ELSEVIER

Journal of Marine Systems 19 (1999) 251–266

JOURNAL OF MARINE SYSTEMS

Daily and seasonal variations of the partial pressure of CO_2 in surface seawater along Belgian and southern Dutch coastal areas

A.V. Borges *, M. Frankignoulle

Université de Liège, Mécanique des Fluides Géophysiques, Unité d'Océanographie Chimique, Institut de Physique (B5), B4000 Sart Tilman, Belgium

Received 5 January 1998; accepted 19 August 1998

Abstract

The variations of the partial pressure of CO_2 (pCO_2) and related parameters were determined in surface seawater along the Belgian coast, from January 1995 to June 1996, at both daily and seasonal time scales. The distribution of pCO_2 in this area is regulated by river input from the Scheldt, biological activity and hydrodynamics. The contribution of each of these processes varies as a function of the considered time scale: (i) the daily variation of pCO_2 depends on the tide although modulated by the biological diel cycle; (ii) the seasonal variation of pCO_2 depends on the input from the Scheldt and the seasonal variations of phytoplanktonic biomass. During winter, the plume of the river Scheldt is oversaturated in pCO_2 with respect to the atmosphere. During spring and summer, phytoplankton blooms occur both in the lower Scheldt estuary and in the river plume and may lead to undersaturation of pCO_2 in the easternmost area of the river plume. However, the degradation of phytoplankton induces oversaturation of pCO_2, in the westernmost area of the plume. Furthermore, the inter-annual variation of pCO_2 depends partly on the fluctuations of the discharge of the Scheldt. Our preliminary results strongly suggest that, on an annual basis, the Scheldt plume behaves as a net source of CO_2 to the atmosphere.

Keywords: pCO_2; Belgian and Dutch coasts; Scheldt river plume; daily and seasonal variations

1. Introduction

The lack of in situ measurements of inorganic carbon in continental shelf seas is at the base of the controversy concerning their role in the global carbon cycle. The estimations of the exchange of CO_2 across the air–sea interface are in these regions mostly based on calculations and they yield from one author to another opposite conclusions (Walsh, 1991; Smith and Hollibaugh, 1993). Continental shelf seas are complex systems characterized by a wide range of specific processes such as: upwelling, tidal fronts, river inputs, exchange with sediments and intense biological processes (Walsh, 1988; Mackenzie, 1991; Wollast, 1991). Large deviations in the partial pressure of CO_2 from the atmospheric equilibrium are expected to occur from these processes, which can furthermore have antagonistic effects. For instance, rivers and upwelling bring to the shelf significant quantities of inorganic carbon, inducing oversaturation of pCO_2 with respect to the atmosphere. Also, rivers bring organic carbon that will be remineralised. On another hand, upwelling and rivers also

* Corresponding author. Fax: +32-4-3662355; E-mail: alberto.borges@ulg.ac.be

0924-7963/99/$ - see front matter
PII: S0924-7963(98)00093-1

bring large quantities of nutrients that favour primary production, which is also enhanced by physical structures such as tidal and river plume fronts and induce undersaturation of the partial pressure of CO_2 (pCO_2) with respect to the atmosphere. To clarify the role of continental shelf seas in the global carbon cycle, more field data of CO_2 air–sea fluxes are then needed (Mackenzie, 1991; Sarmiento and Sundquist, 1992). One approach is to measure pCO_2 in surface seawater, with an adequate spatial and temporal resolution to meet the small scale variations of pCO_2. The net CO_2 air–sea flux can then be estimated from the measurements of pCO_2, salinity, water temperature and wind speed (Liss and Merlivat, 1986; Wanninkhof, 1992).

The Belgian and Dutch coasts (Fig. 1) have been intensely studied from the physical, chemical and biological point of views but pCO_2 data are very sparse. The main features of these regions are the fresh water inputs from the river Scheldt, the river Rhine and the North Sea Channel (Southern IJsselmeer). Along the Belgian coast, the only set of pCO_2 data available so far has been reported by Frankignoulle et al. (1996a,b,c) and values are between 115 and 665 μatm. Along the Dutch coast, pCO_2 data have been reported by Hoppema (1991, 1993), Kempe and Pegler (1991) and Bakker et al. (1996) and values range between 200 and 800 μatm. These authors concluded that in both regions the distribution of pCO_2 is controlled by the fresh water inputs and by biological activity (photosynthesis and mineralisation of organic matter). Yet, more field data are needed to further clarify the seasonal variations of pCO_2 and classify the Belgian and Dutch coastal regions, in the source/sink context. To assess these issues we have performed a seasonal monitoring of pCO_2 in surface seawater of these areas.

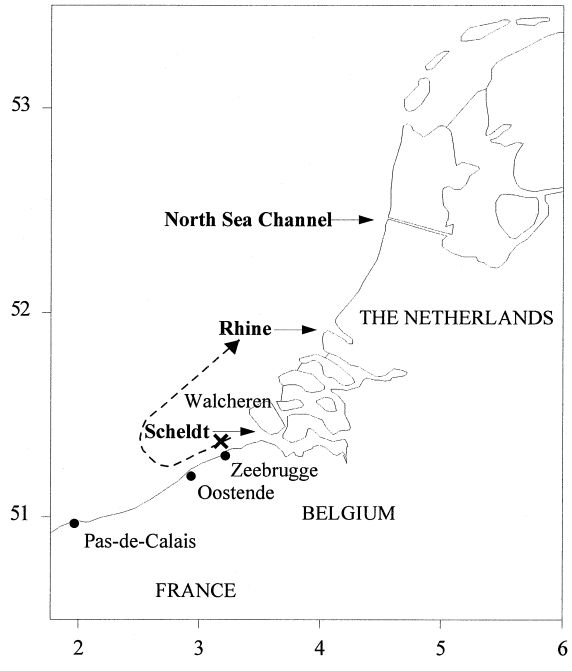


Fig. 1. Map showing the study site. The direction of the residual current along the Belgium coast is schematized by a dotted arrow. The position of the Zeebrugge Station is indicated by a cross.

2. Material and methods

Data presented in this paper were obtained in 1996, on board the R.V. Belgica, during eight cruises: 30 January–2 February (Belgica cruise 96/01), 6–9 February (Belgica cruise 96/02), 22–29 February (Belgica cruise 96/04), 4–8 March (Belgica cruise 96/05), 18–29 March (Belgica cruise 96/07), 15–26 April (Belgica cruise 96/11), 20–24 May (Belgica cruise 96/12) and 3–14 June (Belgica cruise 96/14). A reference station was selected off Zeebrugge, where samples were collected at the start and the end of all the cruises carried out by the University of Liège on board the *R.V. Belgica* (results are available since early 1995).

An IR spectrophotometer (LI-COR®, LI-6252) is used to measure pCO_2 in dry air which is equilibrated with seawater. The LI-COR® spectrophotometer is calibrated using two gas standards of 0 and 350 (± 1) μatm, from Air Liquide Belgium. The equilibrator consists of a Plexiglas cylinder (height: 80 cm, diameter: 10 cm) filled with marbles to increase the exchange surface area. Seawater runs (3 l min^{-1}) from the top to the bottom of the equilibrator and air is pumped upwards (3 l min^{-1}) (for further details: Frankignoulle et al., submitted). The pCO_2 values are corrected for the temperature difference between in situ seawater and water in the equilibrator, using the algorithm proposed by Copin-Montégut (1988).

The measurement of pH is obtained using a Ross combination electrode (ORION®), calibrated on the total proton scale, using the TRIS and AMP buffers proposed by Dickson (1993). The reproducibility of pH measurement is estimated to be 0.004 pH units. Total Alkalinity (TAlk) is determined using the classical Gran electro-titration method, on 100 ml GF/C filtered samples. The reproducibility of TAlk measurements performed on board is 4 μeq kg^{-1}. The pCO_2 data computed from pH and TAlk are calculated using the CO_2 acidity and borate acidity constants from Roy et al. (1993), the CO_2 solubility coefficient from Weiss (1974) and the borate molality obtained from the Culkin (1965) ratio to salinity. The error on the pCO_2 calculation is estimated to be less than 8 μatm.

Dissolved oxygen is measured using a polarographic electrode (ORBISPHERE®), calibrated every 12 h, from discrete samples, using the Winkler method. The O_2 saturation level is calculated using the algorithm proposed by Benson and Krause (1984). Salinity and temperature are measured using a SEABIRD® thermosalinograph. Chlorophyll *a* and phaeopigments concentrations are measured, using the spectrophotometer method described by Lorenzen and Jeffrey (1978).

Underway parameters (pCO_2, pH, dissolved O_2, salinity, temperature) were measured with a sampling frequency of 1 min, using a fully computerised acquisition system, connected to the non-toxic seawater supply of the ship (pump inlet at a depth of −2 m). Samples for TAlk, chlorophyll *a* and phaeopigments concentrations were collected with a frequency of 3 h. The isopleth charts were obtained using SURFER® 6.0 package with the Kriging interpolation method. The tide was calculated using the WORLDTIDE™ package.

3. Results and discussion

3.1. Seasonal variation of pCO_2 at the Zeebrugge station

To describe the seasonal variability in the Belgian coastal area of pCO_2 and its controlling factors, the monitoring of pCO_2 and related parameters was started, in 1995, at a reference station off Zeebrugge (3.18°E, 51.37°N), situated in the Scheldt plume.

Fig. 2 shows that salinity at the Zeebrugge Station is low (mean value of 29.5 in 1995 and 30.9 in 1996) and normalised alkalinity (i.e., TAlk normalised to a salinity of 35, abbreviated TAlk (35)) is high (aver-

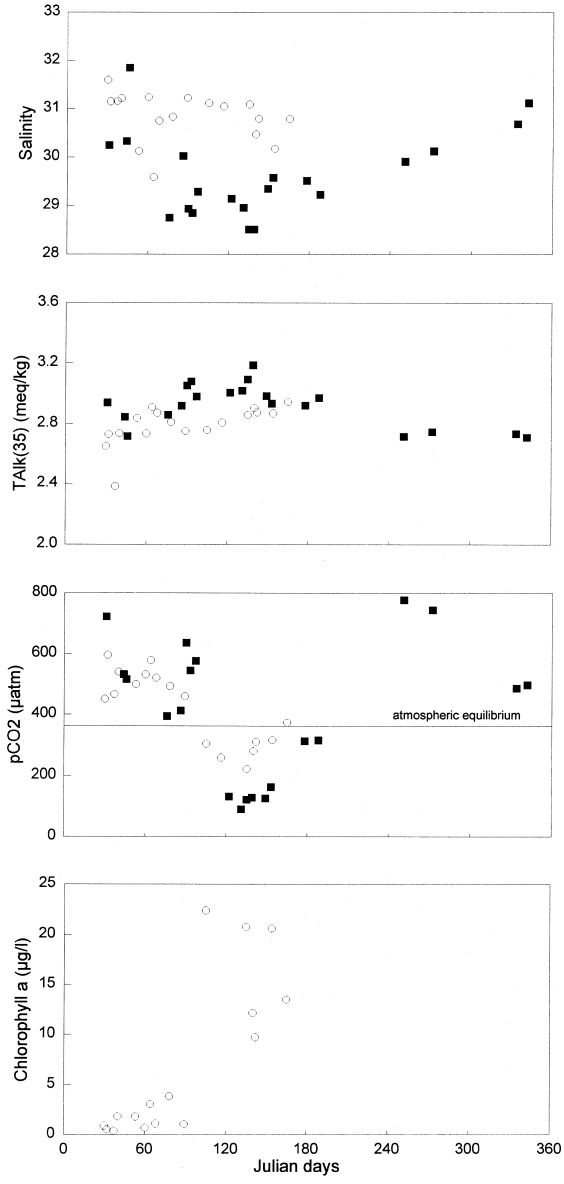


Fig. 2. Variations of pCO_2 (μatm), salinity, TAlk(35) (meq kg^{-1}) and chlorophyll *a* concentration (μg l^{-1}), at the Zeebrugge Station (3.18°E, 51.37°N) in 1995 (black squares) and early 1996 (open circles). pCO_2 was calculated from pH and TAlk.

age values of 2.9 meq kg^{-1} in 1995 and 2.8 meq kg^{-1} in 1996). These two parameters show only slight seasonal variations, so the Zeebrugge Station is, all year round, under the influence of the Scheldt water, characterised by Total Alkalinity higher than the average value for seawater (TAlk(35) ~ 2.3 meq kg^{-1}, Hoppema, 1990; Frankignoulle et al., 1996a,b,c). During winter, the highest observed pCO_2 value was 722 μatm in 1995 and 596 μatm in 1996. This corresponds to an oversaturation of pCO_2 of 200% and 165%, respectively, calculated using the annual mean of atmospheric pCO_2 (361.1 μatm in 1995 and 362.5 μatm in 1996) reported, at Barrow Point, by Keeling and Whorf (1996). During spring, pCO_2 values dropped to 90 μatm in 1995 and to 223 μatm in 1996. In summer 1995, the pCO_2 values increased and attained during fall, a yearly maximum of 778 μatm. To discuss such seasonal variation of pCO_2, three major processes can be envisaged: (i) the river input from the Scheldt, (ii) the biological activity in the water column and/or in the sediment; (iii) the variation of temperature. Frankignoulle et al. (1996b, 1998) showed that important CO_2 production occurs in the Scheldt estuary, induced by intense heterotrophic processes (pCO_2 of 5700 μatm at the turbidity maximum and 600 μatm at the mouth, March 1993). These are related to a high loading of organic matter and a long residence time (1 to 2 months) of the water within the upper part of the estuary (Wollast, 1988). We can conclude that the observed oversaturation of pCO_2 in the Scheldt plume results from the river input of pCO_2 oversaturated water.

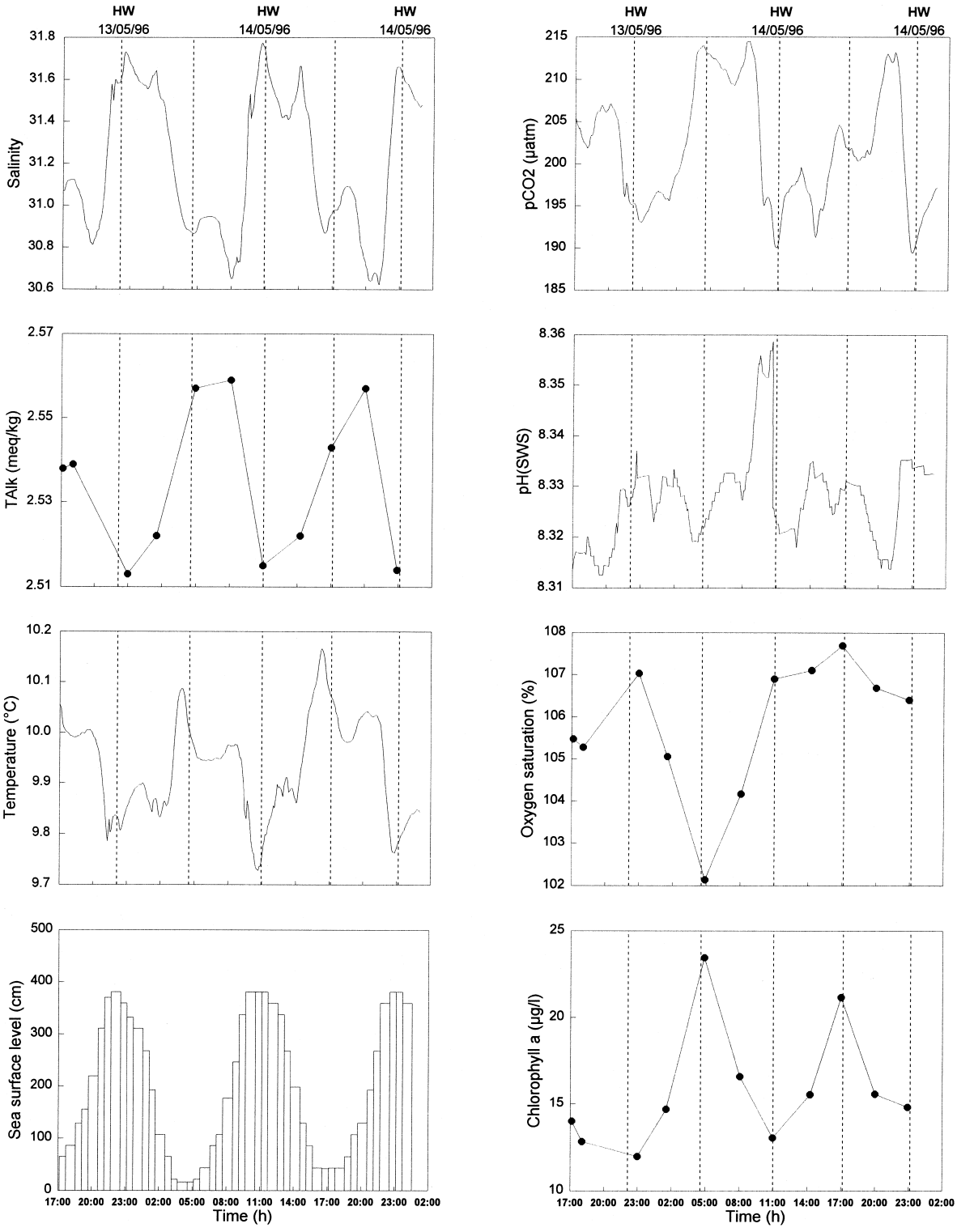
During spring, the pronounced undersaturation of pCO_2 results from phytoplankton blooms and related photosynthetic assimilation of CO_2. Indeed, Fig. 2 shows, in 1996, a correlation between the rise of the chlorophyll concentration and the drop of pCO_2 (no chlorophyll data available for 1995). Our data allow to compute that, on the average, oversaturation of pCO_2 is 150% during 9.5 months, while undersaturation is 60% during 2.5 months.

It is apparent from Fig. 2 that parameters display inter-annual variations: salinity was lower in 1995 than in 1996 and TAlk(35) was higher in 1995 than in 1996. This suggests that the discharge of the Scheldt was higher in 1995 than in 1996. Data from the Ministerie van de Vlaamse Gemeenschap-Anterwerpen Zeehavendiesnt show that, except in January, the Scheldt discharge was on average 10% higher in early 1995 than 1996. Also, the undersaturation of pCO_2 was more pronounced in spring 1995 than in spring 1996. Again, this can be related to the higher Scheldt discharge in 1995 for two reasons: (i) a higher nutrient input that induces a higher phytoplanktonic biomass; (ii) the higher input of pCO_2 undersaturated water (the lower Scheldt estuary becomes undersaturated in pCO_2 during the spring phytoplankton bloom, as discussed below in Section 3.3).

3.2. Daily variations of pCO_2 near Zeebrugge

Fig. 3 gives the variation of pCO_2 and related parameters, during 32 h (from 1700 h on the 13/05 to 0100 h on the 15/05/96), at a mooring site (3.25°E, 51.38°N), near Zeebrugge, during a spring phytoplankton bloom. The variation of seawater level is also given, showing the semi-diurnal signal of the tide, characteristic of this region (Nihoul and Ronday, 1975). The daily variation of chemical parameters must be discussed in relation to physical (tide and wind) and/or biological processes (diel biological cycle) acting at the same time scale. Salinity, TAlk and temperature evolve in a cyclic manner that clearly follows the tidal cycle. The minimum of salinity and the maximum of TAlk and temperature correspond to low tide. As discussed previously, high TAlk is characteristic of Scheldt water and, in May, the plume water is warmer than the offshore water (see below, in Section 3.3). During ebb, the tidal current is south-west bound, transporting Scheldt water (Nihoul and Ronday, 1975). During flood, the tidal current is reversed and transports water with

Fig. 3. Variations of pCO_2 (μatm; direct measurement), salinity, TAlk (meq kg^{-1}), temperature (°C), sea surface level (cm), pH, oxygen saturation level (%) and chlorophyll *a* concentration (μg l^{-1}), during a 32 h measurement cycle, at a mooring point (3.25°E, 51.38°N), near Zeebrugge, from 1700 h on the 13/05 to 0100 h on the 15/05/96.


HW
13/05/96
HW
14/05/96
HW
14/05/96
Salinity
pCO2 (µatm)
TAlk (meq/kg)
pH(SWS)
Temperature (°C)
Oxygen saturation (%)
Sea surface level (cm)
Chlorophyll a (µg/l)
17:00 20:00 23:00 02:00 05:00 08:00 11:00 14:00 17:00 20:00 23:00 02:00
Time (h)

more offshore characteristics (cooler and with lower TAlk).

To discuss the daily variations of pCO_2 and O_2 saturation level, the biological diel cycle must be taken into account. Fig. 3 shows that the variations of pCO_2 and chlorophyll depend on the tidal cycle: the highest pCO_2 and chlorophyll values coincide with low tide. This is in agreement with the fact that the Scheldt water displays higher pCO_2 and chlorophyll values than offshore water, even during the phytoplankton bloom (see below, Section 3.3). However, the diel cycle of primary production/respiration strongly affects the variation of dissolved O_2 as shown by the comparison of two low tide situations: at 0430 h (before sunrise) O_2 saturation level was much lower than at 1710 h (before nightfall). This can be explained by the fact that O_2 saturation level drops during the night in relation to respiration and rises during the day in relation to net primary production. To a lesser extent, this is also shown by the fact that the pCO_2 values observed at low tide are higher at 0430 h than at 1710 h. When we compare the O_2 saturation level at the three high tide situations, the variations due to the biological diel cycle are relatively small: 107.0%, 106.9% and 106.4%, respectively at 2300 h (on the 13th), 1100 h and 2300 h (on the 14th). The important impact of the diel biological cycle on dissolved O_2 in the water mass observed at low tide compared to the water mass at high tide can be related to their respective phytoplanktonic biomass, as shown by the chlorophyll concentration. Billen et al. (1990) have shown that along the Belgian coast, the bacterial biomass is positively correlated to the phytoplanktonic biomass, so the contribution of bacteria to the total respiration will also be higher in the water mass observed at low tide.

3.3. Seasonal variations of pCO_2 and related parameters along Belgian and Dutch coasts

The spatial distribution of pCO_2 and related parameters was established, in 1996, from seven cruises that cover five periods: early February (Fig. 4), early March (Fig. 5), late March (Fig. 6), late May (Fig. 7) and early June (Fig. 8).

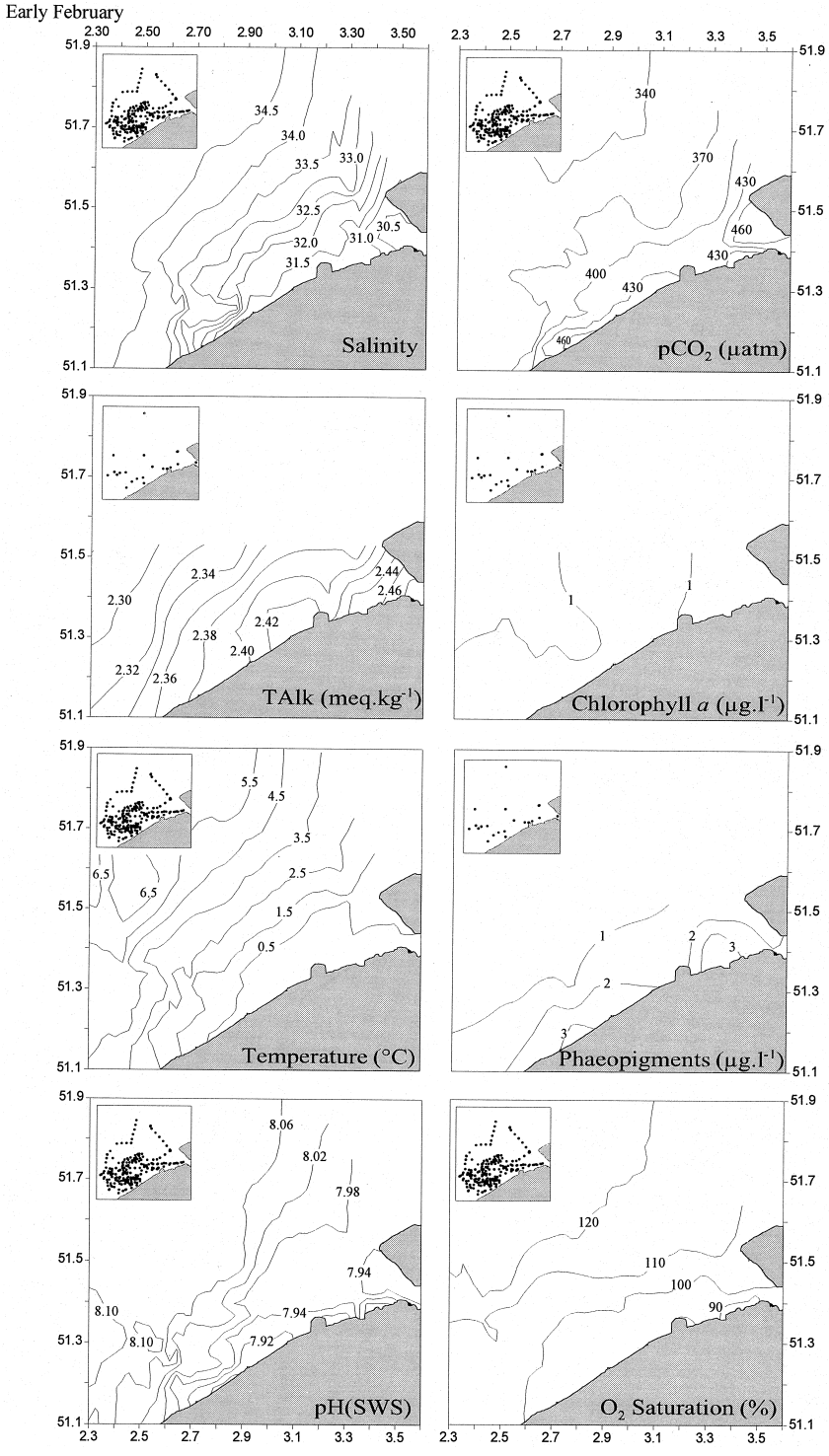
3.3.1. Salinity, TAlk and temperature

Figs. 4–8 show that salinity and TAlk are similarly distributed along a gradient perpendicular to the coast. Temperature often displays the same pattern. The tongue of low salinity, ranging from 30 to 34, and high TAlk, ranging from 2.4 to 2.5 meq kg^{-1}, corresponds to the river Scheldt plume. The position and the extent of the plume is related to a south-bound coastal residual current, that turns west roughly at Oostende to merge, offshore, with the north-bound flow of the North Atlantic current (Nihoul and Ronday, 1975). Our offshore salinity data (around 35) and TAlk (around 2.3 meq kg^{-1}) are typical values for the English Channel Water (Hoppema, 1990; Frankignoulle et al., 1996a,c). In Figs. 5 and 8, the salinity and TAlk gradients show the transport of Scheldt water north of Walcheren, due to the north-bound residual current. Figs. 4–8 show that temperature gradients display important seasonal variations. From early February to late March, the plume water is cooler than offshore water, while from late May to early June, the plume water becomes warmer than offshore water.

3.3.2. pCO_2, pH, O_2 saturation, chlorophyll and phaeopigments concentrations

Figs. 4–6 show that from early February to late March, the distribution of pCO_2 is quite heterogeneous but the Scheldt plume (salinity lower than 34) is clearly oversaturated in pCO_2 with respect to the atmosphere. The distribution of pH is similar to that of O_2 saturation and opposite to that of pCO_2. Such correlation show that along the Belgian coast, the distribution of pCO_2 is strongly affected by the heterotrophic processes taking place in the Scheldt estuary (Frankignoulle et al., 1998). During the cruise carried out in early February, we measured a higher pCO_2 value in the plume (477 μatm at salinity 32) compared to the mouth (470 μatm at salinity 30).

Fig. 4. Distribution of pCO_2 (μatm; direct measurement), salinity, TAlk (meq kg^{-1}), temperature (°C), pH, chlorophyll *a* concentration (μg l^{-1}), phaeopigments concentration (μg l^{-1}) and oxygen saturation level (%), in surface water, along the Belgian coast, from 30/01 to 09/02/96.


Early February
Salinity
pCO2 (µatm)
TAlk (meq.kg-1)
Chlorophyll a (µg.l-1)
Temperature (°C)
Phaeopigments (µg.l-1)
pH(SWS)
O2 Saturation (%)

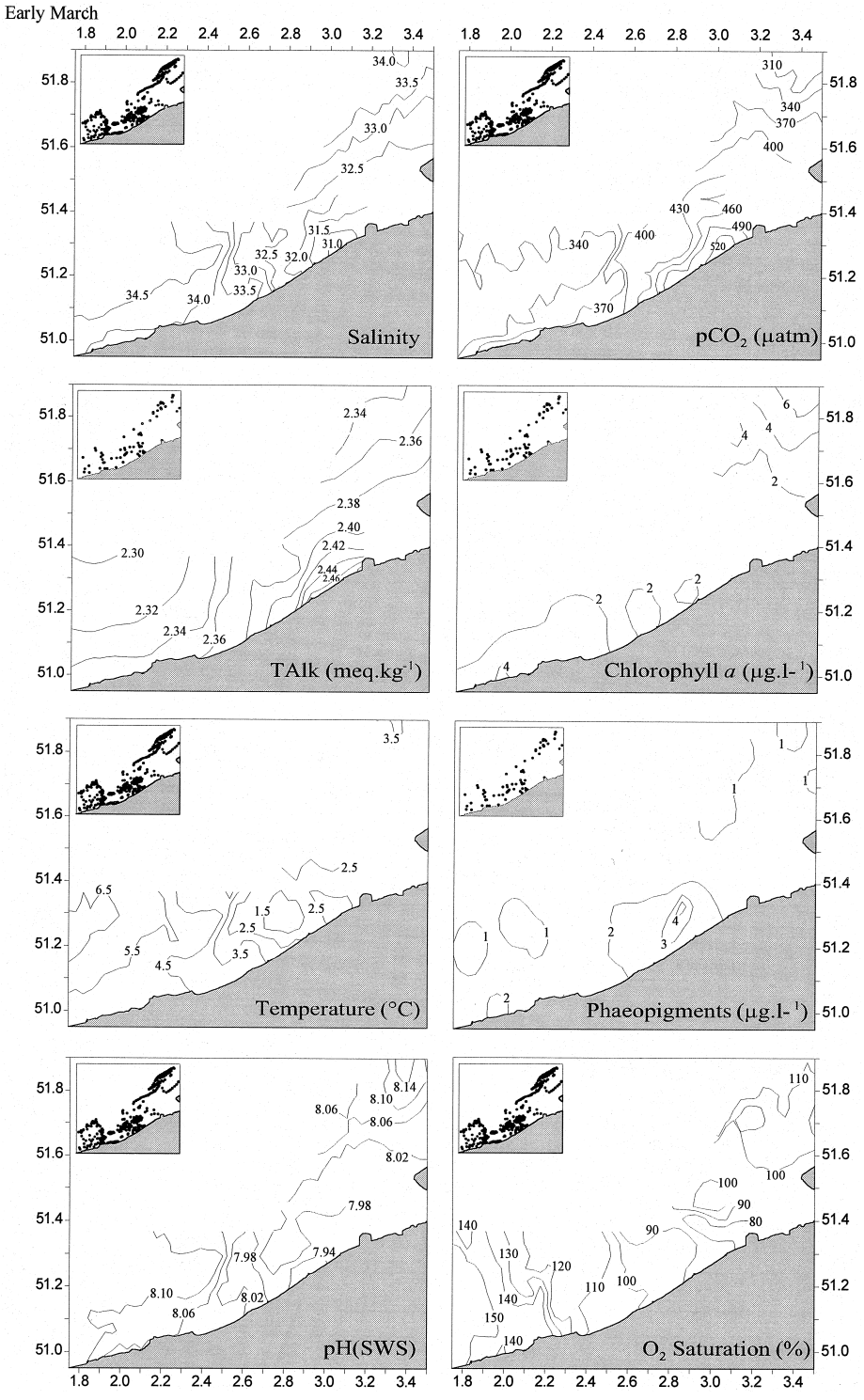
The temperature of the Scheldt water changes during its transit from the mouth (0.8°C) to the plume (1.5°C), in relation to the mixing with offshore water and/or to heat exchange with the atmosphere. This process affects the equilibrium constants of the inorganic carbon species and the CO_2 solubility coefficient resulting in the variation of the original pCO_2 value. This can explain the slight rise of pCO_2 in the river plume: a variation of temperature from 0.8°C to 1.5°C induces a variation of pCO_2 from 470 to 486 μatm, for a salinity of 30. We can conclude that river input and the effect of temperature control the distribution of pCO_2 in the river plume in early February.

In early March, the water masses situated outside the plume (salinity > 34) are undersaturated in pCO_2. The correlation between pH, O_2 saturation level and chlorophyll concentration suggest that, in these areas, the observed undersaturation of pCO_2 is induced by phytoplanktonic activity. Light could then be the limiting factor for primary production within the plume, which is known to be very turbid.

During the late March cruise, again we measured a higher pCO_2 value in the plume (544 μatm at salinity 32) compared to the mouth (463 μatm at salinity 30). In this case, the effect of the variation temperature accounts for a rise in pCO_2 of 9 μatm. To discuss the distribution of pCO_2 in the river plume in late March, we must then consider other processes such as organic matter degradation or exchange with the sediments taking place within the river plume itself. Fig. 6 shows that the chlorophyll concentration, in the river plume, is non-negligible. Furthermore, the highest value of chlorophyll concentration in the river plume was 6.7 μg l^{-1} (for salinities < 33) but only 2.9 μg l^{-1} at salinity 30. This shows that the high phytoplanktonic biomass in the river plume were only in part exported from the Scheldt estuary. However, in spite of the high chlorophyll concentration, oversaturation of pCO_2 is still observed. Finally, the phaeopigments distribution is also clearly different from the two periods previously discussed. In February and early March, high phaeopigments concentrations were correlated to low salinities, then suggesting import from the Scheldt. In late March, a peak of phaeopigments that shows the degradation of phytoplankton is observed within the plume itself (salinity 32) and coincides with the pCO_2 maximum observed. Thus, such organic matter degradation results in the rise of pCO_2 and a decrease of O_2. Future research is needed to determine when this process starts to affect significantly the distribution of pCO_2 in the river plume.

Figs. 7 and 8 give the distribution of pCO_2, in late May and early June. The easternmost area of the plume is undersaturated in pCO_2 (on average: 70% in late May and 95% in early June). Yet, the westernmost area of the plume remains oversaturated in pCO_2 (highest value of 130% in late May and in early June). In late May, in the easternmost area of the plume, high chlorophyll concentrations show the presence of an important phytoplankton bloom that induces undersaturation of pCO_2 in this area. However, we must address the question of the possible contribution to this undersaturation by primary production occurring within the Scheldt estuary itself. During the cruise in late May the lower Scheldt was sampled (data not shown) and undersaturation of pCO_2 was observed between salinities 30 and 26 (respectively 82% and 100%) but the higher estuary was oversaturated in pCO_2. In the river plume, at salinities 32, 33 and 34 the lowest values of undersaturation of pCO_2 were respectively: 61%, 55% and 50%. The effect of the variation of temperature accounts for a diminution of less than 20 μatm (6% of level of saturation). This shows, that during the spring phytoplankton bloom, while the water is already undersaturated in pCO_2 at the Scheldt mouth, the primary production within the plume itself also largely contributes to the observed undersaturation of pCO_2. It should be pointed out that undersaturation of pCO_2 in the lower Scheldt estuary is a very brief event (Frankignoulle et al., 1998). Primary production affects the pCO_2 distribution to a lesser extent, in early June than in late May as shown by the respective levels of undersaturation of pCO_2, as the

Fig. 5. Distribution of pCO_2 (μatm; direct measurement), salinity, TAlk (meq kg^{-1}), temperature (°C), pH, chlorophyll *a* concentration (μg l^{-1}), phaeopigments concentration (μg l^{-1}) and oxygen saturation level (%), in surface water, along the Belgian coast, from 22/02 to 08/03/96.


Early March
Salinity
pCO2 (µatm)
TAlk (meq.kg-1)
Chlorophyll a (µg.l-1)
Temperature (°C)
Phaeopigments (µg.l-1)
pH(SWS)
O2 Saturation (%)

phytoplanktonic biomass declines. This is corroborated by the diminution in early June of the chlorophyll concentrations (highest value of 27 $\mu g\ l^{-1}$ in late May and 15 $\mu g\ l^{-1}$ in early June).

The distributions of pH, O_2 saturation level and pCO_2, in late May and early June, show that in the westernmost area of the plume, respiration dominates primary production. The distribution of the concentration of phaeopigments shows that the oversaturation of pCO_2 is related to the degradation of phytoplanktonic cells. These observations are in agreement with the ecohydrodynamical model of Nihoul and Hecq (1984). These authors attribute the patch of maximum of concentration of phaeopigments to the bacterial degradation of the phytoplanktonic cells, transported from the mouth of the Scheldt by the south-bound residual current.

Finally, Figs. 4–8 show that the reference station off Zeebrugge is quite well representative of the behaviour of the plume in terms of source/sink, i.e., undersaturation during a few weeks in spring and oversaturation for the rest of the year.

Fig. 8 shows the distribution of pCO_2 and associated parameters, along the Dutch coast, in early June. The distribution of salinity shows the extent along the Dutch coast of the Scheldt plume, deflected by the north-bound residual current, as far as 51.8°N. The tongue of low salinity, between 51.8°N and 52.2°N, suggests the input from the Rhine. However, from the distribution of TAlk we cannot discriminate the Scheldt and Rhine plumes. Between 52.2°N and 52.6°N, a distinct tongue of low salinity and high TAlk shows the input from the North Sea Channel, that drains the southern IJsselmeer. This distribution of salinity and TAlk in the North Sea Channel plume, given in Fig. 8, is in agreement with the data of Hoppema (1990). Our TAlk values are, on average, 0.08 meq kg^{-1} higher than the 'typical' values reported by Hoppema (1990) for this region. However, this difference is close to the range of the seasonal and short-term variations of TAlk described by this author. Fig. 8 shows that the Scheldt plume influences the pCO_2 distribution along the Dutch coast as far as 51.8°N. The undersaturation of pCO_2 of the North Sea Channel plume is induced by a phytoplankton bloom, as shown by the chlorophyll concentration distribution.

3.3.3. Relationships of pCO_2 versus chlorophyll

Linear relationships between pCO_2 and chlorophyll have been proposed by Watson et al. (1991) for the North Atlantic (spring 1989), by Frankignoulle et al. (1996a) for the English Channel (summer 1992 and spring 1993) and by Bakker et al. (1997) for the Southern Ocean (austral spring 1992). Watson et al. (1991) obtained three kinds of linear relationships related to the stage of development of the phytoplankton bloom: the 'recent history bloom' characterised by $pCO_2 = 358 - 16.8[\text{Chla}]$ ($r^2 = 0.624$, $p < 0.0001$), the 'peak stage' of the bloom characterised by $pCO_2 = 332 - 10.6[\text{Chla}]$ ($r^2 = 0.372$, $p < 0.0001$) and the 'late stage' of the bloom characterised by $pCO_2 = 299 - 6.6[\text{Chla}]$ ($r^2 = 0.490$, $p < 0.0001$). Frankignoulle et al. (1996a) found in the English Channel, two relationships that fit closely those of Watson et al. (1991). The existence of various relationships in the North Atlantic is related to the fact that before the bloom pCO_2 is relatively close to equilibrium and when the bloom declines chlorophyll values drop rapidly but the air–sea exchange needed to restore equilibrium of pCO_2 occurs at a larger time scale (Watson et al., 1991). Bakker et al. (1997) show that different water masses are characterized by specific pCO_2–Chla relationships that depend on the combination of sea surface temperature variations, primary production rates and the pCO_2 value before start of the bloom. Table 1 gives the relationships calculated from our data set. Only two relationships are significant: in the Scheldt plume, during spring and along the Dutch coast, in early June. As expected, the Scheldt plume relationship yields a quite high pCO_2 value for the zero chlorophyll level. Along the Dutch coast, results are similar to those obtained by Watson et al. (1991) for the 'late stage' of the bloom. For the Belgian coast, we can then conclude that pCO_2 is correlated to

Fig. 6. Distribution of pCO_2 (μatm; direct measurement), salinity, TAlk (meq kg^{-1}), temperature (°C), pH, chlorophyll *a* concentration ($\mu g\ l^{-1}$), phaeopigments concentration ($\mu g\ l^{-1}$) and oxygen saturation level (%), in surface water, along the Belgian coast, from 18/03 to 29/03/96.

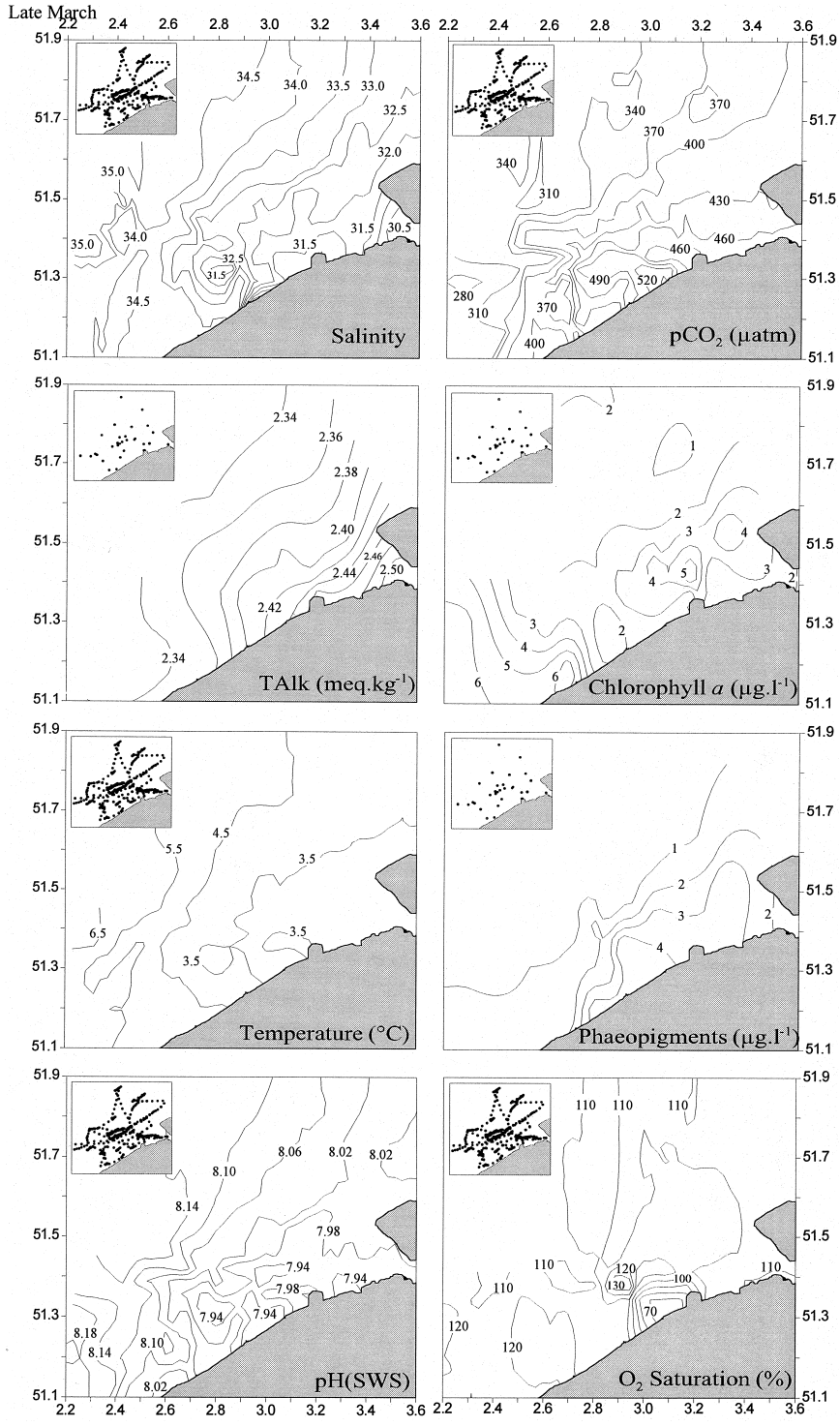

Late March
Salinity
pCO2 (μatm)
TAlk (meq.kg-1)
Chlorophyll a (μg.l-1)
Temperature (°C)
Phaeopigments (μg.l-1)
pH(SWS)
O2 Saturation (%)

Table 1
Linear relationships obtained by plotting surface pCO_2 (μatm) and chlorophyll *a* concentration (μg l^{-1})

	$pCO2 = A + B$ [Chla]	r^2	*n*	*p*
Belgian Coast (Zone A)				
Scheldt plume (Salinity < 33)				
From 30/01 to 29/03	502 − 13.9 (±7.5) [Chla]	0.069	48	0.06942
From 20/05 to 23/05	404 − 13.2 (±3.1) [Chla]	0.675	11	0.00191
From 03/06 to 14/06	376 − 2.8 (±1.2) [Chla]	0.239	19	0.03356
Offshore region (Salinity > 33)				
From 30/01 to 29/03	403 − 11.0 (±3.1) [Chla]	0.165	68	0.00059
From 20/05 to 13/05	No Data			
From 03/06 to 14/06	391 − 10.5 (±3.8) [Chla]	0.260	24	0.01089
Dutch Coast (Zone B)				
From 03/06 to 14/06	331 − 5.9 (±0.88) [Chla]	0.725	19	0.00045

The pCO_2 was calculated from pH and TAlk.
The r^2 is the regression coefficient and *P* the statistical confidence interval.
Zones A and B are defined in Fig. 8.

phytoplanktonic biomass only during the spring bloom. During the rest of the year, other processes are responsible for the distribution of pCO_2.

4. Conclusions

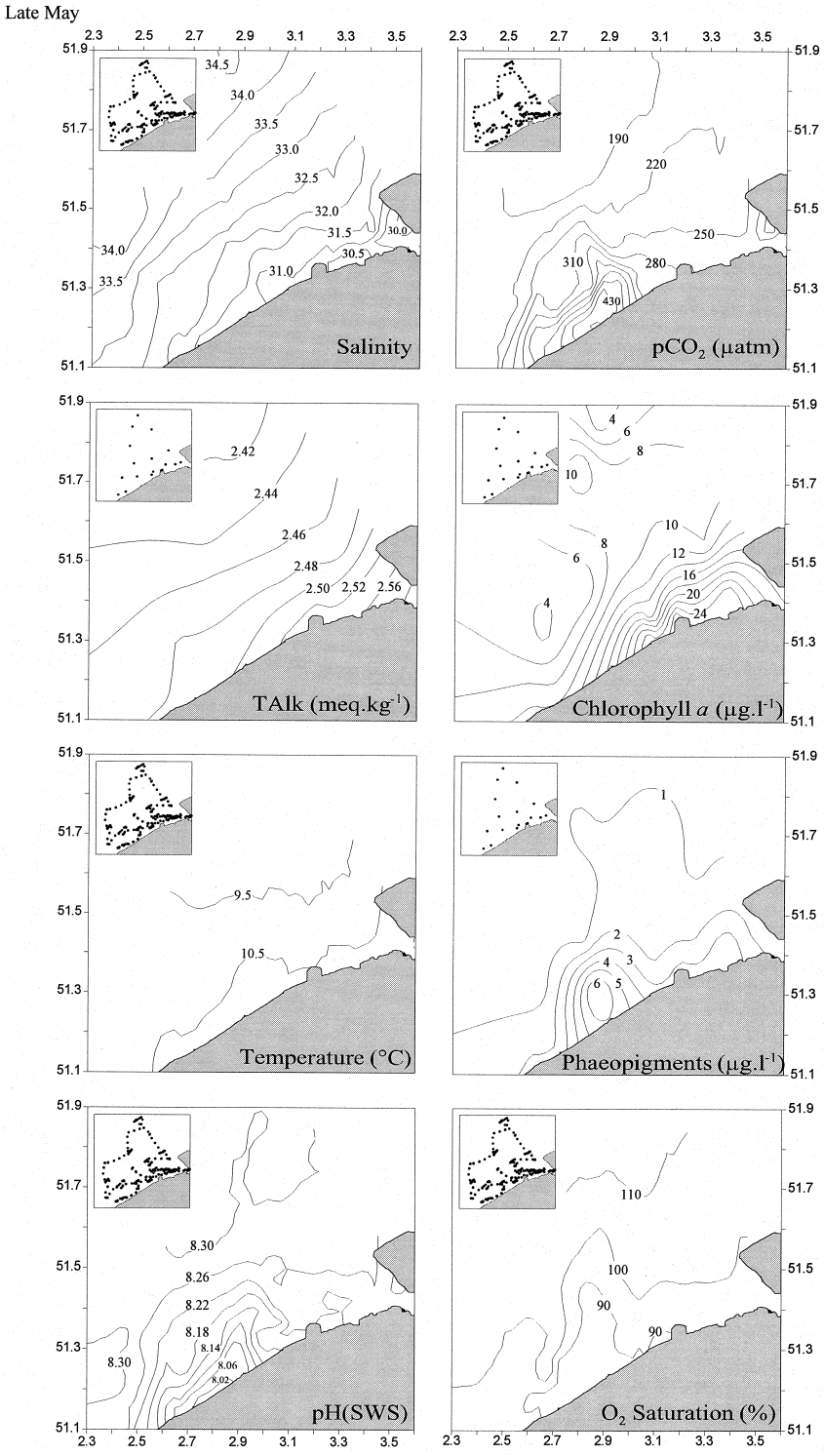
Our study shows the high variability of the distribution of pCO_2 along the Belgian and Dutch coasts and its multiple controlling factors. Indeed, present atmospheric pCO_2 is, on average, 362 μatm and we report pCO_2 values in surface seawater ranging from 90 to 778 μatm. Along the Belgian coast, the main forcing factor is the river input from the Scheldt.

The daily variation of pCO_2 is induced by the tide. During ebb, the tidal current brings Scheldt water, so highest pCO_2 was measured at low tide. However, at this time scale, the variation of pCO_2 is also modulated by the diel biological cycle.

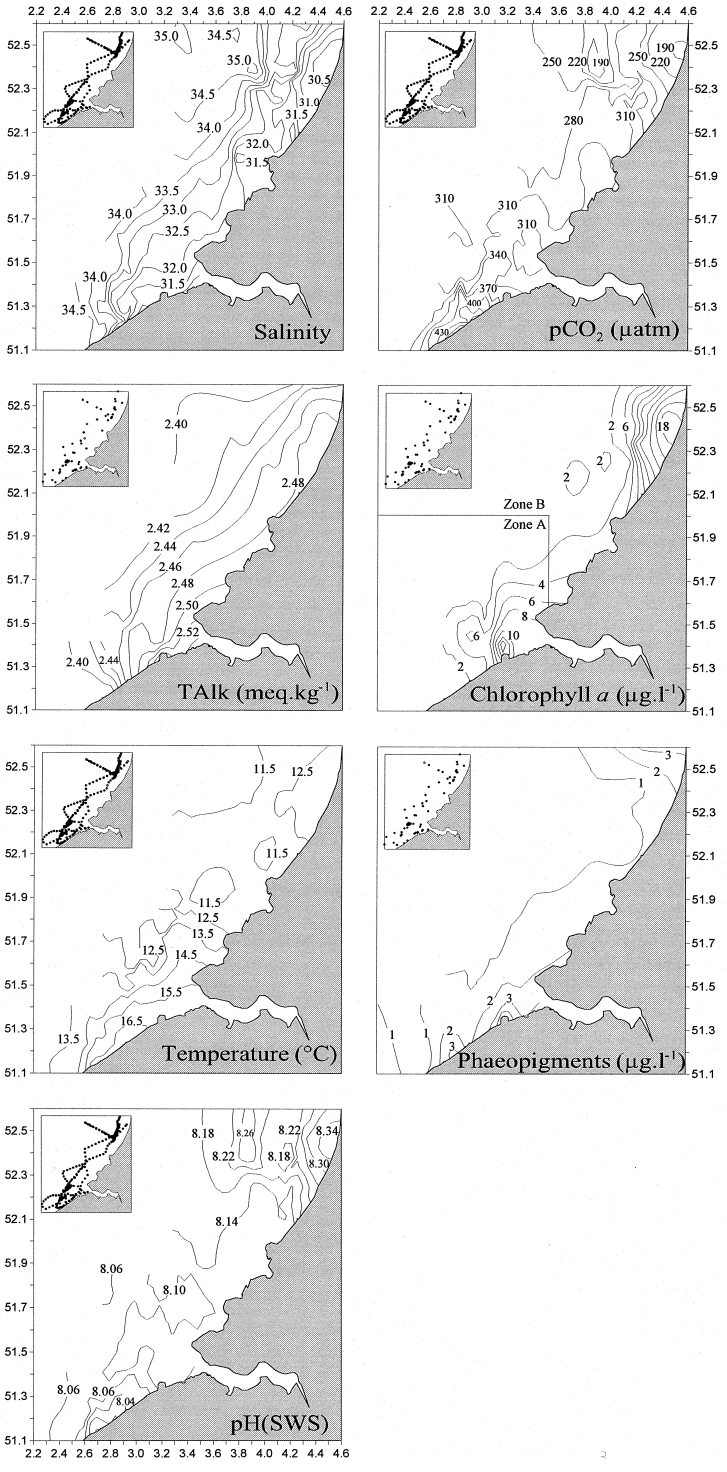
The seasonal variation of pCO_2 is induced by the river input from the Scheldt and the seasonal variation of phytoplanktonic biomass. During winter, the river input of pCO_2 oversaturated water is the major controlling factor, so the Scheldt plume is oversaturated in pCO_2. However, in the areas adjacent to the Scheldt plume, undersaturation of pCO_2 was observed in early March. In late March, the degradation of organic matter within the river plume also contributes to the distribution of pCO_2. During spring, favourable light and temperature conditions and high nutrient contents related to river input induce an important phytoplanktonic biomass within the river plume that is responsible for the undersaturation of pCO_2 in the easternmost area of the river plume. The lower Scheldt estuary also becomes undersaturated in pCO_2 contributing to the undersaturation of pCO_2 observed in the river plume. However, the degradation of phytoplankton, induces oversaturation of pCO_2 in the westernmost area of the river plume. The inter-annual variation of pCO_2 depends, at least partly, on the fluctuations of the discharge of the Scheldt.

The data from the Zeebrugge reference station strongly suggest that the Scheldt plume acts yearly as a net source of atmospheric CO_2. The observed spatial distributions of pCO_2 show that our reference station is representative of the overall distribution of pCO_2 in the plume. On another hand, for all

Fig. 7. Distribution of pCO_2 (μatm; direct measurement), salinity, TAlk (meq kg^{-1}), temperature (°C), pH, chlorophyll *a* concentration (μg l^{-1}), phaeopigments concentration (μg l^{-1}) and oxygen saturation level (%), in surface water, along the Belgian coast, from 20/05 to 24/05/96.


Late May
Salinity
pCO2 (µatm)
TAlk (meq.kg-1)
Chlorophyll a (µg.l-1)
Temperature (°C)
Phaeopigments (µg.l-1)
pH(SWS)
O2 Saturation (%)

Early June


Salinity
pCO2 (µatm)
TAlk (meq.kg-1)
Chlorophyll a (µg.l-1)
Zone B
Zone A
Temperature (°C)
Phaeopigments (µg.l-1)
pH(SWS)

cruises, the off-shore water (English Channel water) was undersaturated in pCO_2. Our data also show that the Dutch coastal region acts, in early summer, as a sink of atmospheric CO_2. Further research is needed to determine whether the Dutch coastal region acts yearly as a source or a sink of atmospheric CO_2 and to quantify in both areas the corresponding carbon flux across the air–sea interface.

Acknowledgements

The authors would like to thank BMM-MUMM (Belgium), for providing thermosalinograph data, Ministerie van de Vlaamse Gemeenshap-Anterwerpen Zeehavendienst for the data of the discharge of the Scheldt, officers and crew of *R.V. Belgica* for helpful collaboration, Renzo Biondo, Isabelle Bourge, for technical assistance, Stephane Desgain for sampling the Zeebrugge Station in 1995, Roland Wollast and an anonymous reviewer for helpful comments on a previous version of the manuscript. This work was funded by the Fonds National de la Recherche Scientifique (Convention F.R.F.C. number 2.4519.95.F), with which Michel Frankignoulle is a research associate and by the European Commission (BIOGEST project number ENV4-CT96-0213). Alberto Vieira Borges is presently a PhD student with a grant from the Fonds pour la Formation à la Recherche dans l'Industrie et l'Agriculture. This is Eloise contribution number 034.

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