

Dissolved inorganic carbon in a highly polluted estuary (the Scheldt)

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Abstract

During 34 months (1996–1999), we studied the dissolved inorganic carbon (DIC) system of the highly polluted Scheldt River and upper estuary. DIC ranged between 3,300 and 7,100 μM , with highest values in winter and lowest in summer. For the brackish and freshwater section of the river $\delta^{13}\text{C}_{\text{DIC}}$ values ranged from -7.5 to -17.5% , the most negative signals were during winter and the least negative during summer. In all seasons, surface waters were significantly supersaturated in CO_2 with respect to the atmosphere (pCO_2 ranged from 2,200 to a maximum of 15,500 μatm) indicating that the system is always heterotrophic. Biological processes (respiration and carbon fixation) and CO_2 evasion to the atmosphere affected the isotopic composition and magnitude of the inorganic carbon pool. In spring and summer 1997 and 1998, large phytoplankton biomasses ($>100 \mu\text{g}$ chlorophyll *a* [*Chl a*] L^{-1}) coincided with lower pCO_2 and CO_2 water–air efflux and less negative $\delta^{13}\text{C}_{\text{DIC}}$ values, indicating considerable CO_2 drawdown by phytoplankton. Mass balance calculations indicated that organic carbon to DIC conversion exceeded CO_2 consumption year round, (net organic carbon conversion ranged from 410 to 520 $\text{g C m}^{-2} \text{ yr}^{-1}$) emphasizing the effect of bacterial respiration. An intermediate river section receiving water from the main tributary (Rupel), which carries wastewater from the densely populated Brussels region, consistently showed decreased DIC, increased pCO_2 , and depletion in $^{13}\text{C}_{\text{DIC}}$ relative to the main river system.

Studies of the carbonate chemistry in some major rivers, such as the Amazon, Yangtze, and Rhine, showed that pCO_2 in river water is 10 to 15 times higher than in the atmosphere (Kempe et al. 1991). Such high values, typically reached in the downstream sections, suggest that rivers and estuaries not only transport carbon from land to the ocean, but also actively degas CO_2 into the atmosphere (Frankignoulle et al. 1998). In a recent review, Cole and Caraco (2001) report that this is the case for a majority of large rivers, which are accordingly categorized as net heterotrophic systems.

European estuaries are subject to intense anthropogenic disturbance. This is especially the case for the Scheldt, which receives an organic matter load estimated at $100 \times 10^9 \text{ g C yr}^{-1}$ (Wollast 1988). Because of the hydrodynamic conditions imposed by the strong tidal regime and the relatively low water discharge, this organic matter accumulates

preferentially in the upper estuary between salinities of 2 and 10‰ (Wollast 1988). There this matter is mainly respired aerobically (Soetaert and Herman 1995; Frankignoulle et al. 1996) and results in significant oxygen depletion, especially in summer (Billen et al. 1988; Heip 1988) and in the production of large quantities of CO_2 (Frankignoulle et al. 1998). Intense bacterial respiration and a long residence time of the river water in the estuarine region lead to the build-up of high partial pressure of CO_2 in the water column. Frankignoulle et al. (1998) reported pCO_2 values as high as 9,425 μatm in the inner estuary of the Scheldt. Such partial pressures exceed by about 26 times the pCO_2 in today's atmosphere (360 μatm), resulting in a large efflux of CO_2 to the atmosphere.

Although the meso- to polyhaline part of the Scheldt Estuary has been extensively studied for its biogeochemical functioning (see Heip and Herman 1995 and references therein), only a few studies have focused on the oligohaline and freshwater tidal reaches. Even fewer studies have focused on the dissolved inorganic carbon (DIC) system. Frankignoulle et al. (1996, 1998) reported partial pressures of carbon dioxide and related atmospheric exchanges in the downstream estuary (km 0–90) and compared these with the situation in other European rivers. The Scheldt system is clearly the most heterotrophic, with highest CO_2 water–atmosphere fluxes per unit surface area. The combined CO_2 efflux from several of these estuaries (including the Scheldt) represented between 5 and 10% of the anthropogenic CO_2 emissions over Western Europe (Frankignoulle et al. 1998), emphasizing the importance of estuaries as CO_2 sources to

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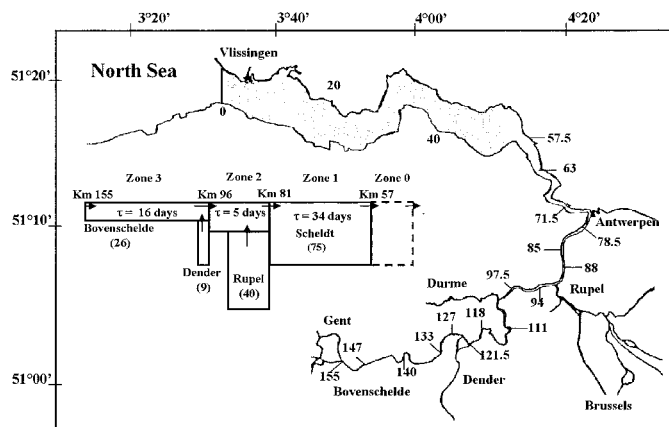


Fig. 1. Map of the study area showing the Scheldt River and the main tributaries, Rupel, Durme, Dender, and Bovenschelde. Positions of the sampled stations are indicated by their distance (km) from the mouth of the estuary (Vlissingen). The insert diagram shows the subdivision of the study area in three boxes with annually averaged residence time (d) of the water in each box as calculated from box volumes and average discharge rates; numbers in parentheses are annually averaged discharge rates ($\text{m}^3 \text{s}^{-1}$) for 1996 to 1998 (Taverniers 1999).

the atmosphere. However, despite a high degree of organic pollution, high levels of primary production can be reached in the Scheldt system (Muylaert 1999).

Because of differing $^{13}\text{C}/^{12}\text{C}$ ratios in various carbon pools and because of the large isotopic shift caused by biologically mediated processes, stable carbon isotope composition is a useful tracer to investigate the processes controlling carbon input and translocation. Changes in the DIC pool size and its isotopic composition reflect temporal changes in the magnitude of sources and sinks (Quay et al. 1986). These can include contributions from tributary streams, biogenic CO_2 uptake and release, and water-air CO_2 fluxes.

The present study focuses on the seasonal fluctuations (monthly resolution) of DIC in the brackish and freshwater parts of the Scheldt Estuary over a 34-month period. Our data document the situation for the upper reaches of the river not investigated previously. We focus on the physical, chemical, and biological processes that affect the inorganic carbon balance with the objective to quantify sources, fluxes, and sinks of carbon.

Study area

Baeyens et al. (1998) give a detailed description of the hydrodynamic features and basin morphology of the Scheldt Estuary. Briefly, the estuary has a mean depth of 10 m, and its width ranges from 7.8 m (Gent; km 160) to 5 km (Vlissingen; km 0) (Fig. 1). Tidal exchange (about $100,000 \text{ m}^3 \text{ s}^{-1}$) is much larger than freshwater discharge (generally $<100 \text{ m}^3 \text{ s}^{-1}$).

Annually averaged discharge rates during the investigated period are shown in Fig. 1. The generally low discharge, compared to the total volume of the estuary, results in a long residence time of the water (50 to 75 d for the entire estuary) and a gradual horizontal salinity gradient (Soetaert and Her-

man 1994). The Rupel is the largest tributary, and in general, its discharge rate exceeds that for the upstream Scheldt basin. The Dender has a much lower discharge, whereas discharge for the Durme is very low to nil.

In the present study, we considered the following zonation for the estuary and river (Fig. 1): a marine zone (Zone 0) from Vlissingen to Zandvliet (km 0–57.5; salinity $>10\text{‰}$); a mesohaline zone (Zone 1) from Zandvliet to Antwerp (km 57.5–78.5; salinity 2–10‰); an oligohaline zone (Zone 2) from Antwerp to just upstream of the mouth of the Rupel (km 78.5–94; salinity $<2\text{‰}$), and a freshwater zone (Zone 3) from the Rupel mouth to Gent (Zone 3; km 94–155). The present work concentrates mainly on Zones 1, 2, and 3, but on three occasions Zone 0 was also studied. Mean tidal level surface and volumes of the studied boxes are (from Soetaert and Herman 1995; Muylaert 1999): Zone 0—surface = $227.07 \times 10^6 \text{ m}^2$, volume = $2,480 \times 10^6 \text{ m}^3$; Zone 1—surface = $20.77 \times 10^6 \text{ m}^2$, volume = $219 \times 10^6 \text{ m}^3$; Zone 2—surface = $3.16 \times 10^6 \text{ m}^2$, volume = $31 \times 10^6 \text{ m}^3$; Zone 3—surface = $8.47 \times 10^6 \text{ m}^2$, volume = $48 \times 10^6 \text{ m}^3$.

Methods

Sampling strategy—The brackish to freshwater tidal estuarine reaches were sampled monthly from January 1996 to August 1998 and also in February and April 1999 along a longitudinal transect comprising 16 stations (Fig. 1). Four stations were sampled in Zone 1, three in Zone 2, and nine in Zone 3. The three zones and the major tributaries (Rupel, Dender, and Bovenschelde; Fig. 1) were sampled within 2 d. In February 1997, February 1999, and April 1999, sampling included the marine zone (Zone 0).

Sampling and field measurements—Surface water samples were collected with a 15-L Niskin bottle 0.5 m below surface. pH was measured with a portable pH-meter (Hanna instruments); two NBS buffers (7.01 and 9.18) were used for calibration. The precision of the pH readings, as stated by the manufacturer, was 0.01. However, precision of the measurements during fieldwork was estimated to be only 0.05. Temperature, dissolved oxygen, and salinity were measured in situ with a Datasonde 3 Multiprobe logger. DIC samples for ^{13}C analysis were collected by gently overfilling a glass bottle from the Niskin bottle, poisoning with HgCl_2 , capping gas tight with a rubber plug and an aluminium cap, and storing at ambient temperature. Water samples for total alkalinity were collected in 500-ml PE bottles, poisoned with HgCl_2 at 4°C , and analyzed within 24 h.

pCO₂ and DIC—pCO₂ and DIC were calculated from pH and total alkalinity (T_{alk}) measurements (e.g., Millero 1996). Alkalinity was determined by an end-point titration on 25-ml samples with 0.01 M HCl (Merck, Titrisol) using an automatic titrator (Mettler-Toledo). Reproducibility for the analysis of different aliquots of the same water sample was $\leq 15 \mu\text{M}$. DIC concentration and partial pressure of CO_2 were calculated using the equations for the first and second dissociation constants K_1 and K_2 from Cai and Wang (1998) fitted for salinities between 0 and 40 and the CO_2 solubility coefficient from Weiss (1974). We estimate the total error

on $p\text{CO}_2$ due to the precision of the pH reading (main contribution to total error) and alkalinity analysis to be on the order of 12%.

CO₂ flux—The magnitude of the CO_2 flux between the aqueous and gaseous phase was calculated as (e.g., Frankignoulle et al. 1996; Cai and Wang 1998)

$$F(\text{CO}_2) = K \cdot K_{\text{CO}_2} [\Delta p\text{CO}_2], \quad (1)$$

where $F(\text{CO}_2)$ is flux ($\text{mol m}^{-2} \text{s}^{-1}$), K is the gas exchange coefficient or piston velocity (m s^{-1}), K_{CO_2} is the CO_2 solubility coefficient ($\text{mol m}^{-3} \text{atm}^{-1}$) (Weiss 1974), and $\Delta p\text{CO}_2$ is the difference in CO_2 partial pressure between water and air, where $p\text{CO}_{2(\text{air})}$ is taken as $360 \mu\text{atm}$ (Cai and Wang 1998; Frankignoulle et al. 1998)

K depends on many environmental factors—primarily wind speed, temperature, and turbulence in air and water (e.g., Liss and Merlivat 1986). Wind speed is probably the most important factor controlling the CO_2 piston velocity, and different empirical relationships relating K to wind speed have been proposed in literature (e.g., Liss and Merlivat 1986; Wanninkhof 1992; Cole and Caraco 1998). For the period between January 1996 and August 1998, daily wind speeds at two meteorological stations located in the vicinity of Antwerp on the Scheldt (Deurne and Brasschaat; <http://ingrid.ldgo.columbia.edu/SOURCES/NOAA>) were 2.7 ± 1.7 and $2.3 \pm 1.2 \text{ m s}^{-1}$, respectively (average 2.5 m s^{-1}). Piston velocity was calculated using the relationship proposed by Wanninkhof (1992) for a smooth liquid interface and situations where long-term average wind speeds are available. Schmidt number dependency on temperature was also calculated according to Wanninkhof (1992). Based on monthly averaged wind speed, our K values, normalized to a Schmidt number of 600 (i.e., the Schmidt number of CO_2 in freshwater at 20°C), ranged from 0.4 to 4.7 cm h^{-1} . Such values are on the low side compared with the value reported by Frankignoulle et al. (1996) for the Scheldt ($8.4 \pm 3.1 \text{ cm h}^{-1}$) and based on floating dome experiments. We utilized the wind speed dependency relationship of Wanninkhof (1992) and the monthly averaged wind speed to calculate water–air CO_2 fluxes. It must be kept in mind that because of the strong dependency of the gas exchange coefficient on wind speed, estimates of CO_2 water–air exchange are potentially subject to large error.

Isotopic analyses—Hellings et al. (1999) describe the method used for the determination of the isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$). Briefly, after acidifying the sample with orthophosphoric acid, evolved CO_2 was extracted in an evacuated system and quantitatively recovered in a liquid nitrogen–cooled trap after eliminating water vapor in traps cooled with isopropanol (-80°C). The glass tubes with trapped CO_2 were sealed using a torch, and samples were introduced into the mass spectrometer (Delta E, Finnigan Mat) via a tube cracker connected to the inlet port. Values are expressed relative to the VPDB (Vienna Peedee Belenite) reference. Reproducibility for different aliquots of the same water sample was generally better than 0.04‰.

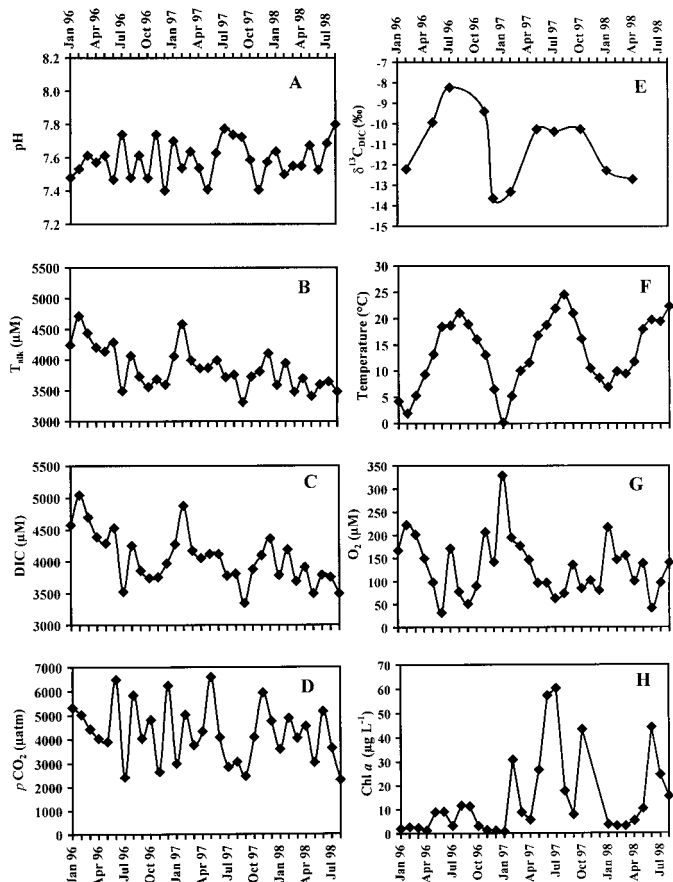


Fig. 2. Zone 1 (km 57.5 to 78.5; four stations); monthly zonal averages (January 1996 to August 1998) of (A) pH; (B) T_{alk} (μM); (C) DIC (μM); (D) $p\text{CO}_2$ (μatm); (E) $\delta^{13}\text{C}_{\text{DIC}}$ (‰); (F) temperature ($^\circ\text{C}$); (G) oxygen (μM); (H) Chl a ($\mu\text{g L}^{-1}$). pH, temperature, T_{alk} , dissolved O_2 for 1996, and $\delta^{13}\text{C}_{\text{DIC}}$ for May, July, November, and December 1996 are from Hellings et al. (1999); Chl a data are from Tackx et al. (1999).

Results

Monthly averaged values—Zonally averaged values of temperature, dissolved O_2 , chlorophyll a (Chl a), pH, T_{alk} , DIC, $p\text{CO}_2$, and $\delta^{13}\text{C}_{\text{DIC}}$ for the mesohaline zone (Zone 1), the oligohaline zone (Zone 2), and the freshwater zone (Zone 3) between January 1996 and August 1998 are shown in Figs. 2 and 3. Temperature, dissolved O_2 , pH, and T_{alk} data for 1996 are from Hellings et al. (1999), as are $\delta^{13}\text{C}_{\text{DIC}}$ results for May, August, November, and December 1996. Chl a data are from Tackx et al. (1999).

Zonally averaged oxygen concentrations showed a clear seasonal variation with highest values (150 to $250 \mu\text{M}$) in winter (Figs. 2, 3G). In spring, summer, and autumn (April to November) significant depletion of oxygen occurred with average concentrations decreasing to as low as $30 \mu\text{M}$ (Zone 1), $15 \mu\text{M}$ (Zone 3), and $0 \mu\text{M}$ (Zone 2). Dissolved O_2 appeared to be predominantly controlled by temperature and was even inversely related to Chl a (Figs. 2, 3G,H).

T_{alk} and DIC showed no regular temporal pattern. In 1996–1997, peak values occurred in late winter (February to

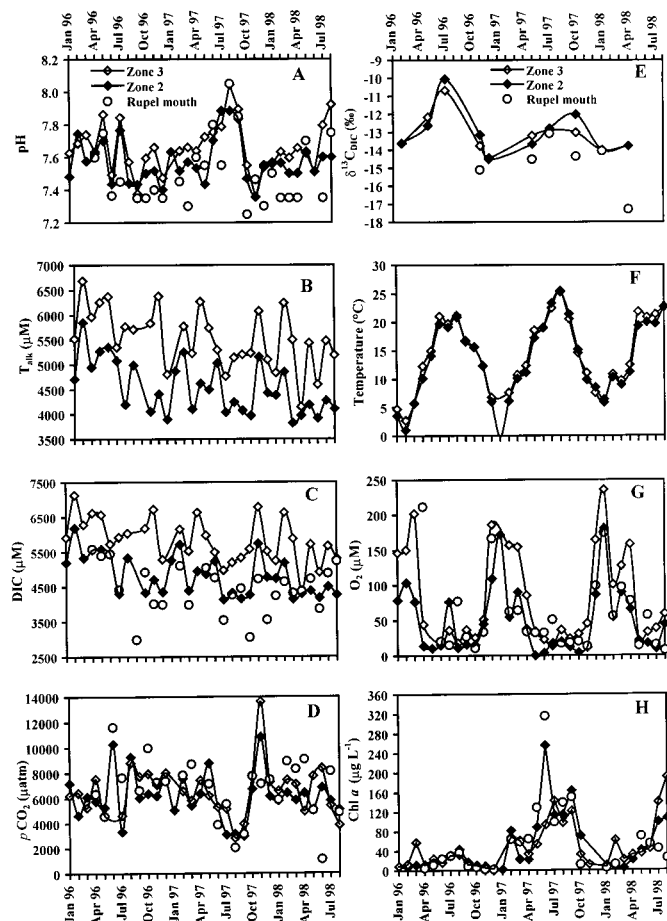


Fig. 3. Zone 2 (km 85 to 94; three stations), Zone 3 (km 97.5 to 155; 9 stations) and mouth of Rupel (one station); monthly zonal averages (January 1996 to August 1998) of (A) pH; (B) T_{alk} (μM); (C) DIC (μM); (D) $p\text{CO}_2$ (μatm); (E) $\delta^{13}\text{C}_{DIC}$ (‰); (F) temperature ($^{\circ}\text{C}$); (G) dissolved O_2 (μM); (H) Chl a ($\mu\text{g L}^{-1}$). pH, temperature, T_{alk} , dissolved O_2 for 1996, and $\delta^{13}\text{C}_{DIC}$ for May, July, November, and December 1996 are from Hellings et al. (1999); Chl a data are from Tackx et al. (1999).

March) and minima in July–September, but in 1997–1998, peaks were in November–December (Figs. 2, 3B,C). Average DIC concentrations for Zone 1 varied between 3,300 and 5,050 μM . Zone 2 had slightly higher DIC concentrations, with average values ranging from 4,100 to 6,200 μM , whereas Zone 3 had highest concentrations ranging between 4,400 and 7,100 μM . DIC values for the Rupel mouth (Zone 2) fell, in general, below those observed for Zone 2.

Zonally averaged $p\text{CO}_2$ values for Zone 1 ranged between 2,200 and 6,600 μatm (Fig. 2D). Lowest $p\text{CO}_2$ values occurred in summer (2,400 μatm , July 1996 and July–September 1997; 2,200 μatm , August 1998) and highest in winter–spring (e.g., 6,300 μatm in December 1997; 6,600 μatm in May 1997, and 5,900 μatm in November 1997). These values are similar to those observed by Frankignoulle et al. (1996, 1998) for the brackish part of the Scheldt, and which were either calculated (from pH and T_{alk}) or directly measured. For the freshwater zone (Zones 2 and 3), zonally averaged $p\text{CO}_2$ values ranged from 2,900 (August 1997) to a

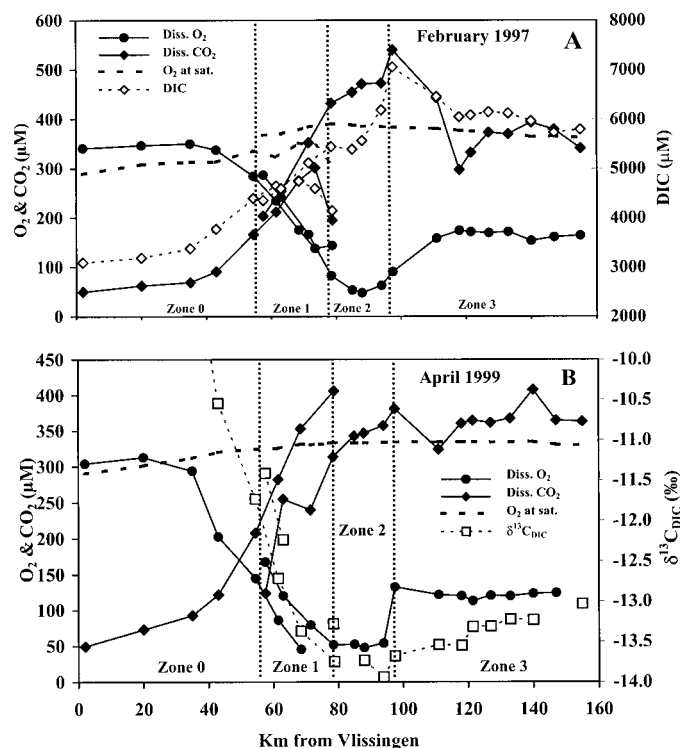


Fig. 4. Concentrations of $p\text{CO}_2$ (μM), dissolved O_2 (μM), and O_2 saturation, vs. distance from Vlissingen in (A) February 1997 and (B) April 1999. Also shown are DIC (μM) in February 1997 (A) and $\delta^{13}\text{C}_{DIC}$ (‰) in April 1999 (B).

maximum of 12,900 μatm (November 1997; Fig. 3D). Other $p\text{CO}_2$ winter values for Zone 2 did not exceed 9,000 μatm . In general, $p\text{CO}_2$ values for the Rupel exceeded those for Zones 2 and 3. The lower values during summer 1997 and 1998 coincided with higher Chl a concentrations and lower pH (Figs. 2, 3A,D,H). Taking the atmospheric $p\text{CO}_2$ to be 360 μatm , the observed oversaturation ranged from 600 to 3,600‰.

Zonally averaged $\delta^{13}\text{C}_{DIC}$ values showed a clear seasonal trend in all three zones (Figs. 2, 3E; not all months were measured). In Zone 1, the most negative $\delta^{13}\text{C}_{DIC}$ values occurred in autumn and winter (−12.2‰ in February 1996, −13.7‰ in November 1996, −12.7‰ in February 1997, and −12.3‰ in January 1998; Fig. 2E). In spring and summer, values were less negative (−8.2‰ in July 1996 and −10.4‰ in July 1997). Likewise, for Zones 2 and 3, the most negative $\delta^{13}\text{C}_{DIC}$ values occurred in winter and autumn (−13.6‰ in February 1996, −14.5‰ in November 1996, −13.8‰ in February 1997, and −14.0‰ in January 1998), whereas in summer, the DIC was more enriched in ^{13}C (−10.5‰ in July 1996 and −12.9‰ in July 1997) (Fig. 3E). In all three zones, seasonal differences were less pronounced in 1997 than in 1996.

Longitudinal profiles of dissolved O_2 , CO_2 , DIC, and $\delta^{13}\text{C}_{DIC}$ —Figure 4 shows longitudinal profiles of dissolved O_2 and CO_2 for February 1997 and April 1999. In the high-salinity region of the estuary (km 0 to 40), dissolved oxygen approached values of 350 and 310 μM in February 1997

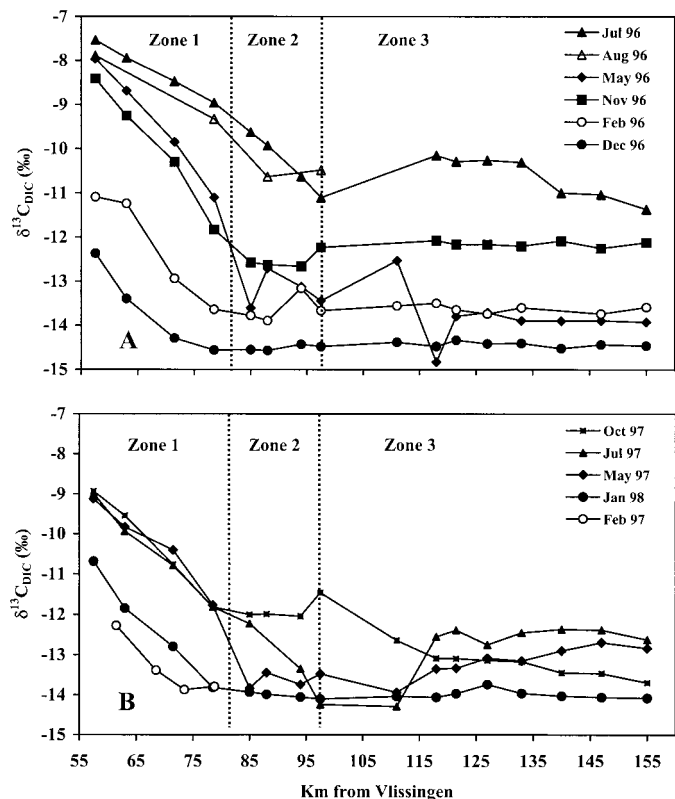


Fig. 5. Values of $\delta^{13}\text{C}_{\text{DIC}}$ (‰) versus distance from Vlissingen for (A) 1996 and (B) 1997–1998.

and April 1999, respectively. From km 40 to 90, concentrations declined significantly and reached a minimum of about $50 \mu\text{M}$ (for both months) in Zone 2 (between km 78.5 and 100) where the Rupel enters the Scheldt. Oxygen concentrations increased again slightly between km 100 and 111, but from km 111 to 155, concentrations remained almost constant at 120 to $160 \mu\text{M}$.

CO_2 was lowest in the marine zone ($\sim 50 \mu\text{M}$). It increased gradually to Antwerp and reached a maximum between km 80 and 100 (400 to $570 \mu\text{M}$ for April 1999 and February 1997, respectively), coinciding with the oxygen minimum. Further upstream, CO_2 concentrations decreased slightly to 350 – $400 \mu\text{M}$. Overall, CO_2 and O_2 profiles are symmetrical; the close stoichiometric ratio suggests strong control by respiration.

$\delta^{13}\text{C}_{\text{DIC}}$ decreased significantly from km 57.5 to 78.5, whereas from km 111 to 155, values were low and relatively constant (Fig. 5). Upstream $\delta^{13}\text{C}_{\text{DIC}}$ values shifted from more negative to less negative between winter and summer. In 1997 and 1998 (Fig. 5B), seasonal variation of $\delta^{13}\text{C}_{\text{DIC}}$ upstream of km 111 was less pronounced than in 1996 (Fig. 5A). In general, upstream $\delta^{13}\text{C}_{\text{DIC}}$ values did not decrease below -14.5‰ . Figure 4B shows for April 1999 that Zone 2 with the CO_2 maximum and the O_2 minimum had a slightly larger ^{13}C depletion ($\delta^{13}\text{C}_{\text{DIC}} = -13.9\text{‰}$) than Zone 3 ($\delta^{13}\text{C}_{\text{DIC}} = -13.3\text{‰}$). For this same month, the Rupel mouth had a $\delta^{13}\text{C}_{\text{DIC}}$ value of -17.5‰ , the lowest value recorded during this study.

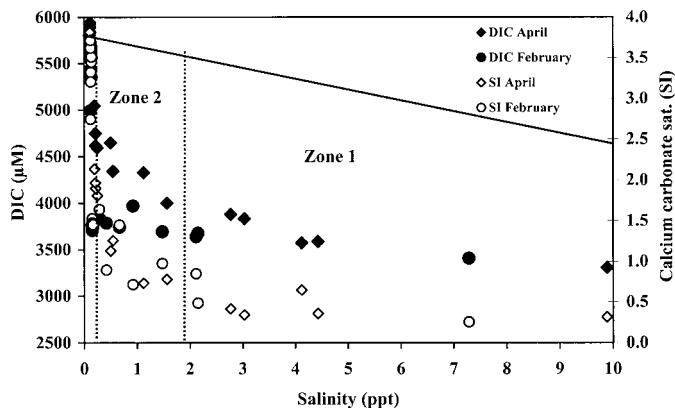


Fig. 6. DIC (μM) and calcite saturation state (SI) versus salinity for February and April 1999. The line represents DIC values that would result from conservative mixing.

Discussion

Distribution of DIC: conservative versus nonconservative processes—Figure 6 shows DIC as a function of salinity for February and April 1999, with the line of conservative mixing between the freshwater (Zone 3) and the marine end-members. There is a clear offset from conservative mixing showing consumption of DIC in Zone 2. This situation is quite different from the one reported by Raymond et al. (2000) for York River entering Chesapeake Bay. That system is characterized by the riverine end-member having lower DIC content than the estuarine end-member and shows internal production of DIC.

The DIC consumption observed in the present study could result from several processes: enhanced phytoplankton activity, CO_2 efflux to the atmosphere, calcium carbonate precipitation, or simply dilution due to the import of Rupel water, which has a lower DIC content (Fig. 3C). Because the low Chl *a* in February and April 1999 in Zone 2 ($7 \mu\text{g L}^{-1}$ compared to $106 \mu\text{g L}^{-1}$ for August 1998; Fig. 3H) reflects winter conditions, it appears unlikely that photosynthetic carbon fixation is responsible for the DIC decrease in Zone 2. Efflux of CO_2 from Zone 2 to the atmosphere in February and April 1999 can account for, at most, 5% of the observed decrease in DIC during transit through Zone 2. To check the next possibility, we calculated the CaCO_3 saturation state using the thermodynamic solubility product of calcite. This calculation was based on: (1) the temperature and salinity dependency equation given by Boudreau (1997), (2) the activity coefficients for Ca^{2+} and HCO_3^- deduced from the extended Debye Hückel dependency of activity coefficients on ionic strength (Stumm and Morgan 1981). We used a dissolved Ca concentration of 3.5 mM for the freshwater end-member (Hellings et al. 2000) and 10 mM for the marine end-member. Ca in the brackish zone was calculated from the salinity profiles and linear interpolation between end-members. Calculations were done for all 34 months and show that the saturation index (SI) varied between 0.1 and 15, with Zone 1 being generally undersaturated and Zone 3 oversaturated (Fig. 6). Zone 2 frequently had SI values < 1 , but in situations of oversaturation, SI did not exceed 5. Al-

though on some occasions saturation of CaCO_3 did occur in Zone 2, DIC consumption due to CaCO_3 precipitation is more likely in Zone 3 (always oversaturated) than in Zone 2 and certainly Zone 1. Thus, at this point, there is no strong evidence that precipitation occurred in Zone 2, where DIC decreased sharply (Figs. 4A, 6). Rupel water generally contains less DIC than Scheldt (Fig. 3C), as confirmed also by the recent work of Abril and Frankignoulle (2001). We therefore calculated the DIC composition of Zone 2 that would result from mixing of Zone 3 water with Rupel water in proportions set by the respective discharges into Zone 2. On average, mixing produces DIC concentrations in Zone 2 that are 1.08 times higher than observed concentrations. This suggests that most of the DIC decrease seen in Zone 2 is the result of dilution rather than CaCO_3 precipitation. The latter process, if it occurs, would contribute only for a relatively small part of the observed decrease of DIC in Zone 2, but clearly, this process needs further investigation.

CO₂ partial pressure and fluxes of CO₂—The pCO_2 values for individual stations ranged from 1,100 to 15,500 μatm . Concentrations in the brackish and freshwater parts of the Scheldt were 3 to 43 times higher than the atmospheric level (360 μatm). Even in the marine zone (Zone 0) pCO_2 values exceeded the atmospheric value by about a factor of three. A similar situation was reported for the Rhine and Amazon rivers (Kempe et al. 1991), but values did not reach the levels observed here in the Scheldt. The Scheldt is subject to high inputs of mainly anthropogenic organic detritus ($100 \times 10^9 \text{ g C yr}^{-1}$; Wollast 1988); bacterial respiration of this material probably accounts for the year-round supersaturation of CO_2 . This is exacerbated by the long residence times of the water (50 to 75 d for the entire estuary; Soetaert and Herman 1994), which also favor the build-up of high pCO_2 . The Rupel, which joins the Scheldt in Zone 2, appears to be a main source of organic waste and mineralized products; this is reflected in the pronounced oxygen minimum and pCO_2 maximum in this zone. This oxygen minimum is present year round, and anoxic conditions have been reported in the summer (Baeyens et al. 1998). The Rupel also advects water that is highly ^{13}C depleted into the Scheldt, resulting in Zone 2 waters being slightly depleted in ^{13}C relative to Zone 3 (Fig. 4B).

The flux of CO_2 to the atmosphere induced by this strong oversaturation was estimated using Eq. 1 with piston velocities calculated according to Wanninkhof (1992) and monthly averaged wind speeds (Fig. 7). In general, CO_2 fluxes per unit surface decreased from Zone 3 to Zone 1, and overall fluxes ranged from 0.01 to $0.45 \text{ mol m}^{-2} \text{ d}^{-1}$. The average efflux of CO_2 ($0.09 \text{ mol m}^{-2} \text{ d}^{-1}$) integrated over Zones 1–3 (i.e., $32.4 \times 10^6 \text{ m}^2$ representing 12% of the surface of the tidally affected section of river and estuary) is $36 \times 10^6 \text{ g C d}^{-1}$, which is equivalent to $13 \times 10^9 \text{ g C yr}^{-1}$. This CO_2 efflux represents 13% of the anthropogenic input ($100 \times 10^9 \text{ g C yr}^{-1}$) reported by Wollast (1988).

$\delta^{13}\text{C}$ signature of DIC—In general, upstream $\delta^{13}\text{C}_{\text{DIC}}$ did not decrease below -14.5‰ (Fig. 5B). If bacterial respiration on organic matter were the dominant process setting the isotopic signature, more negative values, in the range of -20

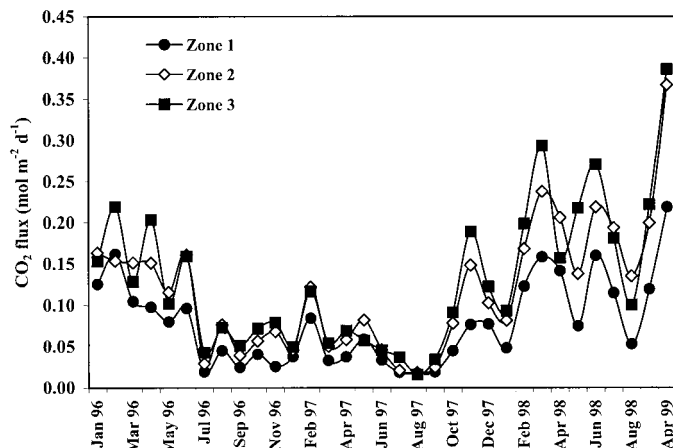


Fig. 7. Monthly averaged CO_2 water-air efflux ($\text{mol m}^{-2} \text{ d}^{-1}$).

to -27‰ , would be expected as observed, for instance, for the Amazon river (Mook and Tan 1991). Such very negative $\delta^{13}\text{C}_{\text{DIC}}$ values were observed in pore waters of freshwater intertidal Scheldt sediments where aerobic decomposition of organic matter of C3 origin is the predominant process (Hellings et al. 2000). Clearly, bulk Scheldt river water must also receive DIC enriched in ^{13}C . Groundwater in large parts of the drainage basin is contained within quaternary and tertiary sand layers, which are often rich in limestone of marine origin (Desmedt 1992). Abril and Frankignoulle (2001) note that Scheldt basin water has about twice the alkalinity of waters draining limestone, with the excess alkalinity partly of anthropogenic origin. Our river $\delta^{13}\text{C}_{\text{DIC}}$ values can reflect about equal contributions of marine limestone dissolution ($\delta^{13}\text{C} \sim 0\text{‰}$) and respiration, and are thus in agreement with this.

Nonconservative behavior of $\delta^{13}\text{C}_{\text{DIC}}$ —In most estuaries, alkalinity and dissolved inorganic carbon are thought to be conservative (Cai and Wang 1998), and $\delta^{13}\text{C}_{\text{DIC}}$ values are largely determined by the mixing ratio of freshwater and seawater (Mook and Tan 1991). In view of the observed intense biogeochemical processing of carbon, this is unlikely to be the case for the Scheldt system.

Variability of $\delta^{13}\text{C}_{\text{DIC}}$ may result from the combined effects of photosynthesis, respiration, physical mixing, and gas diffusion. Preferential uptake of ^{12}C during photosynthesis results in an increase of $\delta^{13}\text{C}_{\text{DIC}}$, whereas release of CO_2 from respired ^{13}C -depleted terrestrial organic matter and local phytoplankton results in a decrease of $\delta^{13}\text{C}_{\text{DIC}}$. In areas of net evasion, bulk transfer of CO_2 across the air-water interface will enrich the DIC in ^{13}C . In summer (e.g., July 1996, 1997) the isotopic composition of DIC was enriched in ^{13}C (especially in Zone 3; Fig. 5), coinciding with an increase of Chl *a* (July 1997; Figs. 2, 3H) and minima in pCO_2 and CO_2 efflux (July 1996, 1997; Figs. 2, 3D, 7). This suggests that enhanced autotrophic carbon fixation combined with reduced input of litter from terrestrial vegetation are predominant processes. Despite high turbidities, the low discharge of the river and the dominance of rotifers in the grazer community, which select for smaller algae, allow huge blooms of larger,

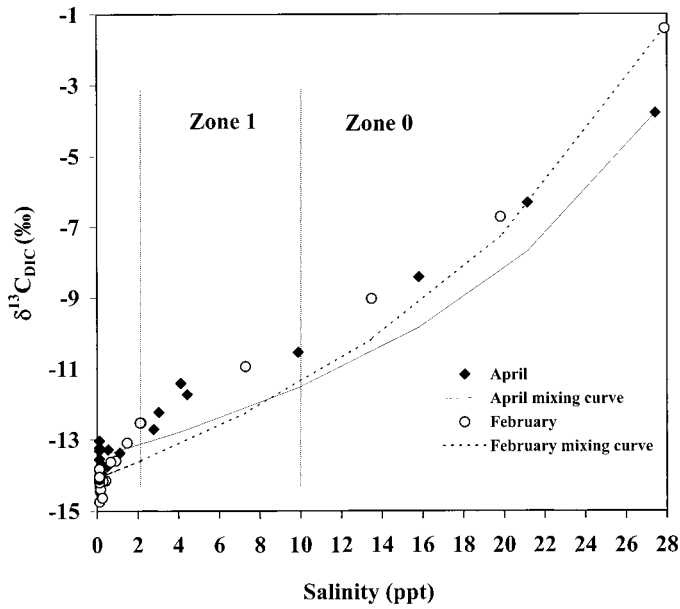


Fig. 8. $\delta^{13}\text{C}_{\text{DIC}}$ (‰) versus salinity for February and April 1999. Lines represent the $\delta^{13}\text{C}_{\text{DIC}}$ values calculated from mass balance equations for February 1999 and April 1999.

diatom-dominated phytoplankton to develop (Muylaert et al. 1997). Gross primary production values for 1996 were estimated to vary between $85 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the brackish region (Zone 1) to $420 \text{ g C m}^{-2} \text{ yr}^{-1}$ in the freshwater reaches (Zones 2 and 3; Muylaert 1999). During the present study, very high Chl *a* concentrations ($>100 \mu\text{g L}^{-1}$) were reached in both summers (Figs. 2, 3H).

We now compare the observed distribution of DIC and $\delta^{13}\text{C}_{\text{DIC}}$ along the estuary with the situation resulting from pure conservative behavior. This requires information for the entire salinity range in the estuary, which is the case for the sampling campaigns in February and April 1999. Conservative mixing requires the $\delta^{13}\text{C}_{\text{DIC}}$ to obey the ^{13}C mass balance equation (Mook and Tan 1991)

$$\begin{aligned} \delta^{13}\text{C} = & [\text{Sal}(\text{DIC}_F \delta^{13}\text{C}_F - \text{DIC}_M \delta^{13}\text{C}_M) + \text{Sal}_F \text{DIC}_M \delta^{13}\text{C}_M \\ & - \text{Sal}_M \text{DIC}_F \delta^{13}\text{C}_F] \\ & \div [\text{Sal}(\text{DIC}_F - \text{DIC}_M) + \text{Sal}_F \text{DIC}_M - \text{Sal}_M \text{DIC}_F], \end{aligned} \quad (2)$$

where Sal is salinity and subscripts F and M refer to freshwater and marine end members, respectively.

Because of the higher DIC content of the freshwater end-member, the mixing line curvature is concave downward (Fig. 8). Values for the marine end-member were: February 1999, $\text{DIC}_M = 2.62 \text{ mM}$, $\delta^{13}\text{C}_M = -1.4\text{‰}$, $\text{Sal}_M = 27.9\text{‰}$; April 1999, $\text{DIC}_M = 2.63 \text{ mM}$, $\delta^{13}\text{C}_M = -3.8\text{‰}$, $\text{Sal}_M = 27.4\text{‰}$. Average values for the area between km 97.5 and 155 (salinity $< 0.18\text{‰}$) were taken as the freshwater end-member situation: February 1999, $\text{DIC}_F = 5.49 \text{ mM}$, $\delta^{13}\text{C}_F = -14.1\text{‰}$, $\text{Sal}_F = 0.13\text{‰}$; April 1999, $\text{DIC}_F = 5.79 \text{ mM}$, $\delta^{13}\text{C}_F = -13.4\text{‰}$, $\text{Sal}_F = 0.11\text{‰}$.

From Fig. 8 it is clear that behavior is nonconservative, with about 1‰ ^{13}C enrichment of the DIC pool throughout

Zones 1 and 0. Because phytoplankton activity was still low during February and April 1999, it seems unlikely that autotrophic carbon fixation is responsible for the observed ^{13}C enrichment of DIC. The isotopic discrimination associated with translocation of inorganic carbon from water to atmosphere varies between -7.4‰ (at 30°C) and -10.8‰ (at 0°C), enriching the dissolved inorganic carbon pool in ^{13}C (Mook et al. 1974; Gruber et al. 1999). In February and April 1999, transit time of water through Zone 1 was 16 d, and we calculated that 37 and $74 \times 10^6 \text{ mol CO}_2$ were lost to the atmosphere over this period in February and April 1999, respectively. This is equivalent to 0.17 and 0.34 mol m^{-3} , considering a Zone 1 water volume of $219 \times 10^6 \text{ m}^3$ and represents between 5 and 9% of the average DIC concentration for Zone 1 (3.8 mol m^{-3}). With a fractional yield of 0.05 to 0.09 and a discrimination related with CO_2 efflux of about 10‰ for water temperatures between 6 and 12°C , we calculated CO_2 efflux could enrich the DIC pool by about 0.5 to 0.9‰ , which is close to the observed ^{13}C enrichment for DIC between arrival to and exit of Zone 1. This simple calculation identifies water-air CO_2 efflux as a further process having the potential to affect the isotopic signature of the river DIC pool.

DIC mass balance—The following DIC mass balance approach is similar to that applied by others (Quay et al. 1986; Herczeg and Fairbanks 1987; Yang et al. 1996). Our approach, however, differs in that we have included a dispersive mixing term (Soetaert and Herman 1995; De Smedt et al. 1998) for the exchange between Zones 1 and 0. The rates of change of the DIC concentrations for the three zones are written as follows.

$$\begin{aligned} V_{Z1} \left(\frac{\Delta \text{DIC}_{Z1}}{\Delta t} \right) = & Q_{21} \text{DIC}_{Z2} - Q_{10} \text{DIC}_{Z1} \\ & - A_{10} E_{10} \left(\frac{\Delta \text{DIC}_{10}}{\Delta x} \right) - F_{Z1} S_{Z1} + J_{\text{DIC}Z1} \end{aligned} \quad (3)$$

$$\begin{aligned} V_{Z2} \left(\frac{\Delta \text{DIC}_{Z2}}{\Delta t} \right) = & Q_{32} \text{DIC}_{Z3} + Q_{\text{RU}} \text{DIC}_{\text{RU}} - Q_{21} \text{DIC}_{Z2} \\ & - F_{Z2} S_{Z2} + J_{\text{DIC}Z2} \end{aligned} \quad (4)$$

$$\begin{aligned} V_{Z3} \left(\frac{\Delta \text{DIC}_{Z3}}{\Delta t} \right) = & Q_{\text{BS}} \text{DIC}_{\text{BS}} + Q_{\text{DE}} \text{DIC}_{\text{DE}} - Q_{32} \text{DIC}_{Z3} \\ & - F_{Z3} S_{Z3} + J_{\text{DIC}Z3} \end{aligned} \quad (5)$$

$V_{Zi}(\Delta \text{DIC}_{Zi}/\Delta t)$ is the time rate of change of DIC calculated from the differences in zonal average DIC content between successive months and the time elapsed. $Q_{i,i-1} \text{DIC}_{Zi}$ represents DIC advection by river flow between successive zones, where Q is the discharge rate. $Q_{\text{RU}} \text{DIC}_{\text{RU}}$, $Q_{\text{DE}} \text{DIC}_{\text{DE}}$, and $Q_{\text{BS}} \text{DIC}_{\text{BS}}$ represent DIC advection by the tributaries, and Ru is Rupel, De is Dender, and BS is Bovenshelde. $A_{10} E_{10} (\Delta \text{DIC}_{10}/\Delta x)$ is the dispersion term, where ΔDIC_{10} is the concentration difference through the interface between Zones 1 and 0, Δx is the dispersion length, A_{10} is the cross-surface area of the interface between Zones 1 and 0, and E_{10} is the tidal dispersion coefficient. $F_{Zi} S_{Zi}$ represents the zon-

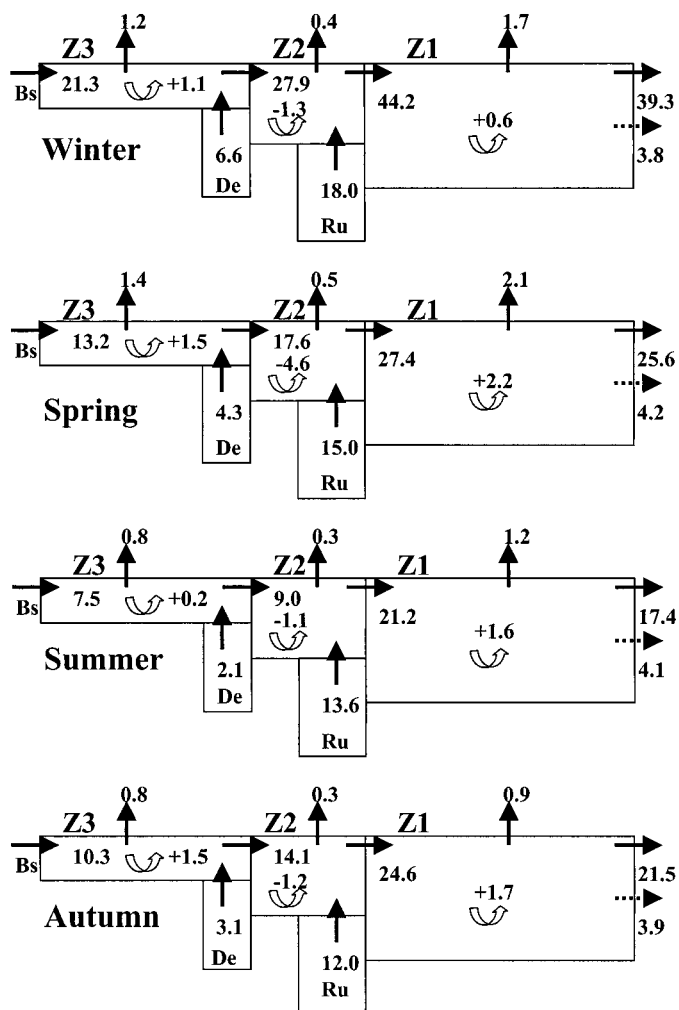


Fig. 9. Inorganic carbon flows (10^6 mol d^{-1}) for average winter, spring, summer, and autumn situations for the period from January 1996 to April 1999. Curved arrow represents net conversion of organic carbon into DIC; broken arrow represents dispersive transport. Tributaries are Bs, Bovenschelde; De, Dender; Ru, Rupel. Zonal areas are: Zone 1, $20.77 \times 10^6 \text{ m}^2$; Zone 2, $3.16 \times 10^6 \text{ m}^2$; Zone 3, $8.47 \times 10^6 \text{ m}^2$.

ally integrated flux of CO_2 from river to atmosphere. $J_{\text{DIC}z_i}$ represents the net conversion of organic carbon to DIC (i.e., DIC production from respiration minus inorganic carbon uptake). This value is set to close the balance.

The dispersion term was considered for the interface between the brackish (Zone 1) and the marine zone (Zone 0) but was neglected for the upstream zones because of very small dispersion coefficients (Soetaert and Herman 1995). We used a value of $130 \text{ m}^2 \text{ s}^{-1}$ for the tidal dispersion coefficient (E_{10}) and of $12,000 \text{ m}^2$ for A_{10} , the cross-surface area (Soetaert and Herman 1995).

Values of the different flux terms were calculated for the whole data set covering 34 months. Figure 9 shows the results for the average winter, spring, summer, and autumn situations. Flux terms were subjected to error calculation according to Miller and Miller (1984). Highest relative error on advective flows and CO_2 efflux is 40%, but in general,

errors on both of these flux terms are smaller ($<20\%$). Relative errors on time rate of change (TRC) and on net conversion of organic carbon to DIC, however, are much larger and frequently exceed 100%. Because overall TRC values were small compared to the advective terms, they were neglected. From Fig. 9, it appears that net conversion of organic carbon into DIC for Zones 3 and 1 is always positive, indicating predominance of heterotrophy over autotrophy. For Zone 3, the seasonally averaged daily net conversion of organic carbon into DIC ranges between 0.2 and $1.5 \times 10^6 \text{ mol d}^{-1}$. Zone 2 consistently shows a net consumption of DIC, ranging between -4.6 and $-1.1 \times 10^6 \text{ mol d}^{-1}$. This consumption of DIC must be related with the process contributing for about 8% of the observed DIC decrease in Zone 2. This process could be CaCO_3 precipitation (see beginning of Discussion).

For Zone 1, daily average net conversion of organic carbon ranges between 0.6 and $2.2 \times 10^6 \text{ mol d}^{-1}$. The yearly averaged net conversion of organic carbon into DIC amounts to $520 \text{ g C m}^{-2} \text{ yr}^{-1}$ for Zone 3 and $410 \text{ g C m}^{-2} \text{ yr}^{-1}$ for Zone 1. These estimates are of the same order of magnitude, but lower than the values estimated by Soetaert and Herman (1995) using the ecosystem model MOSES (between 750 and $1,200 \text{ g C m}^{-2} \text{ yr}^{-1}$). The combined zonally integrated net conversion of organic carbon to DIC for Zones 3 and 1 (i.e., $2.9 \times 10^6 \text{ mol d}^{-1}$ or $12.9 \times 10^9 \text{ g C yr}^{-1}$) represents about 13% of the anthropogenic input of $100 \times 10^9 \text{ g C yr}^{-1}$ reported by Wollast (1988) and is similar to the efflux of CO_2 estimated at $12 \times 10^9 \text{ g C yr}^{-1}$ for both zones combined (see above). Our net organic carbon to DIC conversion rates are clearly in excess of 1996 gross primary production rates, reported to average $420 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the freshwater zone and $85 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the brackish zone (Muylaert 1999). These findings are in agreement with earlier observations for the Scheldt, indicating that the total respiration rate consistently exceeds total primary production (e.g., Billen et al. 1988; Soetaert and Herman 1995; Frankignoulle et al. 1996; Goosen et al. 1997).

This study confirms the marked heterotrophic character of the Scheldt Estuary. The freshwater part of this estuary has higher DIC, pCO_2 , and water-air CO_2 efflux per unit surface, and DIC is depleted in ^{13}C relative to the brackish and marine zones. In winter, DIC and pCO_2 are higher, and DIC becomes depleted in ^{13}C relative to summer, probably as a result of continued bacterial respiration and diminished autotrophic carbon fixation. Phytoplankton blooms reduce pCO_2 and CO_2 efflux during summer and tend to enrich DIC in ^{13}C . Mass balance calculations show a seasonally averaged net conversion of organic carbon to DIC in the upstream and brackish sections of the river, highlighting the heterotrophic status of the river. This conversion is similar in magnitude to the calculated CO_2 efflux. The river section receiving the waters from the main tributary, the Rupel, consistently shows significant decrease of DIC because of dilution. This is accompanied by slightly increased pCO_2 and decreased $\delta^{13}\text{C}_{\text{DIC}}$, indicating dilution of bulk river water with waters having even higher organic carbon load. Finally, net consumption of DIC in the section receiving the waters from the Rupel is possibly related with CaCO_3 precipitation.

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