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Long-term change in dissolved inorganic nutrients in the heterotrophic Scheldt estuary (Belgium, The Netherlands)

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Abstract

We investigated long-term trends (1965–2002) in dissolved inorganic nutrients in the tidal part of the Scheldt estuary (Belgium, The Netherlands). Annually averaged concentrations of dissolved silicate (DSi), dissolved inorganic nitrogen (DIN), and phosphate (DIP) increased significantly until the mid-1970s, after which they declined linearly at rates of 0.6, 2.9, and 0.3 μmol L^{-1} yr^{-1}, respectively. This co-occurred with a deterioration followed by a restoration of water column oxic conditions. Because of the differences in the reduction rate of DSi (1.2% yr^{-1}), DIN (1.7% yr^{-1}), and DIP (5.4% yr^{-1}), the N : P and Si : P ratios more than doubled from 1980 to 2002. The Si : N ratio varied from 0.2 to 0.4 and was positively correlated with river discharge. The part downstream from the confluence of the main rivers was a net sink for DSi during the entire period but evolved from a net sink to a net source for DIP, while the reverse was true for DIN. This differential behavior of the estuary with respect to DIN and DIP strongly buffered the altered loadings to the upper estuary. The input of oxygen-consuming substances at the head of the estuary triggered a sequence of oxidation reactions. In the early 1970s, high loadings of ammonium and organic matter caused oxygen depletion and intense water-column denitrification in the upstream part and intense nitrification downstream, with a nitrate maximum succeeding a nitrite peak. With oxic conditions improving and the input of ammonium decreasing, water-column denitrification declined, the nitrification front migrated upstream, and the estuary evolved from a net producer of nitrite to a net consumer. Now, at the beginning of the 21st century, nitrate behaves almost conservatively over the entire estuary.

Human activity in coastal watersheds greatly increased the fluxes of growth-limiting nutrients from the landscape to receiving waters. This has resulted in highly increased nutrient concentrations in many of the world's rivers (Justic' et al. 1995; Howarth et al. 1996), estuaries (Verity 2002), and coastal ecosystems (Cloern 2001; van Beusekom and de Jonge 2002; Smith et al. 2003).

In clear waters, increases in nutrient loading cause predictable increases in the biomass of algae (Borum and Sand-Jensen 1996), sometimes leading to exceptional algal blooms (e.g., Richardson 1997; Dippner 1998), which affect secondary production (Nielsen and Richardson 1996) and may deplete bottom-water oxygen (Rabalais et al. 1996). In addition, altered proportions between nutrients induce changes in the algal species composition (Officer and Ryther 1980; Lancelot et al. 1987) and food-web structure (e.g., Escaravage and Prins 2002).

In contrast, in turbid waters, the effects of increased nutrient loading may not be as pronounced (Cloern 2001). In these systems, phytoplankton production is often light limited year-round, and growth is low despite the high levels of nutrient input (Heip et al. 1995). Consequently, effects of high nutrient concentrations are often exported downstream to more quiescent nearshore coastal waters, where they may be manifest (e.g., by more intense and longer lasting spring blooms in the plume of large estuaries) (Allen et al. 1998).

Tidal-dominated estuaries along the Atlantic coast of Europe are not only turbid but are also heterotrophic: because of the import of organic matter from external sources, respiration of organic matter is greater than its production by autotrophs (Heip et al. 1995). The heterotrophic consumption of allochthonous organic matter is not coupled to estuarine primary production; therefore, oxygen consumption dominates oxygen production such that most heterotrophic estuaries are characterized by oxygen depletion and carbon dioxide supersaturation. Thus, tidal estuaries emit significant quantities of carbon dioxide (Frankignoulle et al. 1998). Moreover, in heterotrophic systems, release of dissolved inorganic nutrients by mineralization is greater than nutrient incorporation into biomass. Heterotrophic estuaries therefore have the potential to act as a source of dissolved inorganic nutrients (Smith and Hollibaugh 1993). This release of in-

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organic nutrients is added to the inorganic nutrients received from the drainage from adjacent systems, and the eutrophication potential thus increases.

However, there are additional processes that remove nutrients from estuaries; the combined result of all these processes is often termed the estuarine filter. Dissolved silicate (DSi) may be trapped by the growth of pelagic and benthic diatoms followed by sedimentation and incomplete dissolution and burial (Wollast and De Broeu 1971). Dissolved inorganic phosphate (DIP) is strongly particle active and is thus scavenged by metal oxyhydroxides and sorbed on sediments and suspended matter (Froelich 1988; Jensen et al. 1995). These processes are favored under high oxygen conditions and are affected by pH (Smith et al. 2003) and may be reversed under anoxia (Prastka et al. 1998). Dissolved inorganic nitrogen (DIN) is less particle active but may be removed by denitrification, either at the interface between suboxic and more oxygenated waters or in the sediments (Middelburg et al. 1996*b*). Thus, on the one hand, feedbacks that exist between particle and oxygen dynamics and the phosphorus cycle tend to decrease P retention or even promote P release as systems become more anoxic (Cloern 2001) or as phosphate concentration is reduced and becomes limiting (Prastka et al. 1998). On the other hand, the efficiency of N retention may be stimulated by increased denitrification in the water column (Billen et al. 1985) or depressed by nitrate limitation of sedimentary denitrification (Middelburg et al. 1996*b*) as systems move toward hypoxia. Because of this and the complex interactions that exist between redox conditions, nutrient loads, and suspended particle matter, our understanding of the effects of eutrophication in estuarine systems is not as advanced as it is for freshwater systems (Cloern 2001).

While we know about the estuarine biogeochemical processes generally, the net effect of their simultaneous occurrence highly depends on system-specific features. In order to discern the interacting, often confounded effects of these processes, retrospective analyses from varying systems are needed. Such analyses may help quantification and mechanistic understanding and may eventually allow for the forecasting of estuarine behavior.

The Scheldt estuary, located in an area with high population density, is among the most nutrient-rich systems in the world and the only true estuary from the Dutch Delta region. Ineffective local water management and changes in land use led to serious degradation of surface waters in the second half of the 20th century. By the end of the 1970s, symptoms such as temporal anoxia and organism death were common features in the upstream part of the Scheldt. A sanitation scheme was begun during this period, and the scheme included implementation and gradual upgrading of sewage treatment works and imposition of more stringent restrictions on the disposal of wastes by industries. These efforts resulted in a gradual improvement of the surface-water quality in Flanders, West Belgium, in general (Maeckelberge 2002) and improvement of the quality of the water (Soetaert and Herman 1995*a*), suspended matter, and sediments (Baeyens 1998) and the reappearance of higher organisms in the low-salinity region of the Scheldt estuary (Appeltans et al. 2003).

In this article we have compiled water-quality and physical parameters gathered in the Scheldt over the last 40 yr. We investigate decadal and interannual variations in dissolved inorganic nutrient and oxygen conditions between the mid-1960s and now. We look at the biogeochemical alterations that occurred along the estuarine axis as a consequence of changed loadings and we aim to evaluate the effect of these alterations on the functioning of the estuary as a filter for dissolved inorganic nutrients.

Study area

The catchment of the Scheldt (350 km long) covers 21,863 km^2 and is situated in the northwest of France (31%), the west of Belgium (Flanders, 61%), and the southwest of The Netherlands (8%). Most of the river basin area is urban; the total population of the catchment numbers more than 10 million people, with densities varying from 100 to more than 2,000 inhabitants km^{-2} (averaging 400 inhabitants km^{-2}). The Scheldt can be divided into the nontidal Upper Scheldt and the tidal portion (170 km long), which extends from the mouth at Vlissingen to Gent, where sluices stop the tidal influence. The study area comprised the tidal portion of the Scheldt (Fig. 1). This part comprises the riverine part of the Scheldt, from Gent to the confluence of the Scheldt with the Rupel near Rupelmonde, and the brackish-marine part from Rupelmonde to Vlissingen (Fig. 1). The tidal Scheldt is a shallow, well-mixed, and relatively turbid macrotidal estuary. Mean depth varies from about 14 m at the mouth to 7 m near Gent. The tidal regime is semidiurnal, with mean neap and spring ranges of 2.7 and 4.5 m, respectively (Regnier et al. 1998). Residence time from Rupelmonde to Vlissingen is relatively large as a result of the small river discharge and large tidal influence and is estimated at 2–3 months, depending on river flow (Soetaert and Herman 1995*b*; Regnier et al. 1997). The water column is generally well mixed, but the upper estuary (Belgian part) may be slightly stratified during high peak discharges. As a result of tidal asymmetry, sediments accumulate in the upstream part of the Scheldt, as more sediment is transported upstream at high tide than is exported at low tide. The cross-sectional area increases smoothly from the river to the mouth (Fig. 1), giving the estuary a trumpet shape. The Scheldt has undergone substantial hydrological modifications through channeling of the upstream portion and dredging to maintain shipping channels to the harbor of Antwerpen.

Three rivers join the Scheldt: the Dender, the Durme, and the Rupel; the latter carries largely untreated wastewater from the densely populated Brussels region. The Canal Gent-Terneuzen merges with the Scheldt near the mouth at Vlissingen (Fig. 1).

Database and data analysis

The analysis of biogeochemical variables is based on a variety of data sources. They comprise data from research and monitoring cruises performed by The Netherlands Institute of Ecology (NIOO-CEME, 27%), the Dutch governmental agency Rijkswaterstaat (RIKZ—DONAR database, 32%), and several data sets contributed by Belgian univer-

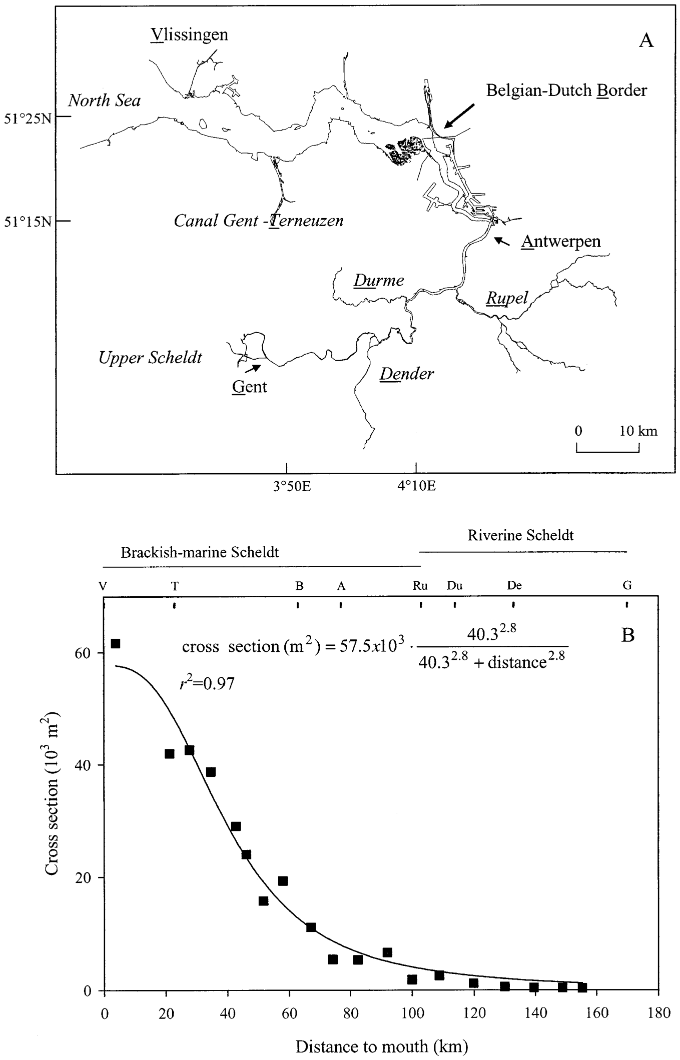

Fig. 1. (A) Map of the Scheldt, with indication of main cities and the tributaries (italic); underlined characters are used in panel B and Fig. 2. (B) Cross-sectional area of the Scheldt, at various positions along the estuarine axis and best-fit sigmoid equation. Characters at the top of the graph denote the positioning of cities or confluences with tributaries, as represented by underlined characters from panel A (e.g., V = Vlissingen, T = Canal Gent-Terneuzen, etc.).

sities (25%) and Belgian governmental agencies (15%). The institutes involved participate in international and internal intercalibration and quality assurance procedures with good results. Discharges at Schelle (downstream from Rupelmonde) and morphological information from the Belgian part were made available by the Flemish Waterways and Maritime Affairs Administration (AWZ). Meteorological information at Vlissingen (at the mouth of the Scheldt) was obtained from the Royal Dutch Meteorological Institute (KNMI). Information on the various sources of waste input was obtained from the Management Unit for the Northsea Mathematical Models (MUMM).

The data used cover the period from 1965 to 2002, but with variable resolution in time and space. Most samples were obtained at random with respect to the tidal phase, and with sampling time not always recorded, it was not always possible to translocate the data to mean tidal level. Moreover, sampling effort was not always equally spaced throughout the year. The following procedure was applied to calculate annual averages while trying to compensate for these effects. The data were first averaged within chlorinity classes of 50 mmol L^{-1} (corresponding to ~3 salinity units) and months within a year. For each chlorinity class, these monthly values were then averaged to provide annual averages. By using yearly averaged values, any transient nonlinear effects induced by fluctuating discharges are removed (Regnier et al. 1998).

When applicable, volume-averaged mean concentrations were calculated by combining these annual mean concentrations per chlorinity class with estimated mean volumes in each class. These volumes were obtained by combining the mean chlorinity distribution (*see* Results) with the mean cross-sectional area along the estuarine axis (Fig. 1). These mean distributions were estimated by fitting a sigmoid function relating chlorinity and cross-sectional area (Y) to the distance from the mouth (x), using nonlinear regression (i.e., minimizing the sum of squared residuals):

$$Y_x = Y_0 \frac{k^p}{x^p + k^p}$$

where Y_0 is the quantity at the mouth, k is the distance from the mouth where the quantity is halved, and p is an exponent that regulates the steepness of the relationship. Because of the quasi-exponential increase in cross-sectional area, only 3% of the total volume resides in the most upstream chlorinity class; around 30% resides in the most downstream chlorinity class. Consequently, the volume-averaged salinity of the tidal Scheldt is 23. As in the Belgian part of the tidal Scheldt, a longer time series was available (extending until 1965); volumetric annual averages were calculated for the entire estuary (comprising both the Belgian and Dutch part, i.e., Gent to Vlissingen) and for the Belgian part separately (i.e., from Gent to the Belgian–Dutch border, comprising ~20% of total volume).

There is a whole suite of approaches and models available to analyze the distribution of reactive components in estuaries (e.g., Nedwell et al. 1999). They differ in sophistication, underlying assumptions, and data requirements. We have chosen to use simple mixing diagrams, representing the constituent distributions along a chlorinity gradient, as a way of assessing whether the brackish-marine part of the estuary (i.e., Rupelmonde–Vlissingen; Fig. 1) acts as a source or as a sink for any dissolved substance according to a procedure similar to the one described in Fisher et al. (1988) and as recently used by Colbert and McManus (2003). First, the actual and conservative total estuarine masses, averaged over a 5-yr period, were calculated. For actual mass, this was accomplished by multiplying the volume in a chlorinity class with the actual concentration and then summing these masses to obtain total estuarine mass. For conservative mass, the (conservative) concentration in a chlorinity class was first estimated by linear interpolation between the end-members, multiplied with volume per class, and summed. Then percent deviation from conservative behavior was estimated as:

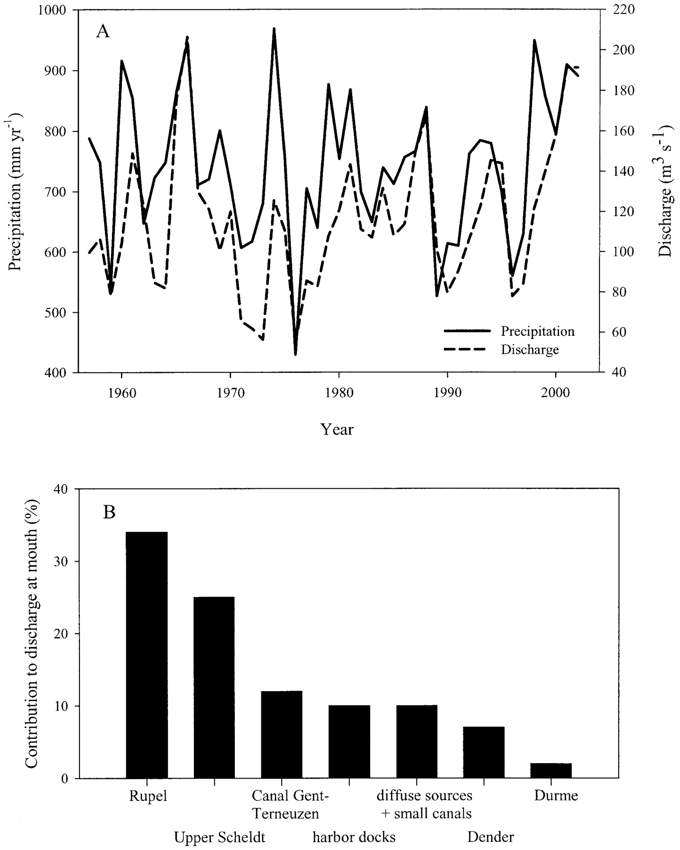

Fig. 2. (A) Annual precipitation measured at Vlissingen (courtesy of KNMI) and annually averaged discharge at Schelle, downstream from the confluence of Rupel and Scheldt (courtesy of AWZ). (B) Contribution of various sources to total discharge at the mouth of the estuary (at Vlissingen); data from 1990–2002 (courtesy of AWZ, Rijkswaterstaat).

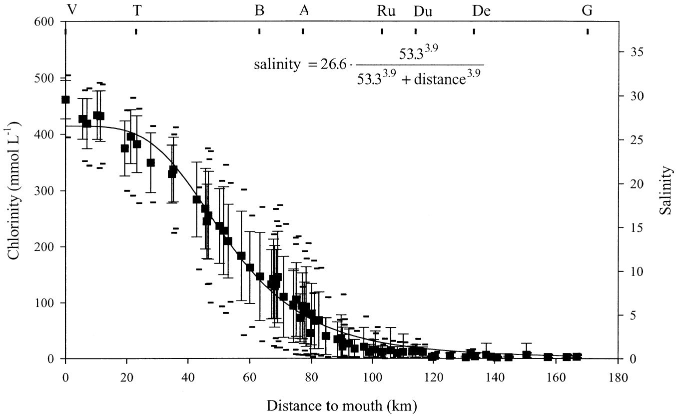

Fig. 3. Chlorinity and salinity along the estuarine axis, with sigmoid best-fit equation. Denoted for each sampling station are the mean values ± standard deviation, and the 5 and 95 percentiles (horizontal dashes); the number of measurements in a station varied from 22 to 2,200. Characters at the top of the graph denote the positioning of cities or confluences with tributaries, as represented in Fig. 1A.

([Actual Mass − Conservative Mass]/Actual Mass) × 100. We favor this method above the so-called apparent zero end-member method (e.g., Boyle et al. 1974; Billen et al. 1985), as it takes into account the full estuarine profile, not just the gradient near the seaward end-member. Moreover, it can be applied in the case of multiple river and lateral sources, as is the case in the Scheldt estuary (Figs. 1, 2). However, this mixing diagram approach does not provide quantitative fluxes of reactive compounds. Its sole intention is to provide an estimate of the relative magnitude and sign of the estuarine filter, with positive values when constituents are added (i.e., the estuary acts as a net source) and negative values in the event of net losses (i.e., it acts as a sink). In addition, since not all freshwater inputs enter at the head of the estuary, 'sink' or 'source' reflects the combination of in situ estuarine processes (retention and liberation), effects of inflowing water from lateral sources (dilution or enrichment), and in case of oxygen air–sea exchange. Conservative mixing cannot be calculated for particulate substances because, depending on their weight, their transport has characteristics both of dissolved matter and sediments, such that salt or chlorinity is not a suitable tracer for these substances. We used 5-yr averages rather than annual averages to derive robust estimates that are less sensitive to variable seasonal and spatial coverage. The last reported period (2000–end of 2002) covers only 3 yr of data.

One important aspect of the mixing diagrams is the positioning of the end-members. By binning of data in 50 mmol L^{-1} chlorinity classes, the most seaward end-member, delimited between chlorinity values of 450 and 500 mmol L^{-1}, comprises all data taken at most 20 km from the mouth of the estuary (*see* Fig. 3, Results). For the upstream boundary, the influence of the Upper Scheldt and all the tributaries needed to be taken into account. Therefore, the entire region upstream from Rupelmonde (102 km from mouth) was excluded from the 'riverine end-member,' which is then defined as the zone of 0–50 mmol L^{-1} chlorinity downstream from the confluence of Rupel and Scheldt. This actually restricts our assessment of the estuarine behavior to the brackish-marine part of the Scheldt only. Detailed studies of the water quality of the Scheldt, including the region upstream of Rupelmonde, are provided by Struyf et al. (2004) and Van Damme et al. (2005).

Results

Yearly averaged river discharge at the confluence between the Scheldt and the Rupel varied from 55 to 207 m^3 s^{-1} (Fig. 2A) during the period extending from 1957 to 2002. The discharge rates are clearly related to total rainfall ($r^2 = 0.50$). The rivers Dender, Durme, and Rupel and the Canal Gent-Terneuzen contribute 7%, 2%, 34%, and 12% of the discharge at Vlissingen, respectively; 25% of the flow is carried by the Upper Scheldt. The docks of the harbor of Antwerp contribute another 10%, while the remaining 10% is from diffuse sources and flow from small canals (Fig. 2B, data from 1990–2001).

The salinity gradient (Fig. 3) along the estuarine axis is best described by a sigmoid equation, as is the case for the estuarine cross-sectional area (Fig. 1). Salinity remains low

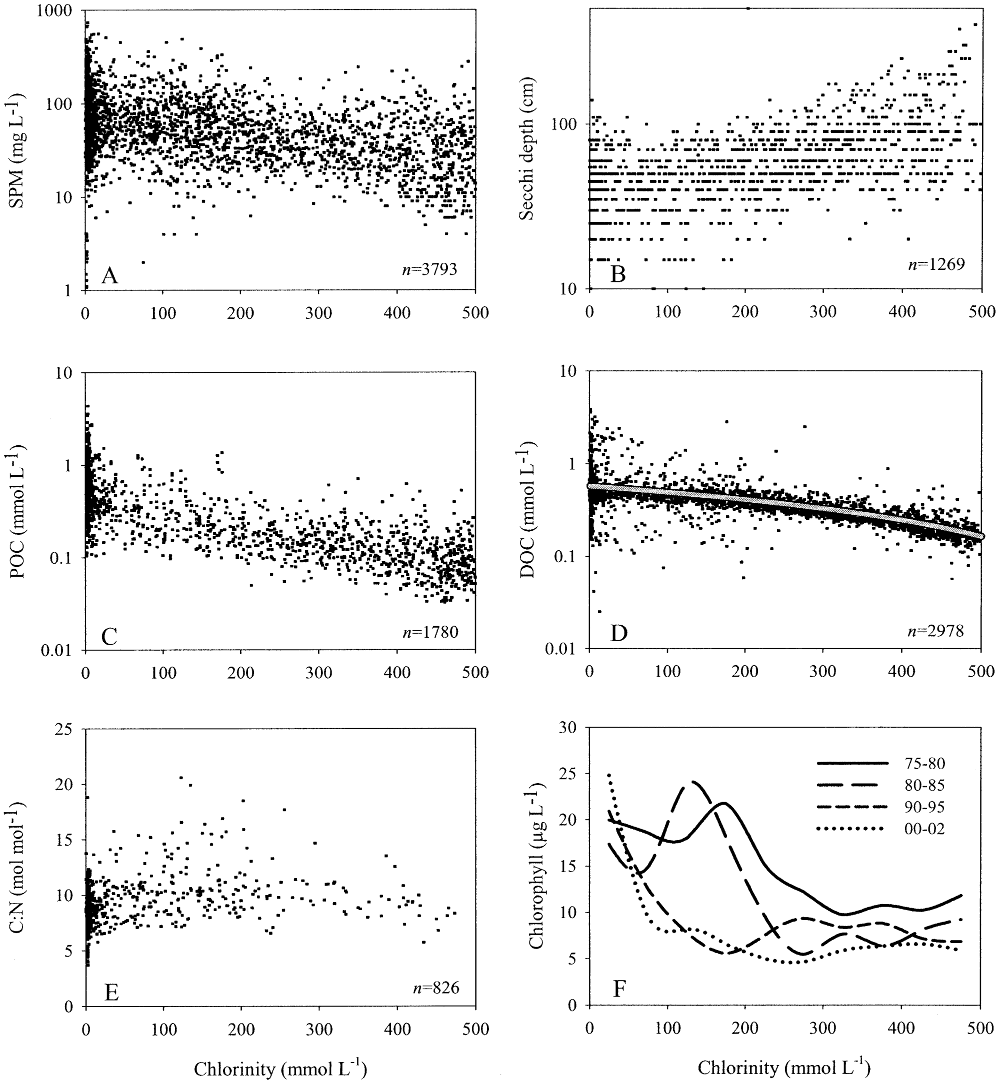

Fig. 4. Constituent distributions along the chlorinity gradient from period 1990–2002. (A–E) All data shown; number of observations (*n*) is indicated. (D) Conservative behavior of DOC indicated with gray solid line. (F) Chlorophyll concentrations in 50 mmol L^{-1} chlorinity intervals averaged over 5 yr; data upstream from Rupelmonde were excluded.

(<3; chlorinity < 50 mmol L^{-1}) in the part upstream from the confluence of Rupel and Scheldt (Fig. 3). Downstream from the Rupel, salinity increases quickly as a result of mixing with seawater. The salinity gradient is largest in the region 50–80 km from the mouth, where the estuary consists of one well-defined channel; this is also the region where the salinity range at any fixed station is largest (range ~15, based on 90% of data points). Downstream from this zone (0–50 km from the mouth) a complex system of ebb-and-flood channels exists; here the salinity gradient is more moderate and the salinity range at any fixed location is lower (~6).

During the period extending from 1990 to 2002, the suspended particulate matter (SPM; Fig. 4A) and secchi depth (Fig. 4B) remained relatively constant (average 93 g m^{-3}, 44 cm, respectively) in the range of 0 to 100 mmol L^{-1} chlorinity (salinity 0–6), which corresponds to the zone upstream from Antwerpen. Downstream, SPM declines and secchi depth increases to a less turbid marine end-member (36 g m^{-3}, 130 cm, respectively). The concentrations of particulate organic matter (POC; Fig. 4C) and dissolved organic matter (DOC; Fig. 4D) decrease from the riverine zone (650 μmol C L^{-1}, 550 μmol C L^{-1}, respectively) to the marine zone (100 μmol C L^{-1}, 180 μmol C L^{-1}; data from 1990–2002); the average DOC : POC ratio increases from 0.9 in the riverine part to almost 3 at 300–350 mmol L^{-1} Cl (salinity 18–22) and then decreases to 1.8 toward the sea. The behavior of DOC is consistent with conservative mixing (Fig. 4D, thick gray line); conservative behavior of POC could not be calculated (*see* Data analysis). The average molar C : N ratio of particulate organic matter (Fig. 4E) is ~8.5 in the upstream and downstream part of the estuary; it increases to ~11 at 150–200 mmol L^{-1} chlorinity, near the Belgian–Dutch border.

To calculate the 5-yr averaged distribution of chlorophyll (Fig. 4F), oxygen, and dissolved inorganic nutrients (Figs. 5, 6), the data upstream from Rupelmonde were excluded (*see* Data analysis). Over the entire period, the number of data points varied between 10,000 (chlorophyll) and 23,000 (oxygen). Before binning the data, an analysis of variance was performed to test for the significant effects of chlorinity class, month of the year, and year on the values of ammonium, nitrate, nitrite, DSi, DIP, and chlorophyll. All were highly significant, except for the effect of month on the values of ammonium. This is because the ammonium concentrations lack a clear seasonal cycle in the upper part of the estuary. As yearly averaging removes all information regarding variance of the data, the standard deviations for the period 1995–2002 were calculated. Standard deviation was between 1.5 and two times the mean for chlorophyll and ammonium and between 0.5 and one times the mean for DSi and nitrite, while it was less than 0.5 times the mean for nitrate, DIP, and oxygen. Similar values were found when each chlorinity class was examined separately.

Averaged chlorophyll concentrations—binned by 5 yr—in the riverine end-member were always higher than in the seaward end-member; in the period after 1990, this riverine chlorophyll is rapidly attenuated and then remains below 10 μg L^{-1}; in the period before 1990, chlorophyll concentrations increased in the region 100–200 mmol L^{-1} chlorphyll.

The distribution of oxygen and DIN along the chlorinity gradient and the estimated percent deviation with respect to the conservative concentration are shown as 5-yr averages in Fig. 5 (*see* Data analysis). Averaging over 5 yr represents the optimal balance between clarity of presentation and robustness of patterns on the one hand and temporal resolution on the other hand.

The oxygen concentrations show that waters were always highly undersaturated in the riverine part (6–35% saturation, 38–116 μmol L^{-1}), while near saturation point (>90% and >250 μmol L^{-1}) in the marine end-member (Fig. 5A). In the period extending from 1970 to 1980, significant oxygen consumption in the most upstream zone caused a prominent drop in oxygen concentrations, which remained rather low until the mid-estuarine reach. An improvement of this situation can be noted from the 1980s onward, although oxygen concentrations during summer often reached very low levels in the most upstream part (e.g., Herman and Heip 1999). During the period extending from 2000 to 2002, oxygen concentrations were restored more quickly upon entering the Scheldt estuary. Within the estuary, oxygen was always net added to the water (re-aeration outcompeting oxygen consumption), although in the period from 1970 to 1975, the oxygen consumption in the entire estuary almost balanced the sources (i.e., the deviation from conservative mixing was almost nil—Fig. 5B). Starting in the 1970s, there is a tendency for the oxygen consumption terms (sinks) to become less important in time (Fig. 5B).

Phosphate concentrations in the riverine end-member declined strongly from around 50 μmol L^{-1} in the early 1970s to ~6 μmol L^{-1} at the start of the 21st century (Fig. 5C). Unfortunately, the downstream part of the estuary was not consistently sampled before 1980. In general the data show a clear consumption of phosphate in the upstream part (0–100 mmol L^{-1} Cl), followed by a net production/input of phosphate in the mid-estuary, after which the behavior of DIP was nearly conservative. The extent of DIP-removal decreased in time (Fig. 5D). Before 1990, the estuary functioned as a net sink for phosphate (i.e., its removal exceeded its production). After 1995, net production exceeded removal (i.e., the % deviation from conservative behavior was positive, Fig. 5D).

Total DIN in the riverine part decreased from 640 μmol L^{-1} in the early 1970s to 430 μmol L^{-1} after 2000 (Fig. 5E), while the most seaward concentration declined from 10 to 5 μmol L^{-1}. Before 1995, mixing plots are convex, indicating that the estuary behaved as a net source of DIN (i.e., its production through mineralization exceeded removal); after that, the mixing plots are concave and the estuary behaved as a net sink (Fig. 5F).

Riverine concentrations of DSi varied from 270 μmol L^{-1} in the 1970s to 160 μmol L^{-1} in the period from 1990 to 1995 (Fig. 5G), while the seaward concentration changed between 14–22 μmol L^{-1}. The estuary always behaved as a net sink of DSi; the percent deviation from conservative mass first increased until 1985 and then decreased again (Fig. 5H).

The ammonium-versus-chlorinity graphs (Fig. 6A), averaged over 5 yr, demonstrate a decrease from the river to the sea. Ammonium was by far the most prominent DIN component in the 1970s, whereas its concentration was rather low from 2000 to 2002. Its contribution to total DIN in the entire estuary decreased from ~70% to <10% (not shown). Similarly, the concentration in the riverine part of the Scheldt decreased from 565 μmol L^{-1} in the 1970s to ~90 μmol L^{-1} in the 21st century, while in the seaward part, concentrations declined from 68 to 5 μmol L^{-1}. In the period extending from 1970 to 1975, there was net production of ammonium in the upstream part, followed by net consumption downstream; in the other periods there was net consumption (almost) everywhere. Overall, the estuary was a net consumer of ammonium (Fig. 6B), and the relative deviation in ammonium with respect to the mean conservative concentration increased in time, indicating more efficient (net) removal; in the early 1970s the sources of ammonium, averaged over the entire estuary, almost balanced the sinks, such that the behavior of ammonium appeared rather conservative.

Nitrite demonstrated more complex behavior (Fig. 6C). Riverine concentrations ranged between 6.7 and 16 μmol L^{-1}, while seaward concentrations declined from about 3.5 in the 1970s to 1.3 μmol L^{-1} in the 21st century. In the period before 1985, nitrite concentrations first dropped in the upstream part of the estuary and then increased again downstream. The increase occurred more downstream in the 1970s. In the early 1990s, the drop in concentrations upstream was not visible anymore; instead, nitrite concentrations increased in the upstream part and then decreased. From 1995 on, nitrite concentration decreased rapidly upon entering the brackish-marine part of the Scheldt and then remained low until the sea. The estuary evolved from a net source of nitrite in the period before 1995 to an increasingly larger relative sink (Fig. 6F).

Nitrate concentrations were considerably lower in the

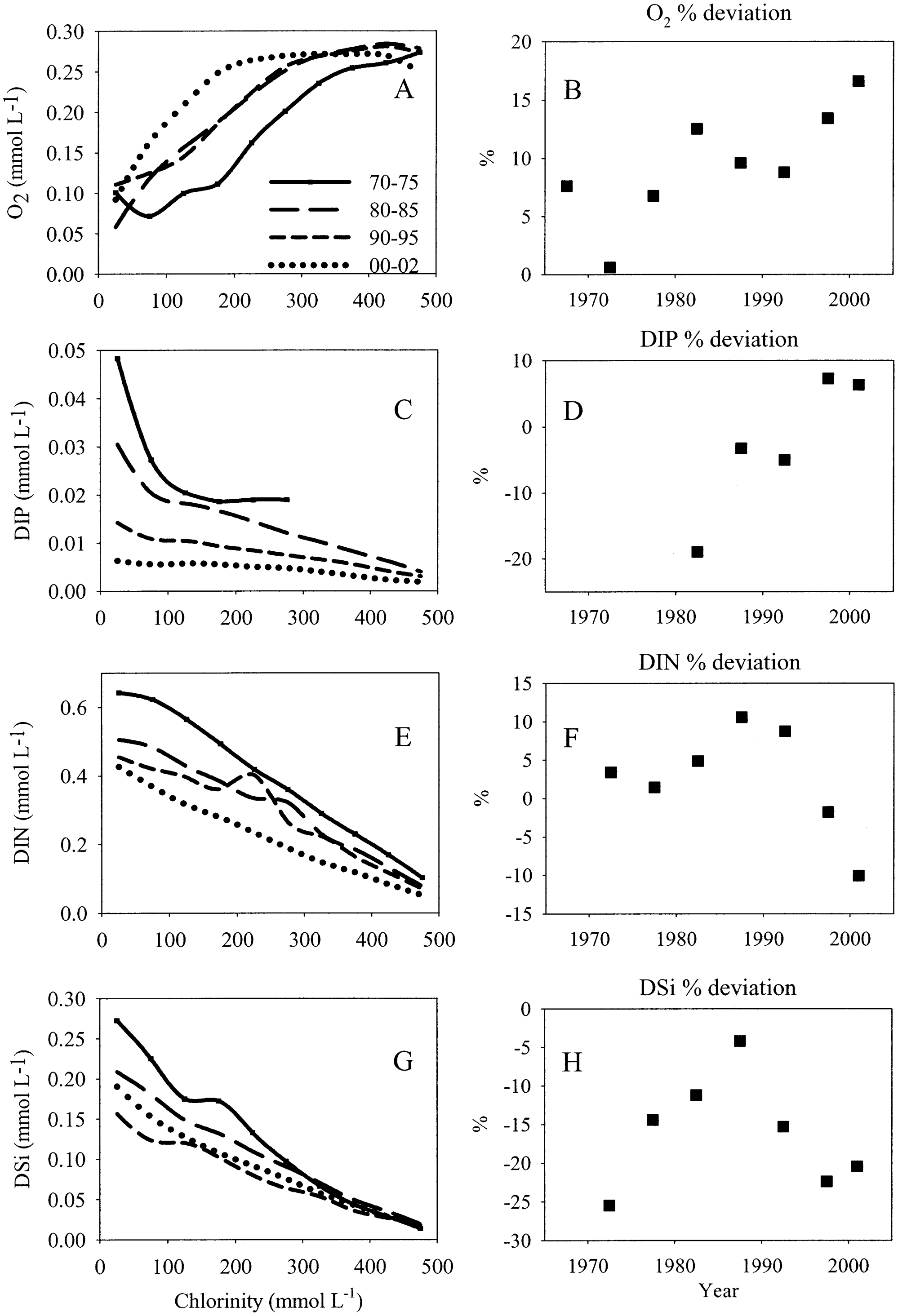

Fig. 5. (A, C, E, G) Five-year–averaged concentrations of oxygen and dissolved inorganic nutrients, binned in 50 mmol L^{-1} chlorinity intervals for four selected periods; data upstream from Rupelmonde were excluded. Plots were smoothed with a spline function. (B, D, F, H) Percent deviation from conservative behavior, for 5-yr intervals (*see* Data analysis for more details). Positive values indicate that sources to the water are larger than the sinks. Data for DIN and DSi were available after 1970, for DIP only after 1980.

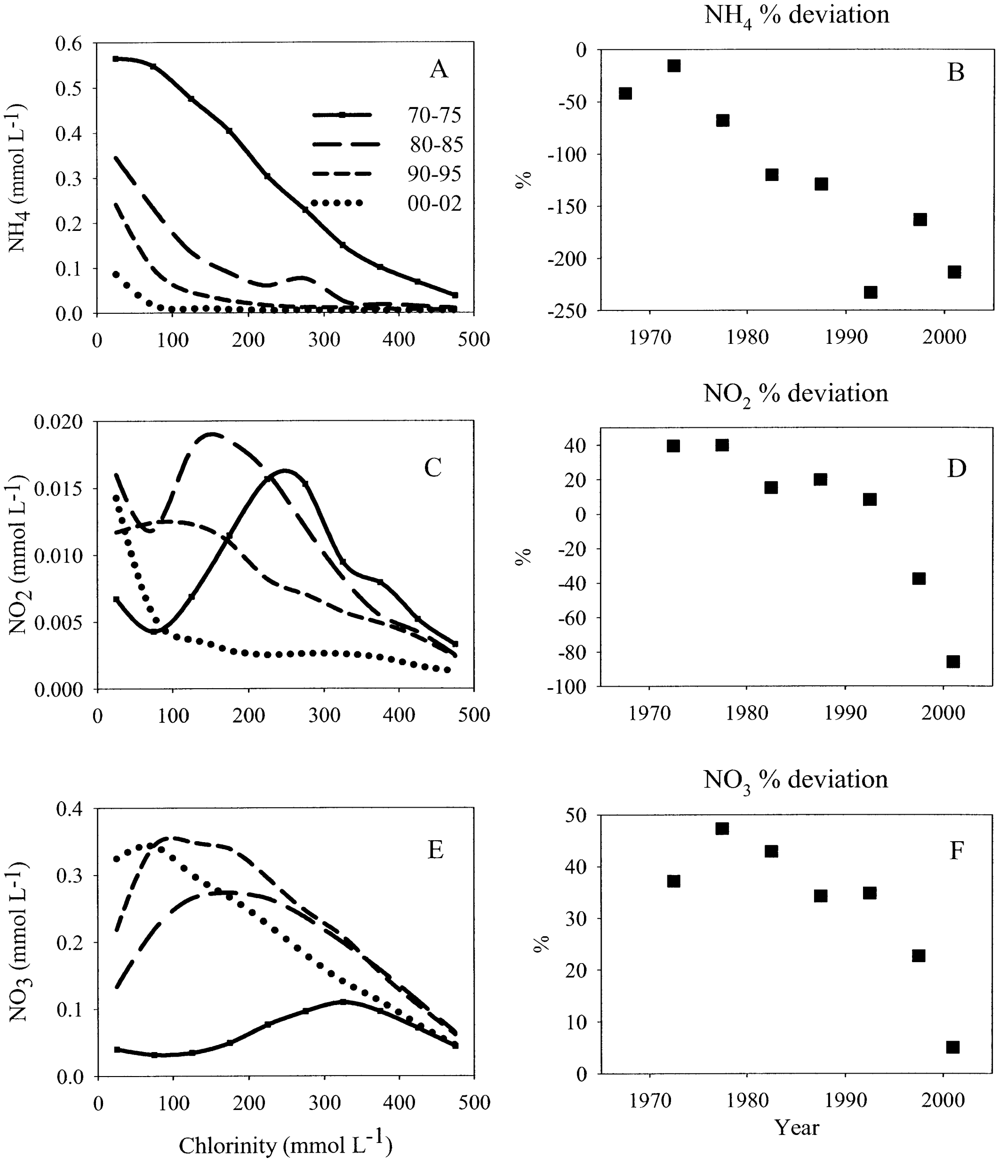

Fig. 6. (A, C, E) Five-year–averaged concentrations of nitrogen species, binned in 50 mmol L^{-1} chlorinity intervals for four selected periods; data upstream from Rupelmonde were excluded. (B, D, F) Percent deviation from conservative behavior, for 5-yr intervals (*see* Data analysis for more details). Positive values indicate a net source, negative values a net sink.

1970s compared to the other periods (Fig. 6E); concentrations declined in the upstream part and then peaked more downstream, after which they declined to marine values. The initial decline of nitrate concentrations upstream was not observed later on, but a clear nitrate peak was still visible, and it moved more toward the river as time progressed. Riverine nitrate concentrations increased from 40 to 324 μmol L^{-1}, while seaward concentrations varied between 44 and 67 μmol L^{-1}. Over the entire period, the estuary behaved as a net producer of nitrate (Fig. 6D), but this net production of nitrate decreased in time. At the start of the 21st century, the estuary behaved almost conservatively with respect to nitrate (i.e., the sinks almost balanced the sources).

The contribution of various lateral waste inputs for the brackish-marine part of the estuary is shown in Fig. 7 for the period from 1980 to 1988 (data from RIKZ, as used in the MOSES model; Soetaert and Herman 1995*a*). Non–point source agricultural land (runoff and precipitation) was the principal lateral source of nitrate (60%) and DSi (76%), while point sources (industrial and communal wastes) were the principal lateral input of ammonium (83%), total DIN (63%), and DIP (81%). Concentrations of nutrients in the inflowing water were always higher than those in the ambient estuarine water, with a factor 5 for ammonium, minimal 1.4 for nitrate + nitrite (Fig. 7). Consequently, lateral discharges were a source of nutrients rather than diluting ambient concentrations during this time period.

For the Belgian part of the Scheldt (Gent to the Belgian–Dutch border), volume-averaged, annual mean concentrations of dissolved inorganic nutrients, their molar ratios, the

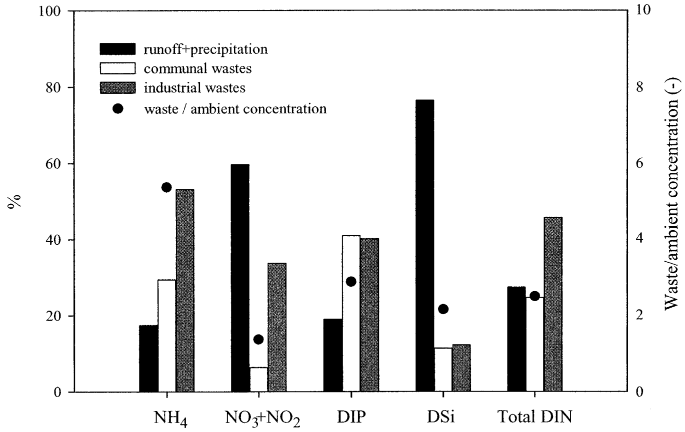

Fig. 7. Relative contribution of various sources to waste inputs to the brackish-marine part of the Scheldt estuary in the period from 1980–1988. Dots give the average proportion of nutrient concentrations in the waste loads versus ambient concentrations (Source: Rijkswaterstaat).

fraction of DIN as ammonium, and the oxygen concentration and biochemical and chemical oxygen demand are shown in Fig. 8. DIN and DIP concentrations increased through the mid-1970s, after which they declined. DSi concentrations were lower in the period preceding 1970 and declined more or less from then on (Fig. 8A). The increase in concentrations in the period from 1968 to 1974 was estimated at a (linearized) rate of 54 and 3.7 μmol L^{-1} yr^{-1} for DIN and DIP, respectively, which represents annual increases of 10% and 16% of their concentration (data not sufficient to calculate for DSi). The consequent decrease (after 1975) was much less pronounced and was calculated at 1.5 μmol L^{-1} yr^{-1}, 7.2 μmol L^{-1} yr^{-1}, and 1.3 μmol L^{-1} yr^{-1} for DSi, DIN, and DIP respectively (i.e., a decrease of the mean concentration per year with 1%, 1.6%, and 6.9%).

The N : P and Si : P ratios were lowest around 1975 (8.7 and 2.9, respectively) and peaked at the turn of the century (61 and 24, respectively). The Si : N ratio changed more erratically and varied between 0.26 and 0.43 (Fig. 8B). Chemical oxygen demand (COD, the concentration of potentially oxidizable substances, Fig. 8C) peaked in 1980, while biochemical oxygen demand (BOD, measured as the amount of oxygen consumed during 5 d at 20°C) peaked somewhat earlier (mid-1970s) and then decreased until 1996; a prominent increase in 1996 was visible (Fig. 8D). The part of total DIN as ammonium increased first from ~40% in 1967 to almost 100% in 1971 and then decreased steadily to less than 10% in the 20th century; an increase in the relative importance of ammonium was visible in 1996 (Fig. 8E). The annual mean oxygen concentration dramatically decreased from 180 μmol L^{-1} (about 50% saturation) in the mid-1960s to less than 100 μmol L^{-1} (~25–30% saturation) in the 1970s and remained low until the end of the 1970s, after which it recovered steadily to 50% saturation in the early 1990s; a second increase in oxygenation is visible from 1995 onward (Fig. 8F).

Similar patterns were observed for the entire estuary (Gent to Vlissingen, Fig. 9), although estuarine averages for phosphate could only be calculated after recovery was already imminent. Overall there was a net decrease in the concentrations of all nutrients with time (Fig. 9A). As phosphate declined more quickly (linearized rate of 0.3 μmol L^{-1} yr^{-1} or ~5.4% yr^{-1}, from 1980–2002) than DIN (2.9 μmol L^{-1} yr^{-1} or 1.7% yr^{-1}) and DSi (0.6 μmol L^{-1} yr^{-1} or 1.2% yr^{-1}), the N : P and Si : P ratios increased from values of about 20 and 6, respectively, in the early 1980s to about 40 and 16, respectively, after 2000 (Fig. 9B). The Si : N ratio varied with a factor 2 during this period (0.22–0.4); there was no clear temporal trend, but the Si : N ratio was significantly and positively correlated with yearly averaged river discharge ($r^2 = 0.53$—Fig. 9B, inset). This relationship was due to the negative correlation that existed between NH_4 and discharge ($r^2 = 0.42$) or DIN and discharge ($r^2 = 0.53$).

Discussion

Nutrient inputs in estuaries come from riverine and agricultural sources, industrial and urban sewage, and atmospheric deposition (Howarth et al. 1996). Before the 1970s, most effluents from industrial and domestic sources were discharged both directly to the Scheldt river and estuary and indirectly, via the sewage systems. Some of these effluents had a very high biochemical and chemical oxygen demand (BOD, COD) and high nutrient concentrations. Since that period, major efforts have been undertaken to reduce this load, and this effort is still increasing, although it is mainly concentrated on point sources of nutrient pollution. The volume-averaged concentration data show how these discharges of agricultural, industrial, and municipal wastewater in the rivers and estuary first caused an increase in nutrient levels and deterioration of the oxygen concentration in the water until the middle or end of the 1970s (Figs. 8, 9). After that period, a marked decrease in nutrient loading and improvement of oxic conditions occurred. In the Belgian part of the Scheldt, the increase in nutrient concentrations from 1967 to 1974 was estimated to occur at a linearized rate of more than 10% per year for DIN and DIP, while the subsequent reduction in nutrient concentrations occurred at a much lower rate. For the whole estuary, the reduction numbered 1%, 1.3%, and 5.4% of the concentrations per year for DSi, DIN, and DIP, respectively. With these rates, the objectives, set by the states of the region, to halve the quantities of nutrients reaching the North Sea by 1995—compared to the base year 1985—were clearly met for phosphorus but not for DIN. We can estimate that, at the current rate of nutrient reduction, it will take at least another decade before the desired goals are achieved for nitrogen.

The initial increase and consequent reduction in nutrient loads that was observed in the Scheldt parallels other findings from nearby eutrophic systems (Colijn et al. 2002; Van Raaphorst and de Jonge 2004). The effect is generally clearer for phosphorus (Van Bennekom and Wetsteijn 1990; Menesguen et al. 1995; Howarth et al. 1996) than for DIN and DSi, which may increase, decrease, or remain virtually constant (Menesguen et al. 1995; Heathwaite et al. 1996; Gowen et al. 2002). This different behavior of P and other nutrients has been attributed to improved point-source treatment and control, particularly for P (e.g., by reduction of industrial

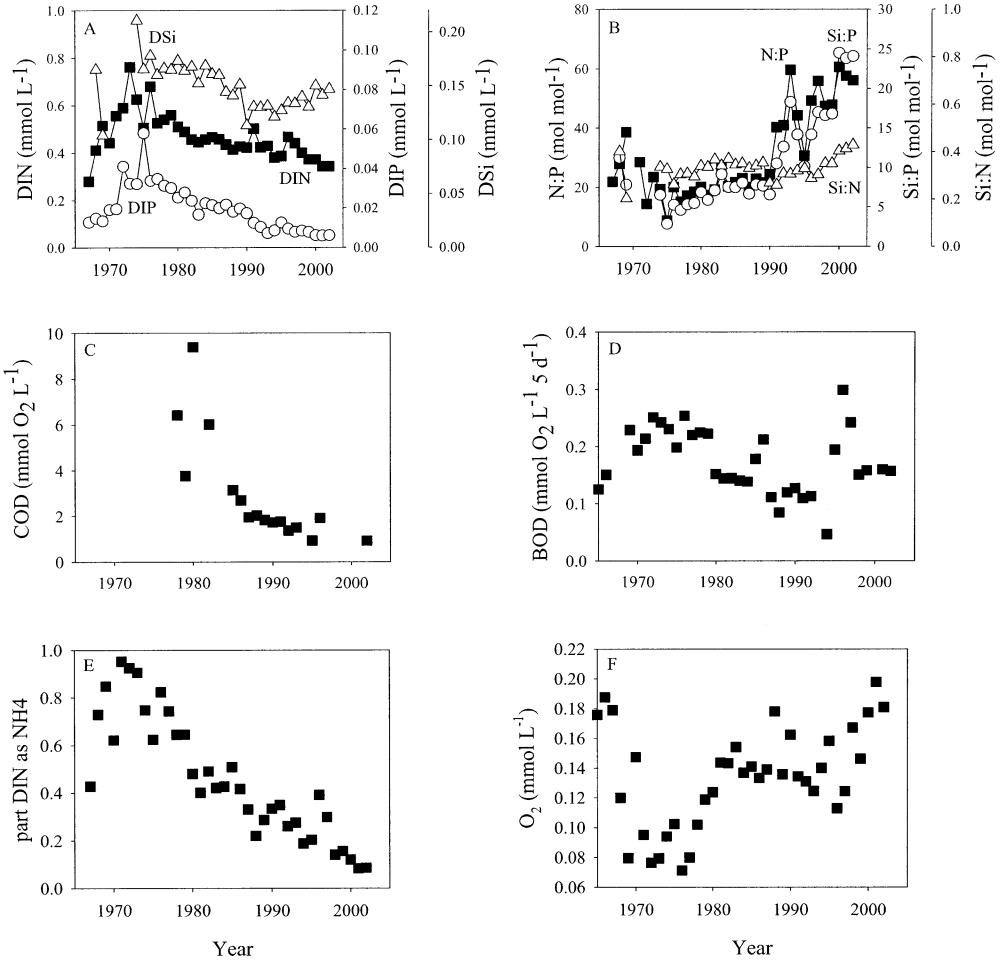

Fig. 8. Long-term changes in annually averaged properties in the Belgian Scheldt (Gent-Belgian–Dutch border). (A) Nutrient concentrations. (B) Nutrient ratios. (C) Chemical oxygen demand. (D) Biochemical oxygen demand (20°C). (E) Relative contribution of NH_4 to total DIN. (F) Oxygen concentration.

effluents from fertilizer factories in the watershed [Menesguen et al. 1995], by the more cost-effective removal of P in wastewater treatment processes [d'Elia et al. 2003], or by replacement of P-containing detergents with other products [Gowen et al. 2002]). Moreover, DIN and DSi are often more prominent in non–point sources, which are more difficult to control (Colijn et al. 2002; Howarth et al. 2002). These factors also explain the trends in the Scheldt. During the period from 1980 to 1988, most of the DSi input was contributed by non–point sources (76%), while this input was only 27% and 19% for DIN and DIP, respectively (Fig. 7). In Flanders, the households connected to a purification plant increased from almost none in 1970 to 30% in 1990, then to 60% in 2002 (Maeckelberghe 2002). This led to important reductions in municipal emissions for phosphorus but not for nitrogen (Source: MUMM). In contrast, the decline in emissions by industries was similar for P and N; it was estimated that the discharge of BOD, COD, P, and N were reduced with 28%, 51%, 60%, and 60%, respectively, from 1994 to 2002 (Maeckelberghe 2002). Finally, the agricultural sources of nitrogen have actually risen (source: MUMM), while they stayed relatively constant for phosphorus.

Nutrient loadings from estuaries to coastal waters are affected both by water discharge and the nutrient concentration. The dependencies are not always straightforward, as water discharge may itself affect the concentration in various ways (e.g., by dilution, leaching of fertilizers from terrestrial systems after heavy rainfall, or increased land erosion) (Johnson 1978). In addition, larger discharges may reduce the residence time within the estuary and thus the effect of resident estuarine processes, such as denitrification (Balls 1994; Colbert and McManus 2003). High nitrate inputs can also occur when wastewater is discharged that has been only partially treated, because the delivery rate to the purification plants exceeds their capacity for treatment. We did not find any evidence for increased concentrations of nutrients with high discharge; however, ammonium and total DIN concentrations were significantly and negatively affected by the yearly discharge, probably through dilution. It is not clear why only DIN concentrations are affected, but as a consequence, there was an increase in the Si : N ratio with increasing discharge (Fig. 9B); overall, annually averaged Si : N ratios varied with a factor 2. The other nutrient ratios were not affected by discharge but displayed a strong temporal pat-

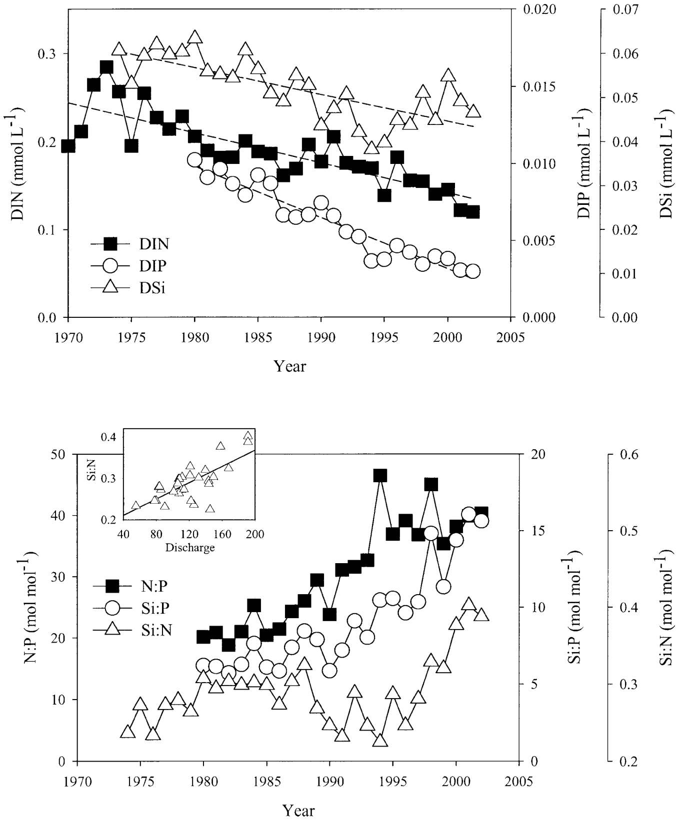

Fig. 9. Long-term changes in annually averaged properties for the total Scheldt (Gent–Vlissingen). (A) Nutrient concentrations. (B) Nutrient ratios. Inset: regression of Si : N ratio (mol mol^{-1}) vs. river discharge (m^3 s^{-1}) ($r^2 = 0.53$).

tern. In the period considered, the molar N : P ratio more than tripled in the Belgian part (from 15 to well above 50, Fig. 8B) and doubled when the entire estuary was considered (from 20 to 40; Fig. 9B). The Si : P ratios increased by similar amounts and now reach 25 and 16 in the Belgian section and entire estuary, respectively. Similar changes in stoichiometric ratios were reported from several nearby systems, including the river Rhine (van Raaphorst and de Jonge 2004), several U.K. estuaries (Nedwell et al. 2002), and the Wadden Sea (Philippart et al. 2000), and this pattern is consistent with observations in the majority of the world rivers (Turner et al. 2003). Analysis of nutrient stoichiometry can indicate potential N, P, or Si limitation of phytoplankton growth when the relative proportion of elements deviates substantially from the ratios required for sustained algal growth (1 : 1 for Si : N, 16 : 1 for N : P and Si : P). Generally it is assumed that ambient molar ratios of dissolved N : P of $<$10 and of Si : N of $>$1 indicate stoichiometric N-limitation, while Si : N values of $<$1 and Si : P values of $<$3 indicate Si limitation of diatoms; an N : P value of $>$20–30 indicates P-limitation (Dortch and Whitledge 1992; Justic' et al. 1995). The N : P and Si : P ratios found in the Scheldt suggest that the conditions have evolved to potential P limitation of the phytoplankton, while the Si : P ratio has exceeded or is very near to the Redfield stoichiometric ratios for diatoms. These alterations in the Scheldt and adjacent systems may also have affected processes and conditions in the southern North Sea, where recent P-limitation of algae, including diatoms, has been reported (Peeters and Peperzak 1990).

In the Scheldt estuary, the SPM concentrations were generally above 10 mg L^{-1} (Fig. 4A—also *see* secchi depth, Fig. 4B), a threshold value above which primary production is usually inhibited (DeMaster et al. 1983; Ragueneau et al. 2002). Because of these high SPM concentrations, and the fact that the nutrient concentrations were most often well above reported half-saturation constants, the algae in the Scheldt are light-limited (Soetaert et al. 1994), and the altered nutrient ratios probably have only limited effects on estuarine functioning. It is not clear whether changes in the light field are responsible for the observed upstream translocation of the chlorophyll (Fig. 5F). The data on SPM are not sufficiently detailed and, as a result of tidal resuspension and deposition, are too variable to discern any long-term changes. However, it is more likely that, with the improvement of oxic conditions and the recolonization of the area by higher animals, such as mesozooplankton (Appeltans et al. 2003), grazing may have depressed the chlorophyll concentration in the area of 100–200 mmol L^{-1} chlorinity from the 1990s onward.

In the freshwater, tidal part of the Scheldt, the rivers Rupel and Upper Scheldt bring water rich in nutrients (Figs. 5, 6) and particulate and dissolved organic matter (Fig. 4) and relatively poor in oxygen (Fig. 5). As this water is carried downstream, ongoing estuarine processes, dilution with seawater, and dilution or enrichment from lateral sources changes its composition.

Along the chlorinity axis, the concentration of dissolved silicate was always lower than would be expected by theoretical mixing lines between marine and freshwater endmembers (Fig. 5G). This indicates that in the estuary, the removal rates (uptake by diatoms and consequent deposition and burial) exceeded nutrient regeneration from dissolution and input from lateral sources. DIP was always consumed in the high-turbidity region of the estuary, the zone most upstream (Fig. 5C), consistent with sorption and colloidal aggregation that remove phosphate in other turbid estuaries (e.g., Sanders et al. 1997). In addition, its concentration increased slightly in the zone downstream, pointing to regeneration by organic matter mineralization plus lateral input exceeding removal there. Such clearly separated zones of removal and regeneration could not be discerned for DIN; instead, there appeared to be a consistent net addition (before 1995) or removal (after 1995) along the estuarine axis (Fig. 5E).

Although DIN and DIP regeneration are both mediated by organic matter mineralization, the relative filtering effect of the Scheldt for these two nutrients was found to be significantly different. Concurrent with improving redox conditions in the estuary and decreasing concentration in the river, the filter function for DIP decreased (Fig. 5D), while the filter became more efficient for DIN (Fig. 5F). The initial decrease of the estuarine filter efficiency for DIN from the mid-1970s until 1985 (Fig. 5F) was expected and follows the reduced importance of water-column denitrification (*see* following section). The consequent increase of the retention efficiency for DIN is probably related to a reduction in the degree of organic matter mineralization, which in turn lowers DIN regeneration. In addition, it may point to an increased importance of sedimentary denitrification, caused by higher nitrate concentrations in the overlying water combined with reduced sediment organic matter deposition rates (Middelburg et al. 1996*a*). The trends in COD and, to a lesser extent, in BOD (Fig. 8), indicate that the input of substances with the capacity to consume oxygen, including organic matter, have decreased since the mid-1970s to 1980s (Fig. 8), although there remains much residual variation. This reduced organic loading may have lowered the regeneration of DIN from organic matter mineralization, with the consequence that the estuary behaved as a net sink for DIN after 1995 (Fig. 5E–F). In contrast, during the same period, the whole-estuary DIP sources were larger than the removal terms and the estuary behaved as a net source for DIP (Fig. 5C–D). This indicates the existence of some other mechanism that has reversed the effects of reduced organic matter loading and improved oxic conditions on phosphate concentrations. This was unexpected, because in general, the retention capacity for P is believed to increase when oxic conditions are restored (e.g., Cloern 2001). A lack of such relation was also recently found in lakes (Gächter and Müller 2003) and attributed to complex interactions between the cycles of iron, S, and P in lake sediments. Moreover, it has been shown that under reduced phosphorus loading in the inflowing water, the (estuarine) P-sink may become phosphate limited, and this may even promote desorption of DIP from relic high-phosphate sediments, deposited under high riverine DIP concentrations (Prastka et al. 1998). The current concentrations of phosphate in the riverine end-member range between values of 5–10 μm L^{-1}, which is still higher than the concentrations of 1–5 μmol L^{-1} for which desorption of phosphate is predicted to occur (Prastka et al. 1998) but which is within the range in which the efficiency of phosphate removal decreases strongly (Sanders et al. 1997; Prastka et al. 1998).

The differential filter behavior of the estuary with respect to DIN and DIP in part counteracted the anthropogenic alterations in the estuarine loadings. By the net addition of DIP and removal of DIN in the Scheldt after the 1990s, the pronounced increase in the molar N : P ratio (15 to 50), as observed in the waters of the Belgian (upstream) part, is significantly alleviated when reaching the mouth of the estuary (20 to 40).

The net nutrient removal efficiency thus depends crucially on the nutrient regeneration from organic matter. Unfortunately, it is not straightforward to estimate levels of nutrient regeneration, but numerical model estimates indicate that they are on the same order of magnitude as input of dissolved inorganic nutrients (Soetaert and Herman 1995*a*). Combining the measured C : N ratio (Fig. 4E) with the concentration of particulate organic carbon (Fig. 4C), we can estimate that the concentration of particulate organic nitrogen is close to 10% of DIN. However, particulate organic matter has a much longer residence time in the estuary than do dissolved substances (Soetaert and Herman 1995*b*), as it is moved downstream with the freshwater flow and upstream by tidal pumping. It has been argued that the estuary imports particulate organic matter both from the river and the sea (Soetaert and Herman 1995*a,c*), consistent with estimates from other estuaries (e.g., Tappin et al. 2003) and observations on the spatial distribution of benthic mineralization in the Scheldt estuary (Middelburg et al. 1996*a*). The increase in the C : N ratio mid-estuary (Fig. 4E), an indication of reduced degradability and extensive modification of the particulate organic matter, is consistent with the mixing and ageing of these two sources of organic matter. We would also remark that these C : N ratios are significantly higher than the ones expected for phytoplankton living in turbid and nutrient-rich environments, giving further evidence that the organic matter is dominated by allochthonous detrital material (Middelburg and Nieuwenhuize 1998; Boschker et al. 2005). The apparent conservative nature of dissolved organic matter (DOM) in the Scheldt (Fig. 4D), although consistent with that of many European estuaries (Abril et al. 2002), may be misleading, as there is evidence that DOM concentration in estuaries is buffered through sorption on suspended matter (Herman and Heip 1999), and this may mask net biological consumption.

The tidal Scheldt is well mixed, has a simple trumpet-shaped morphology (Fig. 1B), and a similarly shaped, gradual salinity gradient that is relatively time-invariant (Fig. 3). Combined with the relatively long residence time of the water (Soetaert and Herman 1995*b*), dissolved inorganic nutrient and organic matter inputs result in the establishment of pronounced biogeochemical gradients. Our data clearly show how this biogeochemical zonation has been altered following reduction in loadings. In the early 1970s, large quantities of ammonium were imported in the most upstream area (Fig. 6A), the annually averaged concentrations in the riverine part exceeding 500 μmol L^{-1}. The decay of organic matter and the oxidation of ammonium in the turbid upstream region caused anoxic conditions in summer and low annually averaged oxygen concentrations in this region (Fig. 5A). The reduction of nitrate concentration in the upstream, low-oxygen zone indicates that important denitrification occurred in the water column during that period (Fig. 6E). Billen et al. (1985) indeed measured significant water-column nitrate consumption in 1976. Major reoxidation of ammonium to nitrite and nitrite to nitrate was postponed until downstream from 100–150 and 150–200 mmol L^{-1} chlorinity, respectively (salinity 6–9, respectively, 9–12; Fig. 6C, E). Starting from 1980 and continuing onward until the present day, a clear reduction of water-column denitrification and a progression of the nitrification front toward the upstream region were observed. This was probably induced by a significant decrease in the concentration of ammonium (Fig. 6A) and an increase in the nitrate concentration in the riverine end-member (Fig. 6E) and reduced loadings of organic matter, as reflected in COD (Fig. 8). In the period extending from 1980 to 1985, the profiles for nitrate lacked any indication of water-column denitrification (Fig. 6E), but the drop in nitrite concentration in the upstream part was still prominent (Fig. 6C), indicating that consumption of nitrite by denitrification was still proceeding. Past 1990, signs of water-column denitrification were absent. This decrease in water-column denitrification probably caused the reduced retention efficiency for DIN observed from 1975 until 1985 (Fig. 5F). From 1975 onward we also observed a gradual progression of the zone of nitrification from mid-salinity to upstream

(Fig. 6C, E). At the beginning of the 21st century, nitrification seemed to be significant only in the upstream region. With ammonium concentrations in the riverine Scheldt estuary having dropped to $<100\ \mu\text{mol L}^{-1}$, signs of net nitrite production were lacking, while the oxidation to nitrate caused an increase of nitrate concentrations in the most upstream region only. Downstream from this region, nitrate behaved quasi-conservatively, mainly reflecting the dilution of the nitrate-rich upstream water with low-nitrate coastal water. Our inferred upstream migration of the nitrification front is consistent with anecdotal measurements of nitrification, nitrous oxide concentrations, and particulate $\delta^{15}N$ signatures. In the 1970s, nitrification activity (Billen 1975), dissolved nitrous oxide concentrations (de Wilde and de Bie 2000), and $\delta^{15}N$ (Mariotti et al. 1984) were high and most pronounced in the mid-estuary, while in the period from 1990 to 1995, nitrification (de Bie et al. 2002*b*), nitrous oxide concentrations (de Bie et al. 2002*a*), and particulate $\delta^{15}N$ (Middelburg and Nieuwenhuize 1998) peaked in the freshwater part of the estuary, declining downstream.

The anthropogenic eutrophication problem requires quantification and eventually mechanistic understanding of processes occurring within estuaries, the main conduits of land-derived nutrients to the coastal zone. Particularly, the retention function of estuaries is of relevance to global change questions, and the simplifications taken in this article should be viewed as a first small step toward increasing our understanding. If anything, we show that the estuarine processes are complex and incompletely understood and may change fundamentally on decadal time scales. Moreover, correct interpretation of the filter effect of estuaries requires knowledge regarding the behavior of organic matter and organic nutrients in addition to dissolved inorganic nutrients. Establishing estuarine nutrient budgets is fraught with difficulties that are best approached by the use of mechanistic models (e.g., Tappin 2002; Tappin et al. 2003). Previous attempts to estimate nutrient budgets or to model the Scheldt estuary have focused on specific time periods (e.g., the 1970s [Billen et al. 1985], the 1980s [Soetaert and Herman 1995*a,c*], or the 1990s [Regnier et al. 1997]). As the Scheldt changed so drastically during these periods, it is not surprising that these authors sometimes reported fundamentally different results. One of the future challenges will be to refine our process descriptions and parameterization of the biogeochemical processes to arrive at one operational model that covers the whole suite of loadings that have affected the Scheldt.

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