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Planktonic and Whole System Metabolism in a Nutrient-rich Estuary (the Scheldt Estuary)

FRÉDÉRIC GAZEAU[1,4,*], JEAN-PIERRE GATTUSO[1], JACK J. MIDDELBURG[2], NATACHA BRION[3], LAURE-SOPHIE SCHIETTECATTE[4], MICHEL FRANKIGNOULLE[4,†], and ALBERTO VIEIRA BORGES[4]

[1] *Laboratoire d'Océanographie de Villefranche, Centre National de la Recherche Scientifique (CNRS)-Université de Paris 6, B. P. 28, F-06234 Villefranche-sur-mer Cedex, France*

[2] *Netherlands Institute of Ecology (NIOO-KNAW) Centre for Estuarine and Marine Ecology, Postbus 140, 4400 AC Yerseke, The Netherlands*

[3] *Department of Analytical and Environmental Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium*

[4] *Unité d'Océanographie Chimique (B5), Interfaculty Centre for Marine Research, (MARE), Université de Liège, B-4000 Sart Tilman, Belgium*

ABSTRACT: Planktonic gross primary production (GPP), community respiration (CR), and nitrification (NIT) were measured monthly in the Scheldt estuary by the oxygen incubation method in 2003. No significant evolution of planktonic GPP was observed since the 1990s with high rates in the freshwater area (salinity 0; 97 ± 65 mmol C m^{-2} d^{-1}) decreasing seaward (22–37 mmol C m^{-2} d^{-1}). A significant decrease of NIT was observed with regard to previous investigations although this process still represents up to 20% of total organic matter production in the inner estuary. Planktonic CR was highest in the inner estuary and seemed to be mainly controlled by external organic matter inputs. Planktonic net community production was negative most of the time in the estuary with values ranging from −300 to 165 mmol C m^{-2} d^{-1}. Whole estuary net ecosystem production (NEP) was investigated on an annual scale using the results mentioned above and published benthic metabolic rates. A NEP of −39 ± 8 mmol C m^{-2} d^{-1} was estimated, which confirms the strong heterotrophic status of this highly nutrified estuary. NEP rates were computed from June to December 2003 to compare with results derived from the Land-Ocean Interaction in the Coastal Zone budgeting procedure applied to dissolved inorganic phosphorus and carbon (DIP and DIC). DIP budgets failed to provide realistic estimates in the inner estuary where abiotic processes account for more than 50% of the nonconservative DIP flux. DIC budgets predicted a much lower NEP than in situ incubations (−109 ± 31 versus −42 ± 9 mmol C m^{-2} d^{-1}) although, as each approach is associated with several critical assumptions, the source of this discrepancy remains unclear.

Introduction

Estuaries are highly dynamic systems with large seasonal and spatial gradients of biogeochemical compounds and processes (Heip et al. 1995). Linking land to the ocean, they are often greatly influenced by human activities, including enhanced organic matter and nutrient loadings. Among other parameters, the balance between organic matter and nutrient loading is critical in determining the balance between autotrophy and heterotrophy at the ecosystem level (Kemp et al. 1997; Eyre and McKee 2002).

An ecosystem is autotrophic when production of organic matter by primary producers exceeds the consumption of this matter by the overall community. Such systems are potentially net sinks for atmospheric carbon dioxide (CO_2) although air-sea CO_2 flux is also controlled by external inputs of dissolved inorganic carbon (DIC; Gattuso et al. 1998; Borges 2005), calcium carbonate ($CaCO_3$) precipitation and dissolution (Wollast et al. 1980), and thermodynamic effects. In a heterotrophic ecosystem, organic matter consumption exceeds primary production, leading generally to high CO_2 partial pressures (pCO_2) and low oxygen (O_2) concentrations in the water column (Frankignoulle et al. 1998). Primary production is light limited in many estuaries due to high turbidity, driving these systems toward heterotrophy (Smith and Hollibaugh 1993; Gattuso et al. 1998).

Estuaries are generally oversaturated in CO_2 with respect to atmospheric equilibrium, with CO_2 effluxes ranging from 10 to 660 mmol C m^{-2} d^{-1} (Abril and Borges 2004; Borges 2005). Such emissions of CO_2 can have a significant effect on

* Corresponding author; current address: Netherlands Institute of Ecology (NIOO-KNAW)–Centre for Estuarine and Marine Ecology, Postbus 140, 4400 AC Yerseke, The Netherlands; tele: +31 (0) 113-577466; fax: +31 (0) 113-573616; e-mail: f.gazeau@nioo.knaw.nl

† Deceased on March 13, 2005

regional CO_2 budgets. European estuaries emit between 5% and 10% of present anthropogenic CO_2 emissions for western Europe (Frankignoulle et al. 1998). Globally, the CO_2 emission from estuaries could balance the CO_2 sink associated with marginal seas, rendering the overall coastal ocean neutral regarding the exchange of CO_2 with the atmosphere (Borges 2005; Borges et al. 2005).

A wide range of techniques have been used to estimate the trophic status of coastal sites. Each of them relies on one or more assumptions and covers different spatial and temporal scales. Metabolic rate measurements based on incubation methods (mainly O_2 and ^{14}C) or open water O_2 measurements (Odum 1956; Kemp and Boynton 1980; Howarth et al. 1992; Caffrey 2004) have been used in numerous studies. Incubations supposedly eliminate the effects of mixing and turbulence that may affect both primary production and respiration (Kemp and Boynton 1980; Howarth et al. 1992). Whole system estimates based on this approach can be biased as some ecosystem components, such as macrophytes or large grazers, are not taken into account. The accuracy of open-water metabolic rates assessments depends critically on accurate air-water exchange parameterization.

Within the Land-Ocean Interaction in the Coastal Zone (LOICZ; Gordon et al. 1996) program of International Geosphere-Biosphere Programme, a stoichiometric budgeting approach has been applied to more than 200 coastal sites. This approach provides system scale estimates and is easily implemented as it is based on usually well studied and available variables. Gordon et al. (1996) recommended dissolved inorganic phosphorus (DIP) as the main variable to be used to compute net ecosystem production (NEP) rates using the LOICZ budgeting procedure but in turbid estuaries, processes of adsorption and desorption to and from suspended particles and sediment (Froelich 1988) can introduce a bias in the estimates. DIC can also be used to compute NEP but it requires knowledge on other processes, besides primary production and respiration, that are likely to have an effect on DIC in coastal systems, such as CO_2 fluxes at the air-water interface and $CaCO_3$ precipitation and dissolution (Gordon et al. 1996).

In order to assess the metabolic status of the coastal zone on a global scale, there is a great need to derive estimates for a wide range of ecosystems. As mentioned above, several techniques are available to attain such an objective but very few studies have focused on comparing different methods (Kemp et al. 1997; Gazeau et al. 2005) and testing their validity in a variety of ecosystem types.

The purpose of the EUROTROPH project (http://www.ulg.ac.be/oceanbio/eurotroph/) was to determine the metabolic status of three European coastal ecosystems (Randers Fjord, Scheldt estuary, and Bay of Palma) using several techniques and to compare the estimates at several time scales. In this paper, we report, compare, and discuss the metabolic status of the Scheldt estuary (Belgium and the Netherlands; Fig. 1) based on in situ incubation measurements and the LOICZ budgeting procedure applied to both DIP and DIC.

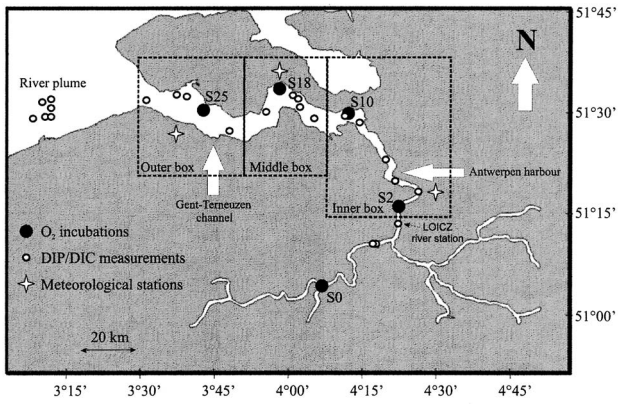

Fig. 1. Map of the Scheldt estuary showing the average position of each fixed salinity where O_2 incubations were performed as well as the location of the monitoring stations where dissolved inorganic phosphorus and carbon (DIP and DIC) concentrations, used in the LOICZ budgets, were measured. The location of the three meteorological stations from where wind speed measurements were obtained are also shown.

Study Site Description

The Scheldt estuary is one of the most eutrophic estuaries in Europe as a result of urban wastewater drainage and runoff from agriculture (Wollast 1988). The river Scheldt, with a catchment area of 19,500 km^2 (Heip 1989), is the most important freshwater source to the estuary. Tidal exchange is, on average, 200 times higher than the freshwater input (Wollast 1988). The freshwater residence time is long, ranging from 70 d in the inner estuary to 10–15 d in the outer estuary (Soetaert and Herman 1995b). Salinity ranges from about 0.5 at Temse to about 28 at the mouth of the estuary. Due to strong tidal currents (up to 1.5 m s^{-1}), the water column is well mixed throughout the estuary (Wollast 1988). Turbidity is high in the entire inner estuary and phytoplankton is light limited rather than nutrient limited (van Spaendonk et al. 1993; Kromkamp and Peene 1995) as ammonium (NH_4), nitrate, and DIP concentrations in the brackish zone usually exceed 100, 300, and 5 mmol m^{-3}, respectively (Soetaert et al. 2005). Intensive bacterial growth has been measured and is among the highest reported in the literature (Goosen et al. 1995); it is fueled

mainly by allochtonous inputs (Boschker et al. 2005). These high levels of bacterial activity coupled with the long freshwater residence time lead to O_2 depletion and a large efflux of CO_2 to the atmosphere in the inner and middle estuary (Frankignoulle et al. 1996, 1998). It is one of the most studied coastal systems in western Europe, and although several biogeochemical models or budgets have been reported and provide estimates of its metabolic status (Soetaert and Herman 1995a; Hellings et al. 2001; Vanderborght et al. 2002), no direct measurements have been carried out in the past.

Following periods of strong summer depletions of O_2 and severe associated fish and invertebrates mortality at the end of the 1970s (Heip 1988), wastewater treatment plants were constructed in the drainage basin of the Scheldt estuary. This resulted in a significant improvement of water quality in the river, its tributaries, and the estuary over the past 20 yr (Billen et al. 2005; Soetaert et al. 2005). The results obtained for 2003 are compared to previous estimates of biogeochemical processes and their relation to water quality improvements is discussed.

Materials and Methods

Water Analysis

From January to December 2003, at 17 fixed stations (hereafter referred to as monitoring stations; Fig. 1), subsurface samples were taken for salinity, nutrient, and pigment analyses. For pigment, water (500 to 1500 ml) was filtered through GF/F filters, which were stored frozen, pending extraction and analysis by high-performance liquid chromatography (Barranguet et al. 1998). Automated colorimetric techniques were used to measure concentrations of DIP, nitrate + nitrite (NO_x), NH_4, and silicates (Si).

Total alkalinity (TA) and pH were measured at the beginning of each planktonic incubation (see below) and, from June to December 2003, at each of the 17 monitoring stations. TA was measured by Gran electro-titration on 50-ml GF/F filtered samples with a reproducibility of ± 2 μmol kg^{-1} and an estimated accuracy of ± 3 μmol kg^{-1}. pH was measured using a combined electrode (Metrohm) with a reproducibility of ± 0.004 pH units. Frankignoulle and Borges (2001) provide details on the pH calibration procedure and pCO_2 and DIC computation from the pH and TA measurements. O_2 concentrations were measured at each monitoring station from January to December 2003 using an automated Winkler titration technique with a potentiometric end point detection. Analyses were performed with a Mettler Toledo DL50 titrator and a platinum (Pt) redox electrode. O_2 percentages of saturation ($O_{2\%sat}$) were computed using O_2 concentrations at saturation estimated with the algorithms given by Benson and Krause (1984).

Planktonic O_2 Incubations

Planktonic gross primary production (GPP), community respiration (CR), and O_2 consumption due to nitrification (NIT) were measured monthly from January to December 2003, except in April, at five fixed salinities (± 1): 0, 2, 10, 18, and 25. Figure 1 shows the annual average geographical position of the stations corresponding to each salinity. Surface water samples (at least 3 replicates) were incubated in a 5-compartment on deck incubator for at least 6 h in transparent 60-ml biochemical oxygen demand bottles. Samples were kept at in situ temperature by flowing water, and irradiance was controlled in each compartment with filters having a shading capacity of 0%, 81%, 87%, 92%, and 100%. In order to avoid sedimentation of particulate material, bottles were fixed on a rotating device (1 rpm).

Concentrations of dissolved O_2 were measured before and after incubation using an automated Winkler titration technique with a potentiometric end point detection. Analyses were performed with an Orion redox electrode (9778-SC) and a custom built titrator from January to June 2003 and with a Mettler Toledo DL50 titrator and a Pt redox electrode for the rest of the study period. Reagents and standardizations were similar to those described by Knap et al. (1996). The O_2 consumption due to CR and NIT (both expressed as negative values) was partitioned by incubating samples in the dark compartment with and without addition of the nitrification inhibitors N-serve (Nitrapyrine; 5 mg l^{-1}) and chlorate (10 mmol l^{-1}), as described in Berounsky and Nixon (1993) and Brion et al. (2000). As the N-serve inhibitor is dissolved in ethanol, its addition might enhance bacterial respiration, so control samples were also incubated in the dark with addition of ethanol only. Hourly NIT and CR rates were estimated as:

$$\mathrm{NIT} = \left[\frac{\Delta O_{2d\_eth} - \Delta O_{2d\_inh}}{\Delta O_{2d\_eth}} \times \Delta O_{2d}\right]/t \quad (1)$$

$$\mathrm{CR} = \frac{\Delta O_{2d}}{t} - \mathrm{NIT} \quad (2)$$

where ΔO_{2d}, ΔO_{2d_eth}, and ΔO_{2d_inh} are O_2 variations during the incubations in the dark and with addition of ethanol and inhibitors, respectively; t is the duration of the incubations (h). ΔO_{2d_eth} was, on average during the annual cycle, 45 ± 40% higher than ΔO_{2d}, illustrating the need for control incubations.

At each irradiance level, hourly net community production during daylight (NCP_d) was estimated as the difference between O_2 concentrations before and after incubations. Hourly planktonic GPP rates for each irradiance level were calculated as:

$$GPP = NCP_d - (CR + NIT) \quad (3)$$

Light in the water column was measured using LI-COR LI-193SA Spherical Quantum Sensor that was connected to a LI-COR LI-1400 data logger. Surface irradiance data were obtained every hour at the Netherlands Institute of Ecology (Yerseke, The Netherlands) using a LI-COR LI-190SA quantum sensor coupled to a LI-COR LI-1000 data logger. Light attenuation in the water column was estimated using the formulation:

$$K = -\frac{\ln(I_z/I_0)}{z} \quad (4)$$

where K is the light attenuation coefficient (m^{-1}), I_z is the irradiance measured at depth z ($\mu mol\ m^{-2}\ s^{-1}$), I_0 is surface irradiance ($\mu mol\ m^{-2}\ s^{-1}$), and z is depth (m).

For each station, relationships between hourly GPP rates ($mmol\ O_2\ m^{-3}\ h^{-1}$) and average irradiances during the incubations in each compartment (I in $\mu mol\ m^{-2}\ s^{-1}$, estimated using data of surface irradiance) were established by fitting the model of Platt et al. (1980) to our data:

$$GPP = GPP_{max}[1 - \exp(-I/I_k)] \quad (5)$$

where GPP_{max} is the maximal GPP rate ($mmol\ O_2\ m^{-3}\ h^{-1}$) and I_k is the irradiance at which the initial slope and GPP_{max} intersect ($\mu mol\ m^{-2}\ s^{-1}$).

Because of the duration of the incubations (usually less than 10 h) and to correct for the daily variability of surface irradiance, hourly GPP rates were recalculated using a mean daily surface irradiance for each month. Daily planktonic CR and NIT rates were calculated by multiplying the hourly rates by 24. Hourly GPP rates were multiplied by the daylight duration during each month to estimate daily planktonic GPP.

These volumetric rates were depth integrated using a bathymetric study of the estuary carried out with the Arcview 8.3 software package. The depths corresponding to irradiance levels available in each compartment of the on deck incubator were estimated using collected data of light attenuation in the water column (K; see above). At each station, 9 depth intervals were considered and all metabolic parameters were integrated using a simple trapezoidal procedure with regard to the depth gradient (i.e., percentage of area covered by each depth interval) although GPP rates were integrated only up to the depth of 1% of surface irradiance.

These oxygen based values were converted into carbon units using a photosynthetic quotient (PQ) of 1.3, a respiratory quotient (RQ) of 1, and a NIT O_2:C ratio of −14. This latter conversion factor was estimated from simultaneous N-serve-sensitive ^{14}C bicarbonate NIT measurements (Andersson et al. 2005) on four occasions in 2003. Planktonic daily net community production (NCP) rates were estimated as the sum of GPP, CR, and NIT.

Whole System Metabolism Using In Situ Incubations

In order to compare with results obtained using the LOICZ procedure, the estuary was divided into three boxes (see Fig. 1). As no benthic measurements were performed during the whole annual cycle, NEP based on in situ incubations was estimated using planktonic metabolism results detailed above and published benthic intertidal metabolic rates (Middelburg et al. 1996; Barranguet et al. 1998). Planktonic GPP, CR, and NIT rates in the inner box were estimated by averaging results obtained at salinities 2 and 10, and in the middle and outer boxes results obtained at salinity 18 and 25 were used, respectively. In November 2002 and April 2003, Barrón and Duarte (unpublished data) measured benthic mineralization rates in subtidal areas of the Scheldt estuary using the O_2 incubation method. These values correspond, on average, to 20% of intertidal CR rates measured by Middelburg et al. (1996) in 1991, based on CO_2 and methane (CH_4) fluxes, during the same periods of the year. As subtidal CR data from Barrón and Duarte do not cover an annual cycle, subtidal mineralization was assumed to represent 20% of intertidal rates derived from the annual values of Middelburg et al. (1996). The percentage of area covered by the intertidal flats was estimated by a bathymetric study in each box (40%, 23%, and 17% in the inner, middle, and outer boxes, respectively). Benthic intertidal GPP rates available for one station (Molenplaat; Barranguet et al. 1998) located in the middle box were used, assuming a zero primary production by microphytobenthos in subtidal areas due to light limitation.

Using all data described above, NEP rates were estimated both on an annual scale and for the period June to December 2003 that allows direct comparison with the LOICZ approach (see below).

Whole System Metabolism Using the LOICZ Budgeting Procedure

Biogeochemical modelling according to Gordon et al. (1996) was applied monthly using salinity,

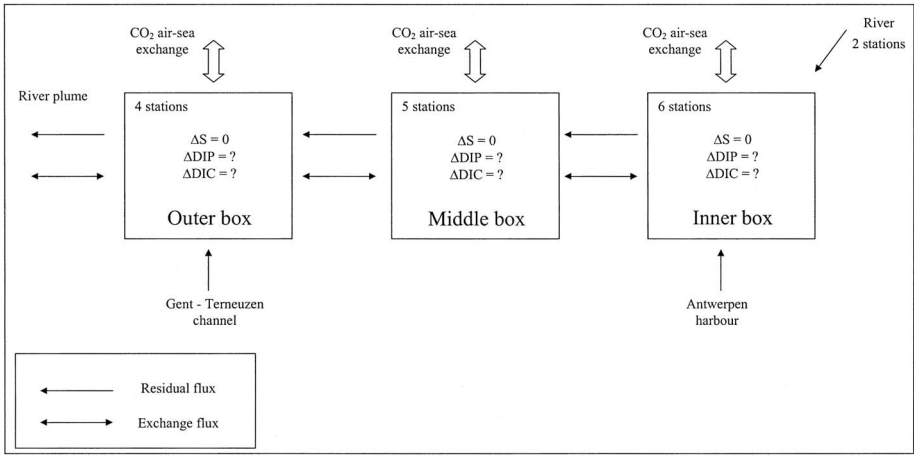

Fig. 2. Land-Ocean Interaction in the Coastal Zone (LOICZ) budgeting procedure for the Scheldt estuary from June to December 2003.

DIP, DIC, and pCO_2 data obtained at each monitoring station (Fig. 1) from June to December 2003. Water in the Scheldt estuary is well mixed throughout the year and a 3-box model was considered using the same division of the estuary as described above. The monitoring station located upstream of the inner box and stations located in the river plume were used as the riverine and marine end members, respectively. The river plume data of DIC and DIP were collected during several cruises from June to December 2003 (carbon, nitrogen, and phosphorus cycling in the North Sea CANOPY project, Federal Office for Scientific, Technical and Cultural Affairs, Research Project EV/12/20C, 2002–2006).

Daily freshwater fluxes were provided by the Ministerie van de Vlaamse Gemeenschap, Belgium (http://www.vlaanderen.be). Soetaert et al. (2005) estimated that 32% of the total freshwater flow to the Scheldt estuary comes from lateral sources (12% from the Gent-Terneuzen channel, 10% from the Antwerpen harbour, and 10% from diffuse sources and small canals). Monthly data of DIP in the Gent-Terneuzen channel (station Zelzate; 51.2°N, 3.82°E), as well as at several stations in the Antwerpen harbour, were provided by the Flemish Environmental Agency, Belgium (http://www.vmm.be). DIC concentrations at these stations were estimated from reported $O_{2\%sat}$ data using an empirical DIC versus $O_{2\%sat}$ relationship established during the study period in the Scheldt estuary:

$$\mathrm{DIC} = -21\mathrm{O}_{2\%\mathrm{sat}} + 4738 \quad \left(r^2 = 0.88, p < 0.001, n = 116\right) \tag{6}$$

where DIC is expressed in mmol m^{-3}. No data of DIP and DIC loadings from diffuse sources and small canals were available for the year 2003. Representing 10% of the total water input, this source of nutrient was neglected in the budget.

Residual and exchange fluxes were estimated using data of water flow (Scheldt river, Antwerpen harbour, and Gent-Terneuzen channel) assuming that water and material inputs and outputs from precipitation and evaporation are negligible and salinity (conservative parameter) considering steady state over a tidal cycle ($dS/dt = 0$; Fig. 2). Using these residual and exchange fluxes as well as data of DIP and DIC concentrations in each budgeted box, nonconservative fluxes (basically, deviation from the dilution-mixing line) of DIP (ΔDIP) and DIC (ΔDIC) were estimated as the difference between DIP and DIC outputs and inputs in each budgeted box (Gordon et al. 1996).

NEP (p-r in the LOICZ terminology) was calculated from the nonconservative fluxes of DIP, assuming that these fluxes are only related to biological activity:

$$\mathrm{NEP} = -\Delta\mathrm{DIP} \times (\mathrm{C:P})_{\mathrm{part}} \tag{7}$$

where NEP is expressed in mmol C m^{-2} d^{-1}, ΔDIP is in mmol P m^{-2} d^{-1}, and $(C:P)_{part}$ is the particulate C:P ratio (a value of 106:1 was used).

NEP was also computed from the nonconservative fluxes of DIC (Gordon et al. 1996). These DIC fluxes (ΔDIC) are attributed not only to the difference between production and mineralization of organic matter ($NEP = -\Delta DIC_o$), but also to net CO_2 exchanges with the atmosphere (ΔDIC_g) and precipitation and dissolution of $CaCO_3$ (ΔDIC_c):

$$\mathrm{NEP} = -\left(\Delta\mathrm{DIC} - \Delta\mathrm{DIC_g} - \Delta\mathrm{DIC_c}\right) \tag{8}$$

As, to our knowledge, no information on precipitation and dissolution of $CaCO_3$ is available in the saline Scheldt estuary, this process was assumed negligible ($\Delta DIC_c = 0$) in the present study.

The air-water CO_2 flux was computed according to:

$$F = \alpha k \Delta pCO_2 \quad (9)$$

where F is the air-water CO_2 flux (mmol m^{-2} d^{-1}), α is the CO_2 solubility coefficient (mmol m^{-3} ppm^{-1}), k is the gas transfer velocity (m d^{-1}), and ΔpCO_2 is air-water gradient of CO_2 ($pCO_{2water} - pCO_{2air}$, in ppm). A positive flux corresponds to a transfer of CO_2 from the water to the atmosphere, so in Eq. 8, ΔDIC_g equals $-F$.

To compute ΔpCO_2, we used monthly values of atmospheric CO_2 molar fraction from Weather Station Mike (66.00°N, 2.00°E), representative of the open North Sea waters (from the National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory air samples network, available at http://www.cmdl.noaa.gov/) to which was added a value of 27 ppm that corresponds to the average observed increase of the atmospheric signal in the Scheldt basin (Borges et al. 2004b). The CO_2 molar fraction values were converted to partial pressure values in wet air (pCO_{2air}) using the procedure described in DOE (1994).

k was computed according to a parameterization as a function of wind speed, water current, and depth established from 295 floating chamber interfacial CO_2 flux measurements carried out during 2 cruises in November 2002 and April 2003 (Borges et al. 2004b):

$$k_{600} = 0.24 + 0.4126 w^{0.5} h^{-0.5} + 0.619 u_{10} \quad (10)$$

where k_{600} is the gas transfer velocity of CO_2 normalized to a Schmidt number (Sc) of 600 in m d^{-1}, w is the water current (cm s^{-1}), h is the water depth (m), and u_{10} is the wind speed (m s^{-1}) referenced at a height of 10 m.

Monthly averages of k_{600} were computed from hourly wind speed measurements and modelled water currents at three reference stations representative of the three boxes (Fig. 1). Wind speed data at Hansweert and Hoofdplaat were provided by Hydro Meteo Centrum Zeeland (http://www.hmcz.nl/) and by the Institut Royal de Météorologie de Belgique at Antwerp. Hourly water currents were computed using a 1-dimensional hydrodynamic model of the Scheldt estuary (Regnier et al. 1997). The boundary conditions for the simulation are obtained from a tide prediction routine taking into account the spring-neap oscillation at the estuarine mouth and the daily value of the freshwater discharge measured at the upper limit of the tidal rivers. The k_{600} values were converted to in situ conditions assuming a k dependency proportional to $Sc^{-0.5}$. Sc was computed for a given salinity from the formulations for salinity 0 and 35 given by Wanninkhof (1992) and assuming that Sc varies linearly with salinity.

Error Estimates

Error propagations were performed for each approach (in situ incubations and LOICZ budgets applied to DIP and DIC) using the Monte-Carlo procedure of Matlab 6.5. Each parameter used in the computation of NEP with these methods was randomly changed within reasonable boundaries (95% confidence intervals in case of averaged values) and 1,000 iterations were performed. It should be mentioned that these parameters were assumed to be normally distributed and independent of each other. Averaged values and deviations from the mean (SD) were estimated and are presented in the next sections.

Using the incubation method, analytical errors based on at least triplication in the planktonic compartment and SD provided by Middelburg et al. (1996) and Barranguet et al. (1998) were considered, as well as errors attributed to the averaging of two stations to compute rates for the inner estuary and the averaging to compute either annual or June to December values.

The uncertainty in NEP values based on the LOICZ procedure, both with DIP and DIC, was estimated assuming the SD of the freshwater flow over each month as well as errors attributed to the averaging of several stations for salinity, DIP, and DIC values in each compartment considered in these budgets. Using the LOICZ method applied to DIC, the uncertainty on the CO_2 atmospheric flux was computed assuming the error attributed to the averaging of hourly u_{10} data to compute monthly values. Errors associated with the averaging of monthly budgets outputs to estimate NEP rates from June to December were also considered.

Results

Water Characteristics

Figure 3 presents the annually averaged decrease of NH_4, NO_x, DIP, and Si along the salinity gradient. Dilution lines were drawn between the values at the most marine station and the values obtained at the station used as the riverine end member with the LOICZ budgets (Fig. 1). Seasonal variations in NH_4 and Si concentrations were larger than those of NO_x and DIP concentrations. High values were observed in the freshwater area (>100,

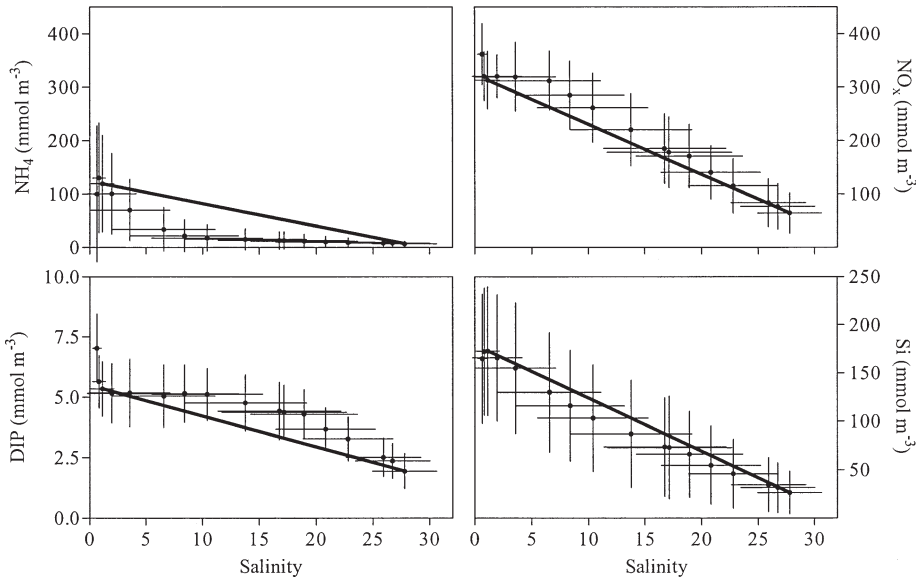

Fig. 3. Annually averaged ammonium (NH_4), nitrate + nitrite (NO_x), dissolved inorganic phosphorus (DIP), and silicate (Si) concentrations in the Scheldt estuary against salinity in 2003. Horizontal and vertical bars represent standard deviations of means.

about 300, >5, and about 150 mmol m^{-3} for NH_4, NO_x, DIP, and Si, respectively). A significant depletion of NH_4 and corresponding enrichment of NO_x with regard to the dilution line were observed in the inner estuary. At low salinities (0–5), DIP values followed the dilution line while production is observed seaward. On an annual basis, the Scheldt estuary appears to be a very small sink for Si.

The annual variation of several parameters at the five salinities sampled during the incubation experiments is presented in Fig. 4. It must be stressed that, as pigment concentrations were not measured at the freshwater station, values obtained at the two most upstream stations (salinity 0–1; see Fig. 1) are presented for these variables.

Along the estuary, pCO_2 was lowest in winter and increased until the end of summer to reach a maximal value of about 10,000 ppm (Fig. 4). pCO_2 was always highest at the freshwater station except in summer when values strongly decreased to reach a minimal value in August (<5,000 ppm). Values were always above atmospheric equilibrium except during an algal bloom in May at salinity 18.

$O_{2\%sat}$ was higher in winter than in spring or summer, especially in the brackish part (salinity 2; Fig. 4). The lowest $O_{2\%sat}$ were measured, almost throughout the year, at salinity 2. In summer, as noted for pCO_2, a strong increase of $O_{2\%sat}$ was observed in the freshwater area. O_2 supersaturations were only measured in the mesohaline part of the estuary (salinity 18) in May.

Planktonic and Whole System Metabolism Using Incubations

Planktonic GPP was high in the freshwater area in summer, where high chlorophyll *a* (chl *a*; Fig. 4) and low phaeopigments concentrations were measured, with a maximal value of 272 mmol C m^{-2} d^{-1} in August (Fig. 5). Seaward, the highest rates were observed in May and July at salinity 18 and 25, respectively. Averaged from January to December 2003, planktonic GPP rates were 97 ± 65, 31 ± 22, 22 ± 13, 37 ± 23, and 35 ± 19 mmol C m^{-2} d^{-1} at salinity 0, 2, 10, 18, and 25, respectively.

Nitrification was always highest in the brackish part with a maximal value of 20 mmol C m^{-2} d^{-1} in May (Fig. 5) and was related to high NH_4 concentrations in the freshwater area. Low nitrification activities were observed seaward with a minimal value in October at salinity 18 (0.2 mmol C m^{-2} d^{-1}). On average, annual NIT represented 5%, 20%, 5%, 3%, and 2% (6 ± 3, 8 ± 5, 1 ± 1, 1 ± 1, and 1 ± 1 mmol C m^{-2} d^{-1}) of total organic production at salinity 0, 2, 10, 18, and 25, respectively.

Planktonic CR was high especially in the freshwater and brackish parts (Fig. 5). Maximal values were observed in May and October, well related to high phaeopigments (Fig. 4) and total organic carbon concentrations (data not shown). The highest rate was measured in October at salinity 2 (−313 mmol C m^{-2} d^{-1}). On an annual scale, CR values of −131 ± 37, −200 ± 83, −48 ± 19, −48 ± 25, and −56 ± 18 mmol C m^{-2} d^{-1} were obtained at salinity 0, 2, 10, 18, and 25, respectively.

Planktonic NCP was negative during most of the year with lowest values in the brackish part

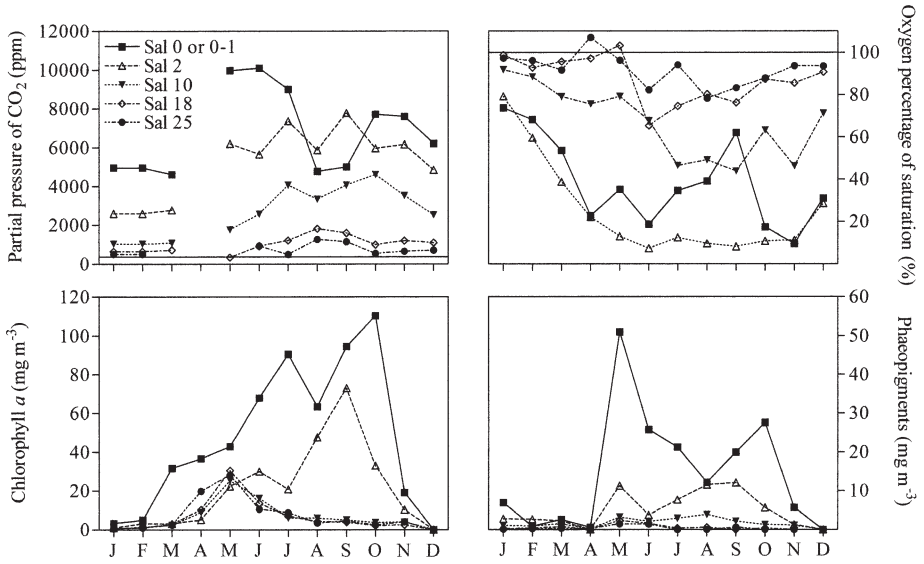

Fig. 4. Surface partial pressure of CO_2, oxygen percentage of saturation, chlorophyll *a*, and phaeopigments concentrations from January to December 2003 at fixed salinities (±1) in the Scheldt estuary. Solid lines correspond to the atmospheric equilibrium.

(minimum in October: −300 mmol C m^{-2} d^{-1}; Fig. 5). In the freshwater area, positive NCP values were recorded in summer (maximum in August; 165 mmol C m^{-2} d^{-1}). Seaward, positive NCP were also measured in April, July, and August. On an annual scale, NCP was −30 ± 4, −158 ± 28, −24 ± 3, −8 ± 3, and −20 ± 4 mmol C m^{-2} d^{-1} at salinity 0, 2, 10, 18, and 25, respectively.

Our results imply that the planktonic compartment was strongly heterotrophic both on an annual scale (−31 ± 4 mmol C m^{-2} d^{-1}) and from June to December (−31 ± 6 mmol C m^{-2} d^{-1}; Table 1). Multiplying intertidal benthic CR rates measured by Middelburg et al. (1996) by the intertidal flats surface area yields June to December mean benthic CR of −35 ± 20, −16 ± 8, and −5 ± 0 mmol C m^{-2} d^{-1} in the inner, middle, and outer estuary, respectively. Benthic GPP values as reported by Barranguet et al. (1998) are rather low and the benthic compartment is heterotrophic except in the

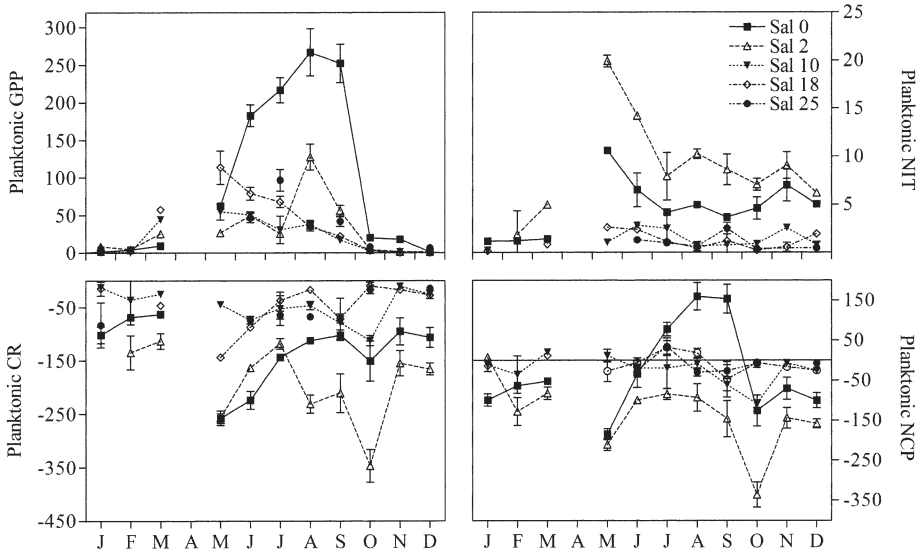

Fig. 5. Metabolic performances from January to December 2003 at fixed salinities (±1) in the Scheldt estuary. Planktonic net community production (NCP) is the sum of phytoplankton gross primary production (GPP), nitrification (NIT), and community respiration (CR). All rates are expressed in mmol C m^{-2} d^{-1}.

TABLE 1. Integrated gross primary production (GPP), community respiration (CR), nitrification (NIT), and net community production (NCP) in the planktonic and benthic compartments of the Scheldt estuary on an annual scale and from June to December 2003 (means ± SD). Benthic metabolic rates were taken from Middelburg et al. (1996) and Barranguet et al. (1998). Computed net ecosystem production (NEP; sum of planktonic and benthic NCP) rates for the same periods are also shown. All rates are expressed in mmol C m^{-2} d^{-1}.

	Plankton				Benthos			
	GPP	CR	NIT	NCP	GPP	CR	NCP	NEP
Annual								
Inner	26 (4)	−122 (27)	4 (2)	−91 (14)	12 (5)	−35 (20)	−23 (20)	−114 (33)
Middle	38 (2)	−47 (2)	1 (0)	−8 (3)	7 (3)	−16 (8)	−9 (8)	−17 (9)
Outer	35 (2)	−55 (4)	1 (0)	−20 (4)	5 (2)	−5 (0)	0 (2)	−20 (5)
Whole estuary	34 (1)	−66 (6)	2 (0)	−31 (4)	7 (3)	−15 (5)	−8 (6)	−39 (8)
June–December								
Inner	29 (6)	−146 (29)	5 (1)	−112 (30)	12 (5)	−43 (21)	−31 (21)	−143 (37)
Middle	29 (1)	−38 (3)	1 (0)	−8 (3)	7 (3)	−21 (9)	−14 (9)	−22 (10)
Outer	40 (2)	−51 (2)	1 (0)	−10 (2)	5 (2)	−5 (0)	0 (2)	−10 (3)
Whole estuary	34 (1)	−66 (6)	2 (0)	−31 (6)	7 (3)	−18 (5)	−11 (6)	−42 (9)

outer estuary with NCP values of −23 ± 20, −9 ± 8, and 0 ± 2 mmol C m^{-2} d^{-1} in the inner, middle, and outer estuary respectively. Integrating all of these metabolic parameters led to a whole estuary NEP of −42 ± 9 mmol C m^{-2} d^{-1} for June to December and −39 ± 8 mmol C m^{-2} d^{-1} on an annual scale.

Whole System Metabolism Using the LOICZ Budgeting Procedure

Characteristics of the modelled boxes (surface area, mean depth, and volume), as well as mean salinity, pCO_2, and DIP and DIC concentrations, are presented in Table 2. The whole estuary acted as a net source of DIP (0.17 ± 0.1 mmol P m^{-2} d^{-1} or 500 ± 294 tP yr^{-1}) and DIC (9 ± 37 mmol C m^{-2} d^{-1} or about 10,000 ± 42,000 tC yr^{-1}; Table 3). NEP computations based on the DIP budget led to an integrated NEP of −19 ± 11 mmol C m^{-2} d^{-1}. It should be noted that the DIP budget revealed a slightly heterotrophic status of the inner estuary with a NEP of −9 ± 4 mmol C m^{-2} d^{-1}. NEP computations based on DIC budgets led to integrated negative NEP of −109 ± 31 mmol C m^{-2} d^{-1}. Estimated CO_2 release to the atmosphere was 118 ± 20 mmol C m^{-2} d^{-1} (135,000 ± 23,000 tC yr^{-1}).

Discussion

Environmental and Metabolic Characteristics of the Scheldt Estuary

Surface water pCO_2 values did not change significantly since the period 1993–1996 (Frankignoulle et al. 1998). In 2003, pCO_2 ranged from 349 ppm (May, outer estuary) to more than 10,000 ppm (or more than 25 times the atmospheric value; June, salinity 0). pCO_2 was generally higher in the freshwater part and decreased along the salinity gradient due to dilution with low pCO_2 marine waters, degassing at the air-water interface, and increasing NEP. O_2 concentrations did not follow a similar pattern along the estuary as lower values were generally found in the inner estuary than in the freshwater zone. This discrepancy between pCO_2 and O_2 can be attributed to high nitrification rates found in the inner estuary as this process consumes more O_2 than it produces CO_2. Although O_2 conditions have improved in the Scheldt estuary since the 1970s (Soetaert et al. 2005) due to a decrease of NIT (see below), $O_{2\%sat}$

TABLE 2. Freshwater flow, surface area, mean depth, and volume of each estuarine box budgeted using the LOICZ procedure. Salinity and other environmental parameters in each budgeted box as well as for the lateral inputs and in the freshwater and river plume areas are also shown. DIP, DIC, and pCO_2 are dissolved inorganic phosphorus, dissolved inorganic carbon, and partial pressure of CO_2, respectively. Each value is an average of several stations (Fig. 1) from June to December 2003 and numbers in parentheses refer to the associated standard deviation.

Compartment	Freshwater flow (m^3 d^{-1})	Area (km^2)	Mean depth (m)	Volume (km^3)	Salinity	DIP (mmol m^{-3})	DIC (mmol m^{-3})	pCO_2 (ppm)
River	5.62×10^6	—	—	—	1.9 (1)	6.37 (0.57)	4349 (99)	5480 (540)
Gent-Terneuzen channel	9.9×10^5	—	—	—	14	17.10	3314	—
Antwerpen harbour	8.26×10^5	—	—	—	4	5.58	3030	—
Inner		54	8.8	475	8.9 (2.2)	6.31 (0.64)	3822 (128)	3551 (634)
Middle		93	9.5	884	20.9 (2)	5.24 (0.59)	3039 (97)	1137 (319)
Outer		113	12.9	1455	28.6 (1.1)	2.88 (0.59)	2550 (73)	682 (176)
River plume		—	—		32.3 (0.5)	1.43 (0.33)	2333 (181)	570 (136)
Whole estuary		260	9.7	2814	—	4.21 (1.6)	2931 (578)	1360 (1496)

TABLE 3. Budgeting of nutrient fluxes, air-sea CO_2 fluxes, and net ecosystem production (NEP) of the Scheldt estuary for the period June to December 2003 using the LOICZ budgeting and the O_2 incubation approaches (means ± SD). ΔDIP and ΔDIC (mmol m^{-2} d^{-1}) are the nonconservative fluxes of dissolved inorganic phosphorus and carbon. F is the CO_2 flux (mmol C m^{-2} d^{-1}) at the air-water interface computed using the parameterization of the gas transfer velocity of Borges et al. (2004b). NEP (mmol C m^{-2} d^{-1}) was estimated from ΔDIP (NEP DIP), ΔDIC (NEP DIC), and direct processes measurements (NEP incubations).

Compartment	ΔDIP	ΔDIC_t	F	NEP DIP	NEP DIC	NEP incubations
Inner	0.09 (0.04)	16 (88)	341 (58)	−9 (4)	−356 (66)	−143 (37)
Middle	0.32 (0.14)	5 (44)	92 (26)	−34 (15)	−97 (37)	−22 (10)
Outer	0.14 (0.22)	−34 (58)	32 (12)	−15 (24)	2 (56)	−10 (3)
Whole estuary	0.17 (0.10)	−9 (37)	118 (20)	−19 (11)	−109 (31)	−42 (9)

was below 15% from May to November 2003 in the brackish part.

Planktonic Photosynthesis

Planktonic GPP rates based on O_2 incubations in the present study are close to ^{14}C based rates reported for the 1990's by Kromkamp and Peene (1995) for the salinity mixing zone and by Muylaert (1999) for the tidal river (Fig. 6), indicating no clear evolution over this time period. Phytoplankton growth in the Scheldt estuary is primarily light controlled and Soetaert et al. (2005) reported that suspended particulate matter (SPM) concentrations did not significantly change from 1990 to 2002. This explains the similarity between our results and previous ones. Significant decreases of Si were observed in the freshwater and brackish areas in August and the marine part in May, coinciding with high GPP rates. In the freshwater and inner parts of the estuary, GPP was highest in summer when irradiance and water temperature were also highest. Chl *a* and phaeopigment data showed that high loads of riverine phytoplankton were imported from March to May and degraded in the inner estuary when salinity increases (Boschker et al. 2005). In summer, high chl *a* concentrations were still observed but phaeopigments concentrations dropped to low values indicating a much more active phytoplanktonic community in agreement with the higher GPP. This is consistent with the findings of Muylaert et al. (2000) who suggested that salinity, irradiance, and temperature were the main driving forces of the distribution and dynamics of phytoplankton communities in the inner and freshwater parts of the Scheldt estuary. The phytoplanktonic GPP rates measured in this estuary are in the range of published estuarine rates reviewed by Heip et al. (1995) and Gazeau et al. (2004) for European estuaries (1.7–153.3 mmol C m^{-2} d^{-1}).

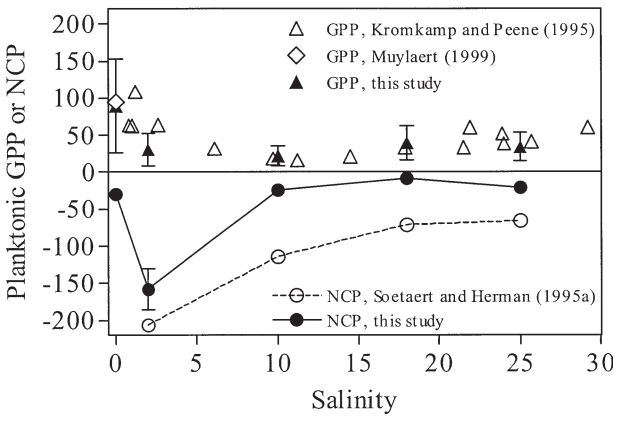

Fig. 6. Upper panel: Comparison of annual phytoplankton gross primary production (GPP) rates measured in the Scheldt estuary in 2003 with previous measurements (Kromkamp and Peene 1995; Muylaert 1999 in the tidal river). Lower panel: Comparison of annual planktonic net community production (NCP) rates measured during this study with the model outputs of Soetaert and Herman (1995a). All rates are expressed in mmol C m^{-2} d^{-1}.

Planktonic Nitrification

In 1997–1998, de Bie et al. (2002) reported a mean NIT rate over the whole estuary of 1.1 (range: 0–7.5) mmol C m^{-3} d^{-1} while we estimated a rate of 0.5 (range: 0–2.2) mmol C m^{-3} d^{-1}. Over the same time period, averaged NH_4 concentrations in the estuary decreased from 90 to 60 mmol N m^{-3}. It seems that the decrease in NH_4 loading in the Scheldt estuary induced a significant decrease of nitrification and led to improved O_2 conditions as reported by Soetaert et al. (2005). Rates of NIT measured in the Scheldt estuary in 2003 are still higher than or similar to the ones reported by Owens (1986) in the Tamar estuary (max: 0.8 mmol C m^{-3} d^{-1}), Berounsky and Nixon (1993) in Narragansett Bay (0–1.9 mmol C m^{-3} d^{-1}), and Brion et al. (2000) in the Seine river estuary (0.2–1.9 mmol C m^{-3} d^{-1}).

Planktonic Organic Matter Mineralization

To the best of our knowledge, no measurements of planktonic CR have been published for the Scheldt estuary to compare with our data. In 2003, planktonic CR was generally highest in the brackish area with maximal rates observed in May and October. These high rates are related to enhanced total organic carbon inputs during these two months (data not shown). Freshwater flow alone cannot explain these

elevated organic matter loads, but daily precipitation data at Vlissingen (51.27°N, 3.36°E) and Stabroek (51.19°N, 4.21°E) reveal that the highest precipitation events occurred in May and October (data not shown). These peaks of planktonic CR might be explained by an increase of lateral organic matter inputs from water runoff and show that planktonic CR in the Scheldt estuary is mainly driven by inputs of allochtonous organic matter rather than by local production, consistent with the compound specific isotope data of Boschker et al. (2005). Hopkinson and Smith (2005) reviewed planktonic and benthic CR rates in 22 estuaries around the world and report planktonic CR between −1.7 in the Gulf of Finland to −84 mmol C m^{-3} d^{-1} in the Fly River delta with an arithmetic mean value of −17.8 mmol C m^{-3} d^{-1}. In the Scheldt estuary, we measured annually averaged planktonic CR rates ranging from −4.7 in the outer estuary to −19.1 mmol C m^{-3} d^{-1} in the inner part with a volume weighted mean value in the whole estuary of −6.6 mmol C m^{-3} d^{-1}. It must be stressed that most of the CR rates reported by these authors do not take into account the O_2 consumption by nitrifiers and CR might be overestimated in highly nutrified systems. The mean rate estimated in the Scheldt estuary is close to the ones measured by Witek et al. (1999) in the Gulf of Gdánsk and Rudek and Cloern (1996) in San Francisco Bay.

Planktonic Net Community Production

We report the first measurements of planktonic NCP (including nitrifiers) based on incubations in the Scheldt estuary, which to date has been estimated only through modelling by Soetaert and Herman (1995a). Rates measured along the salinity gradient in 2003 follow the same trend but measured data are significantly higher than those estimated by Soetaert and Herman (Fig. 6). Their model was calibrated on data gathered in 1980–1985 and it is difficult to conclude whether this difference results from an increase of the planktonic NCP over 20 yr or from differences in methodology.

Whole System NEP Based on In Situ Incubations

Based on these planktonic measurements and published benthic primary production and mineralization rates, a total GPP (including NIT) and CR of 43 ± 4 and −81 ± 10 mmol C m^{-2} d^{-1}, respectively, are estimated leading to a NEP of −39 ± 8 mmol C m^{-2} d^{-1}. In the compilation by Gattuso et al. (1998), almost all estuarine sites are heterotrophic with NEP rates ranging from −62 to 6 mmol C m^{-2} d^{-1} (mean of −16 ± 20 mmol C m^{-2} d^{-1}). Caffrey (2004) reported annual NEP estimates based on the in situ diel O_2 method for 42 estuarine sites in the United States. All sites are heterotrophic in term of carbon with NEP ranging from −11 to −278 mmol C m^{-2} d^{-1} and a mean value of −110 ± 66 mmol C m^{-2} d^{-1}, indicating stronger heterotrophy in these systems than in the Scheldt estuary based on the incubation method. Caffrey's O_2 based rates were converted to carbon units using the same O_2 to carbon conversion factors (PQ and RQ); the validity of these factors and the discrepancy between incubation and open-system approaches will be discussed in detail below. Kemp et al. (1997) found a significant positive relationship between NEP estimates in several systems and the ratio between dissolved inorganic nitrogen and organic matter loadings. The NEP computed in the Scheldt estuary based on in situ incubations does not follow this pattern with a low NEP and high inputs for both nutrient and organic matter. This is not surprising since, as mentioned above, primary producers in the Scheldt estuary and similar macrotidal estuaries are mainly limited by light availability (Heip et al. 1995) and NEP in these systems cannot be predicted from only nutrient and organic matter loadings.

Whole System NEP Based on LOICZ Biogeochemical Models versus In Situ Incubations

NEP estimates obtained using the three approaches (LOICZ biogeochemical budgets applied to DIP and DIC, in situ incubations), in the Scheldt estuary from June to December 2003, are summarized in Tables 3 and 4.

LOICZ Biogeochemical Budgets Applied to DIP

The LOICZ modelling procedure applied to DIP concentrations leads to a significant overestimation of NEP (i.e., biased toward autotrophy) compared to the two other methods, especially in the inner part of the estuary. This method is based on the assumption that all nonconservative fluxes of DIP are attributed to net uptake into organic matter during primary production or release from organic matter by regeneration. The primary shortcoming of this method is that systems with high amounts of suspended material may show evidence for DIP adsorption onto particulate materials or desorption from them (Smith 2001). High suspended matter concentrations are encountered in the inner Scheldt estuary (average over the investigated period: 74 ± 55 g m^{-3}) and processes of DIP sorption on these particles are likely (Zwolsman 1994). We attributed the discrepancy between this method and the two others to DIP particle and sediment exchange processes. Total nonconservative flux of DIP estimated by the LOICZ approach applied to DIP is equal to the sum of biotic (NEP)

TABLE 4. Summary table (means ± SD) of computed net ecosystem production (NEP) in the Scheldt estuary from June to December 2003 using three methods: LOICZ budgets based on dissolved inorganic phosphorus (DIP), LOICZ budgets based on dissolved inorganic carbon (DIC), and in situ incubations. Computed abiotic DIP fluxes and NEP estimates using the LOICZ procedure applied to DIC and in situ incubations modified as described in the text also are presented.

Compartment	NEP DIP	DIP abiotic fluxes†	NEP DIC	Modified NEP DIC*	NEP incubations	Modified NEP incubations**
Inner	−9 (4)	−3.3 to −1.3	−356 (66)	−129 (39)	−143 (37)	−338 (89)
Middle	−34 (15)	−0.6 to 0.1	−97 (37)	−48 (36)	−22 (10)	−36 (14)
Outer	−15 (24)	0.05 to 0.2	2 (56)	19 (52)	−10 (3)	−29 (7)
Whole estuary	−19 (11)	−0.8 to −0.2	−109 (31)	−36 (24)	−42 (9)	−96 (19)

† Range of DIP abiotic fluxes estimated by difference with NEP values computed either with the LOICZ method applied to DIC or from in situ incubations.

* Estimated using the gas transfer velocity (k) parameterization of Raymond and Cole (2001).

** Estimated assuming that planktonic incubations underestimate metabolic rates by a factor of 2.75.

and abiotic (sorption and desorption) processes. By using NEP values derived from incubations, we estimated net abiotic DIP fluxes in the inner, middle, and outer estuary of −1.3, 0.1, and 0.05 mmol P m^{-2} d^{-1}, respectively (Table 4). Considering NEP rates computed with the LOICZ procedure applied to DIC, net abiotic DIP fluxes of −3.3, −0.6, and 0.2 mmol P m^{-2} d^{-1} are estimated (Table 4). This is consistent with observations of Zwolsman (1994) who mentioned that net sorption of DIP onto particle and sediment is likely in the inner estuary and that regeneration (desorption) of phosphorus from sediment or particulate matter occurs in the middle and outer estuary due to the increase of pH. Considering either NEP rates derived from incubations or from the LOICZ approach applied to DIC, net DIP abiotic removals of 600 and 2,500 tP yr^{-1} are estimated, respectively, corresponding to 35% and 65% of river imported and biologically produced DIP. These values are close to the ones reported by Rendell et al. (1997) and Sanders et al. (1997) in the Great Ouse and Humber estuaries (55% and 31%, respectively).

LOICZ Biogeochemical Budgets Applied to DIC

Estimates of NEP based on the LOICZ modelling procedure applied to DIC (−109 ± 31 mmol C m^{-2} d^{-1}), are significantly lower than those derived from in situ direct measurements for the same period (−42 ± 9 mmol C m^{-2} d^{-1}). Using this approach, it was assumed that $CaCO_3$ precipitation and dissolution processes can be neglected. As mentioned above, no measurements have been carried out in the saline portion of the Scheldt estuary. Hellings et al. (2000) estimated dissolution rates in two freshwater intertidal sediments (Appels and Durme) and found that $CaCO_3$ dissolution does not represent more than 15–17% of DIC production. Middelburg et al. (1996) compared sulphate reduction rates measurements and CO_2 effluxes at a brackish tidal flat and concluded that calcite dissolution was not significant. Assuming that $CaCO_3$ dissolution accounts for about 15% of benthic CR (2 mmol C m^{-2} d^{-1}), this clearly cannot explain the discrepancy between the two methods.

Another critical point should be the violation of the steady-state assumption for salinity in our system. In the calculations using the LOICZ method, we considered that the volume and more importantly the salt content of the system are constant. Increases of 0.5, 1.8, and 1.9 of salinity in the inner, middle, and outer estuary, respectively, are observed between June and December, which correspond to average dS/dt of 2.5×10^{-3}, 9.8×10^{-3}, and 10.5×10^{-3} d^{-1}, respectively. Recomputing the budgets using these salinity variations leads to a NEP increase of only 3% and in this system and for the time period considered in our study, the violation of the steady-state assumption is not critical.

Our procedure to estimate lateral DIC inputs in the estuary is certainly prone to large errors and we observed that episodic organic matter inputs due to runoff can have a significant effect on planktonic CR (see above). But recomputing these budgets assuming a 50% variation in lateral inputs will only imply a 8% variation of the predicted NEP. As shown in Table 3, the magnitude of NEP is mainly governed by CO_2 fluxes that are much higher than the nonconservative DIC fluxes, especially in the inner and middle estuary. Hellings et al. (2001), in their DIC budget, estimated CO_2 fluxes in the inner area using the gas transfer velocity parameterization by Wanninkhof (1992) and found an annual CO_2 efflux significantly lower than the one reported in the present study: 71 versus 341 mmol C m^{-2} d^{-1}. These authors estimated the NEP in this zone to be −73 mmol C m^{-2} d^{-1}, a value significantly higher than the −143 ± 37 and −356 ± 66 mmol C m^{-2} d^{-1} based on the incubation and LOICZ-DIC approaches of this study. Integrated over the entire estuary, a CO_2 flux to the atmosphere of ~370 ± 60 tC d^{-1} is estimated, slightly lower than the estimate of 456 tC d^{-1} given by Frankignoulle et al. (1998). Vanderborght et al.

(2002) estimated a CO_2 flux to the atmosphere for July 1996 of 225 tC d^{-1} using the coupled, networked, transport-reaction algorithm for strong tidal estuaries (CONTRASTE) model and the gas transfer parameterization of O'Connor and Dobbins (1958) that only accounts for water current contributions to turbulence (ignoring wind stress). This value is half the one estimated in the present study for July 2003 (455 ± 80 tC d^{-1}) and also lower than the one given by Frankignoulle et al. (1998) for July 1996 (550 tC d^{-1}) from floating dome field data. The estimation of the flux of a gas across the air-water interface depends on the air-water gradient, the solubility coefficient, and the transfer velocity of the considered gas. While the two first variables can be easily constrained, estimating the gas transfer velocity, which depends on the surface water turbulence, is more problematic and has been, most of the time, parameterized as a function of wind speed. The gas transfer velocity parameterization used in this study (Borges et al. 2004b) is based on the floating dome technique that has been dismissed by some authors (Liss and Merlivat 1986). Within certain known bounds of application the floating dome technique appears to provide fair estimates (Kremer et al. 2003a), although this matter will remain unresolved until a consistent comparison of techniques is carried out in several estuaries with different physical characteristics. Raymond and Cole (2001) established a gas transfer velocity parameterization based on a compilation in various estuaries and using different tracer methods. Recomputing CO_2 fluxes and NEP rates using the parameterization of Raymond and Cole (2001) leads to whole estuary values of 47 ± 12 and -36 ± 24 mmol C m^{-2} d^{-1} for these two parameters, respectively (see Modified NEP DIC in Table 4). NEP computed using this gas transfer parameterization is closer to the one derived from the in situ incubations (-42 ± 9 mmol C m^{-2} d^{-1}) and could explain the observed discrepancy between the two methods using our nominal settings. The gas transfer velocity has been shown to be site specific in estuaries (Kremer et al. 2003b; Borges et al. 2004a). This is in part related to the contribution of tidal currents that, in macrotidal estuaries, strongly enhances water turbulence and the gas transfer velocity in addition to wind stress (Zappa et al. 2003; Borges et al. 2004a). As shown by Gazeau et al. (2005) for open-system methods, the computation of NEP based on a LOICZ budget applied to DIC is strongly dependent on the estimation of the gas transfer velocity to derive the air-water CO_2 fluxes. This budgeting approach will remain subject to large uncertainties until a consensus on measurement techniques and parameterizations of the gas transfer velocity is achieved.

In Situ Incubation Measurements

The use of the incubation approach is also dependent on several assumptions. In order to convert planktonic O_2-based rates to carbon units, we assumed a PQ of 1.3, RQ of 1, and NIT O_2:C ratio of -14. The PQ corresponds to the ratio of O_2 released per DIC consumed assuming that nitrate is the primary nitrogen source and that the organic matter produced has a Redfield composition. Assuming that NH_4 is the principal source of nitrogen for phytoplankton growth leads to a PQ closer to 1. Based on the C:N:P molar elemental composition given by Hedges et al. (2002) and nitrate as nitrogen source, one can compute a PQ of 1.45, higher than the one used in this study. Assuming a PQ of 1 or 1.45, NEP of -31 ± 8 and -45 ± 9 mmol C m^{-2} d^{-1} are estimated, respectively. This shows that, due to the low rates of GPP in this estuary, the computed NEP is relatively insensitive to the choice of PQ value, so the uncertainty in PQ values does not explain the discrepancy between incubations and LOICZ budgets based on DIC. A RQ of 1 corresponding to the oxidation of carbohydrates (Richardson 1929) was used to convert mineralization rates into carbon units. Williams and del Giorgio (2005) reported RQ values for different respiratory substrates ranging from 0.5 to 1.33. Using these extreme values leads to NEP estimates of -9 ± 7 to -64 ± 10 mmol C m^{-2} d^{-1}, respectively. Although the computed NEP is very sensitive to the choice of RQ value, assuming the highest one (1.33) gives a NEP still far above the value derived from the LOICZ procedure applied to DIC (-109 ± 31 mmol C m^{-2} d^{-1}). Although the conversion of O_2 consumption due to NIT into carbon units may be prone to some uncertainties, its variation will not significantly modify our NEP values since NIT is more than ten-fold lower than CR. In order to convert hourly values to daily rates, we assumed that both CR and NIT rates are constant over 24 h and this might have introduced a bias in our results. Several authors have stated that CR is likely to be enhanced in the presence of light (Grande et al. 1989b; Martinez 1992; Langdon et al. 2003) although such observations were not always corroborated (Grande et al. 1989a,b). NIT has been found to be inhibited by a factor of 40% to 50% in light (Horrigan and Springer 1990; Ward 2005). In the Scheldt estuary, the euphotic zone (1% surface irradiance) is very shallow due to high SPM concentrations and does not represent a major portion of the water column. Integrated values are not likely to be very sensitive to these assumptions.

Using the incubation method, based on benthic CR data for intertidal areas from Middelburg et al.

(1996) and subtidal rates measured using the O_2 method by Barrón and Duarte (unpublished data), we assumed that benthic mineralization on subtidal areas represents 20% of the intertidal flats rate. As anoxic mineralization is likely to occur in this area, the values of Barrón and Duarte, based on O_2 fluxes, might be underestimated (CH_4 production, denitrification, and burial of reduced sulfur; Heip et al. 1995) and the computed NEP might be overestimated. Assuming that rates of mineralization on intertidal and subtidal areas are equal will decrease the whole estuary NEP to -70 ± 14 mmol C m^{-2} d^{-1}. This is insufficient to explain the discrepancy between NEP derived from incubations and LOICZ budgets applied to DIC.

More importantly, as mentioned above, several studies have shown that incubation methods are likely to underestimate metabolic rates compared to open-system methods due to the inhibition of turbulence and the neglect of some active components of an ecosystem (Pomeroy 1960; Bender and Jordan 1970; Kemp and Boynton 1980; Howarth et al. 1992). Open water techniques usually provide estimates 1.5 to 4 times higher than incubation methods (Kemp and Boynton 1980). Assuming that planktonic metabolic rates predicted by incubation methods were underestimated in our study by a factor of 2.75, effectively leads to a whole estuary NEP of -96 ± 19 mmol C m^{-2} d^{-1}, much closer to the value estimated using the LOICZ procedure applied to DIC (see Modified NEP incubations in Table 4).

Both the incubation method and the LOICZ procedure applied to DIC are associated with several assumptions, some very critical that could explain the observed discrepancy in the computed NEP derived from the two approaches. It seems premature and unreasonable to state whether one or the other method is the most appropriate in this system and only a range of NEP, from June to December 2003, can be provided: -109 to -42 mmol C m^{-2} d^{-1}.

Conclusions

This study confirmed that, due to high inputs of allochtonous organic matter, residence time, and turbidity, the Scheldt estuary is a strongly heterotrophic system and that phytoplankton production is light rather than nutrient limited. As a consequence of permanent high suspended matter concentrations (and light limitation), GPP values estimated in 2003 are very similar to rates measured in the 1990s, despite a significant decrease of nutrient inputs over the last decade. A significant decrease of NIT was observed in the past 6 yr and is correlated with a decrease of the NH_4 loading. NIT is still important in terms of nitrogen, carbon, and O_2 dynamics and represents 20% of the total organic matter production around the maximum turbidity zone. As no previous published direct CR or NEP estimates are available to compare with, no conclusion on the evolution of these parameters can be drawn.

Several approaches were tested to estimate the NEP in this estuary. The LOICZ method based on nonconservative DIP fluxes cannot be applied in this turbid system, as abiotic processes such as sorption and desorption from and to suspended particles and sediment can have a strong effect on these fluxes. The LOICZ method based on DIC yielded more negative NEP estimates than the ones derived from incubations. It is not possible to state which method is the more appropriate in this ecosystem, but the major caveats of each approach to measure metabolic rates in estuaries were identified.

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