Chapter 4

Possible effects of climate change on estuarine nutrient fluxes: a case study in the highly nutrified Schelde estuary (Belgium, The Netherlands)

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Abstract

Global change models predict effects of climate change on hydrological regimes at the continental scale in Europe. The aim of this study was to gain a better understanding of the possible effect of changing external forcing conditions on the functioning of estuarine ecosystems. In densely populated areas, anthropogenic nutrient enrichment and consequent alteration of nutrient biogeochemical cycles have already had a big impact on these ecosystems. The average yearly discharge of the upper Schelde estuary increased nearly threefold over the period 1996-2000, from 28 $m^3 s^{-1}$ in 1996 to 73 $m^3 s^{-1}$ in 2000. The continuously rising discharge conditions over the 5-year period were used as a reference situation for possible future effects of climate on ecological functioning through increase of discharge. At high discharges, nutrient (NH_4^+, NO_3^-, dissolved silica and PO_4^{3-}) concentrations in the tidal fresh- and brackish water showed a decrease of up to 50% while total discharged nutrient loadings increased up to 100%. Opposite effects of increasing discharge on NH_4^+-, NO_3^-- and dissolved silica concentrations in summer and winter, resulted in the flattening out of seasonal cycles for these nutrients. Under high discharge conditions, silica uptake by diatom communities was lowered. Dissolved silica loadings to the coastal area increased concurrently with total silica loadings upstream. Salt intrusion to the marine parts of the estuary decreased. This

resulted in a downstream shift of the salinity gradient, with lower salinity observed near the mouth. As a result, TDIN-, NO_3^-- and dissolved silica concentrations doubled at the mouth of the estuary.

4.1 Introduction

Coastal zones and shallow marine areas are among the most productive systems in the world (Mann, 1988; Glantz, 1992). They form the main fishery grounds on Earth (Postma & Zijlstra, 1988; Sherman *et al.*, 1991). One of the major worldwide problems, in densely populated areas, is the eutrophication of these estuarine and coastal waters (Nixon, 1990; Gray, 1992; Doering, 1996; Boesch 2002). For most temperate estuaries and coastal ecosystems, N is the element most limiting to primary production and most responsible for eutrophication (Howarth, 1988; Howarth *et al.*, 1996, Nixon *et al.*, 1996). Since the reduction of phosphorus inputs from polyphosphate-containing washing powders, phosphorus concentrations in estuarine environments have decreased, while nitrate concentrations remained high (Van Damme *et al.*, 1995; Billen & Garnier, 1997; Zwolsman, 1999). In contrast to N and P, the silica concentration in estuaries is only indirectly influenced by human pollution. Diatom communities require about equal amounts of N and Si. Diatoms are an essential element of coastal water food chains. Increased N-concentrations can lead to a succession from phytoplankton communities dominated by diatoms to phytoplankton communities dominated by species that are not taken up by higher trophic levels (*e.g. Phaeocystis* sp., *Gonyaulax* sp., *Chrysochromulina* sp.) (Schelske *et al.,* 1983; Smayda, 1990; Smayda, 1997). The North Sea, with extensive input of nutrients from rivers (Rhine, Elbe, Schelde) and its isolated nature, has been characterized by increasing eutrophication events (Lancelot *et al.*, 1987; Brockmann *et al.*, 1988; Richardson, 1989; Lancelot, 1995; Ducrotoy *et al.*, 2000).

Coastal zone ecosystems are strongly affected by natural variations in climate (Holligan & Reiners, 1992). Human induced climatic changes can accordingly have a further effect on the ecology of estuarine environments. Regional and global shifts in temperature, changes in cloud cover, increasing or decreasing precipitation regimes and sea level rise are among the most commonly cited alterations due to human impact on the trace gas composition of the atmosphere (Mitchell, 1989, Wigley & Raper, 1992). A reliable forecasting of global change effects on the land-ocean interface is one of the key aspects in the Land-Ocean-Interactions-in-the-Coastal-Zone-programme (LOICZ), a core project of the International Geosphere-Biosphere Programme (IGBP)

(Kondratyev & Pozdnyakov, 1996). Studies, both observational and theoretical, addressing the issue of material fluxes to coastal zones under changing external forcing conditions, have a critical international importance.

Our aim is to focus on the impact of changing hydrological conditions on estuarine water quality and fluxes of nutrients to coastal waters. Generally, in river basins in temperate regions (Belgium, Quebec, Scotland), an increase in discharges and flooding events is predicted (Gellens & Roulin, 1998; Roy *et al.,* 2001; Werritty, 2002). Although different scenarios exist, all scenarios of global change models, at the continental scale of Europe, predict an increased run-off in North and Western Europe (Arnell, 1999). Schelde freshwater discharges could increase up to 28 % during the next century (source: AWZ, Flanders Waterways and Maritime Affairs Administration). Increased precipitation results in a larger proportion of rainfall transferred directly to surface waters by surface run-off as soil storage capacity is exceeded (Wanielista 1990). It is hypothesized that the diffuse nutrient and sediment inputs to the estuary are positively related to the surface run-off and predicted climate change will result in larger loads of nutrients transported towards the estuary.

Higher freshwater discharges can further influence estuarine ecology by decreasing water residence times in the main estuarine channel. The upstream tidal freshwater regions are likely to be most affected by changing freshwater discharges as the impact of marine waters is negligible and advective freshwater flows dominate over dispersive tidal flows. Muylaert *et al.* (2001) have shown how short-term freshets can result in the flushing of entire diatom communities from the freshwater reach. Nutrients and organic material are transferred more rapidly to coastal waters, and important ecological processes (*e.g.* denitrification, nitrification, mineralisation, nutrient uptake) in nutrient cycling have less time to act upon the large volumes of nutrients, which could lead to alterations of fluxes of N, P and Si downstream to coastal waters.

Recent studies have mainly focused on predicting the impact of climate induced hydrological changes on estuarine ecosystem functioning based on modeling different scenarios (Schirmer & Schuchardt, 2001; Nijssen *et al.*, 2001; Justic *et al.* 1997). This study is based on observations made during a period of continuously rising discharge. The period 1996-2000 was characterised by steadily increasing flow conditions in the Schelde estuary, caused by interannual precipitation variability. Detailed time-series of nutrient concentrations in the marine, brackish and freshwater reaches of the Schelde estuary (1996-2000) where studied under these continuously increasing discharge conditions. Covariation between long-term nutrient and oxygen concentrations on the one hand and freshwater discharges on the other hand was examined using standard least-squares linear regression to assess correlation between nutrient concentrations or nutrient fluxes and discharge.

4.2 Materials and Methods

4.2.1 Study area

The Schelde estuary (Fig. 4.1), located in Northern Belgium (Flanders) and the Southwest Netherlands, has a long history of extensive anthropogenic pollution (De Pauw, 1971; Bakker & Heerebout, 1971; Wollast, 1988; Boderie *et al.*, 1993, Baeyens, 1998). It is known as extremely eutrophic and receives large inputs of nutrients from non-point as well as point sources (Heip, 1988). A large freshwater tidal area characterizes the Schelde. This is approximately situated between Gent (km 155, *i.e.* 155 km upstream of the estuarine mouth) and Temse (km 100). The major tributaries to the Schelde, situated respectively at Dendermonde (120 km upstream the mouth) and at the interface between the freshwater and brackish zone near Temse (100 km upstream the mouth), are the Dender and the Rupel. The Rupel receives large inputs of untreated waste from the city of Brussels.

Upstream of Dendermonde, the tidal freshwater zone is characterized by small channel width (30 m) and depth (5-10 m). The volume of freshwater in this zone is only about 30% of total freshwater volume in the estuary. Consequently, the residence time is short and relatively strongly influenced by freshwater discharges compared to downstream regions (Van Damme, pers. comm.). Changes in freshwater discharge can induce a threefold decrease in residence times in this tidal freshwater (2-6 days).

The brackish part of the estuary is situated between Temse and the Dutch-Belgian border (km 55). The Dutch part of the estuary is the marine region. Dendermonde is situated centrally in the freshwater tidal area. Water quality between Temse and Gent usually shows little longitudinal variation compared to the downstream estuarine regions (Van Damme *et al.*, 1995). Measurements at Antwerp and Vlissingen represent respectively the brackish and the marine area.

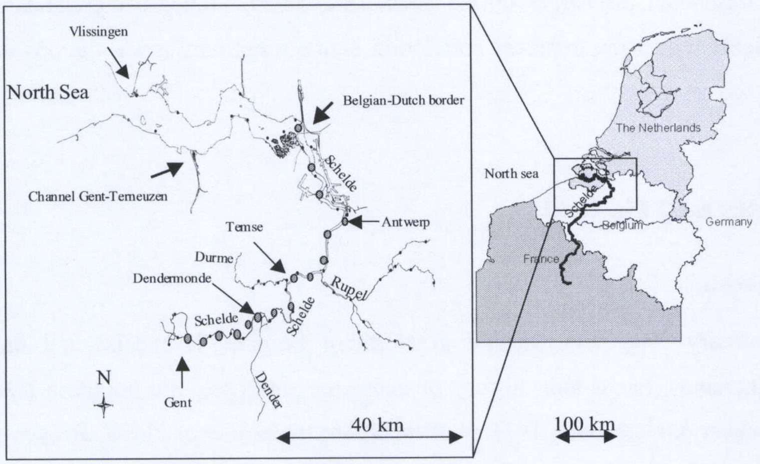

Fig. 4.1: The Schelde estuary and its tributaries; • = monitoring measuring point

4.2.2 Sampling

Between January 1996 and December 2000, surface water samples were taken monthly in the middle of the river from a boat at 16 stations along the longitudinal gradient of the Schelde estuary and in the mouth of the Rupel (from April 1996 on). No samples were taken on the Zeeschelde and Rupel in January 1997 because of ice formation on the rivers. Discharges were measured by AWZ. Discharge of the Bovenschelde (the Schelde just upstream Gent, where tidal influence is stopped by sluices), the Dender and the Rupel was continuously measured, and daily means were calculated. Freshwater discharge at Dendermonde is the sum of discharges of Bovenschelde and Dender, freshwater discharges downstream Antwerp are the sum of Rupel and Dendermonde discharges. The marine (Dutch) estuary is sampled by NIOO-CEME (National Institute of Ecological Research, Centre for Estuarine and Marine Ecology). NIOO-CEME did initially not sample at the same frequency as for the Belgian sampling, especially in winter 1996 and 1997. Some analyzing methods are different for the NIOO-CEME, but intercalibrations were performed to ensure reproducibility.

4.2.3 Analysis

Oxygen was measured *in situ* with a 'WTW OXI 91' oxygen-meter. All other variables were analysed *ex situ* within 24 hours after sampling. Specific conductivity was measured with a 'WTW LF 91' conductivity-meter. Chloride, ammonium (NH_4^+-N), nitrite (NO_2^--N), nitrate (NO_3^--N) and DRP (PO_4^{3-}-P) concentrations were analyzed colorimetrically on a 'Segmented Flow Analyzer Skalar®'. Kjeldahl-N (NH_4^+-N + organic N) and totP were analyzed after digestion in H_2SO_4. Dissolved silica concentration measurement was conducted on an 'Inductively Coupled Plasma Spectrophotometer Iris®'. Silica was monitored since July 1996.

Water quality and discharge data were analyzed for Dendermonde, Antwerp and Vlissingen, respectively 120 km and 80 km upstream of the mouth of the estuary and at the mouth, as well as for the Rupel tributary (Fig. 4.1). Winter and summer were defined as January-March and June-September respectively. These periods were chosen because they show the least intra-annual variation in water quality and low and high chlorophyl a-concentrations (biological activity) respectively (Van Damme, pers. comm.). To measure the influence of discharge on quality trends, it is important to make a seasonal distinction, as nutrient concentrations and discharge show similar seasonal trends.

Discharged loads per time unit (g s^{-1}) were calculated from equation (1):

$$F = Q * s - EA\frac{\partial s}{\partial x} \qquad (1)$$

in which F is flux (mol s^{-1} over cross-surface), Q is freshwater discharge (m^3 s^{-1}), s is concentration (mol m^{-3}), E is dispersion coefficient (m^2 s^{-1}) and A is cross-surface (m^2). This equation is at the basis of the model used in Soetaert & Herman (1985). At Dendermonde and Antwerp, dispersive transport is negligible, discharged loads were essentially calculated by multiplying monthly measured concentration (mg L^{-1}) and monthly averaged discharge (m^3 s^{-1}). A recent standardization study of the dataset within tidal, vertical and longitudinal water quality variation, has shown that measured nutrient concentrations are very good indicators for conditions throughout the whole month (Van Damme *et al.*, 2005). The consistence of the measuring methods ensures that bias (if present) on calculated loads was similar throughout the study period.

For regression analysis on the concentration and freshwater discharge data, these data were log-transformed (log (x+1)). (Log-transformed concentrations were in mg N L^{-1}, mg P L^{-1}, mg O2 L^{-1}, mg Cl^{-1}, mg Si L^{-1}). This is an effective transformation to normalize estuarine water quality data (Jordan *et al.*, 1991; Doering, 1996).

4.3 Results

4.3.1 Hydrology

The average yearly discharge at Dendermonde showed a large variation from a minimum of 28 m^3 s^{-1} in 1996 to a maximum of 73 m^3 s^{-1} in 2000 (Fig. 4.2a). There was a clear seasonal variation with maxima in winter and minima in summer (Fig. 4.2b). Absolute discharge increase was much higher in winter than in summer (Fig. 4.2c). Average monthly discharge was strongly related to total monthly rainfall in winter (R^2 = 0.64, $p<0.001$, Fig. 4.2d)). In summer this relationship was less pronounced but still significant (R^2=0.39, p=0.003, Fig. 4.2d). The same increase in rainfall results in bigger discharge differences in winter than in summer. Discharge data from Antwerp show a similar pattern.

4.3.2 Nutrient concentrations and fluxes

In general, concentrations decreased at Dendermonde and Antwerp as water discharged increased, and this decrease was mainly apparent in winter (Table 4.1). Average winter concentrations in 1999-2000 (average of all winter period observations in period 1999-2000, period with high discharges) of ammonia and totP were only half the concentrations observed in 1996-1997 (period with lower discharges). TDIN, totN and DRP concentrations decreased by around 20-30%. In summer (average of all summer observations in periods 1996-1997 vs. 1999-2000), concentrations did not drop likewise. In Antwerp, totN and TDIN even increased. A Wilcoxon Rank-Sum test was performed to test the significance of the observed differences (Table 4.1). In contrast to other nutrients, nitrate concentrations increased by around 20 % in Antwerp in winter

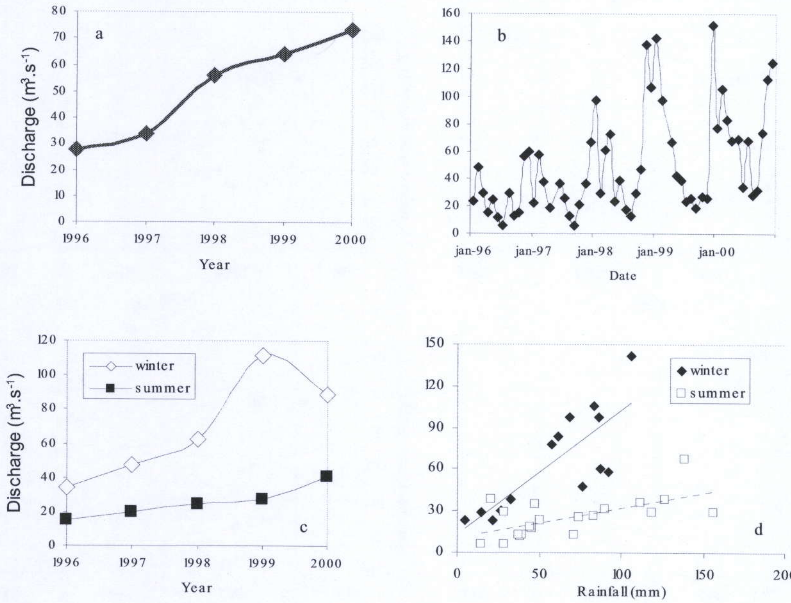

Fig. 4.2: Discharge at Dendermonde 1996-2000 (source: AWZ); a) Yearly averaged discharge; b) Seasonal patterns; c) Yearly winter and summer averages; d) Discharge dependence (least-squares regression) on rainfall. Monthly averaged discharged at Dendermonde versus total monthly rainfall at Geraardsbergen (source: KMI, Royal Meteorological Institute) (Least-squares regression: summer p=0.003, R^2=0.39, F=12; winter p=0.0006, R^2=0.64, F=22).

and summer and in Dendermonde in winter. Summer nitrate concentrations in Dendermonde slightly decreased, while oxygen conditions tripled in the freshwater zone. However, this improvement was not observed farther downstream. Winter concentrations of dissolved silica (DSi) remained virtually constant, but summer concentrations greatly increased over the 5-year study period, especially in Antwerp. Water quality over the studied period in the Rupel showed similar patterns as in Antwerp. No Wilcoxon-test was performed for the Rupel for winter data, due to less frequent data in the 1996-1997 period. In contrast to the other sites, at Vlissingen nitrate, silica, DRP and TDIN concentrations greatly increased, while totP concentrations were stable (Table 4.1, Fig. 4.3). No yearly average is shown for 1996, because in winter there was no sampling at Vlissingen.

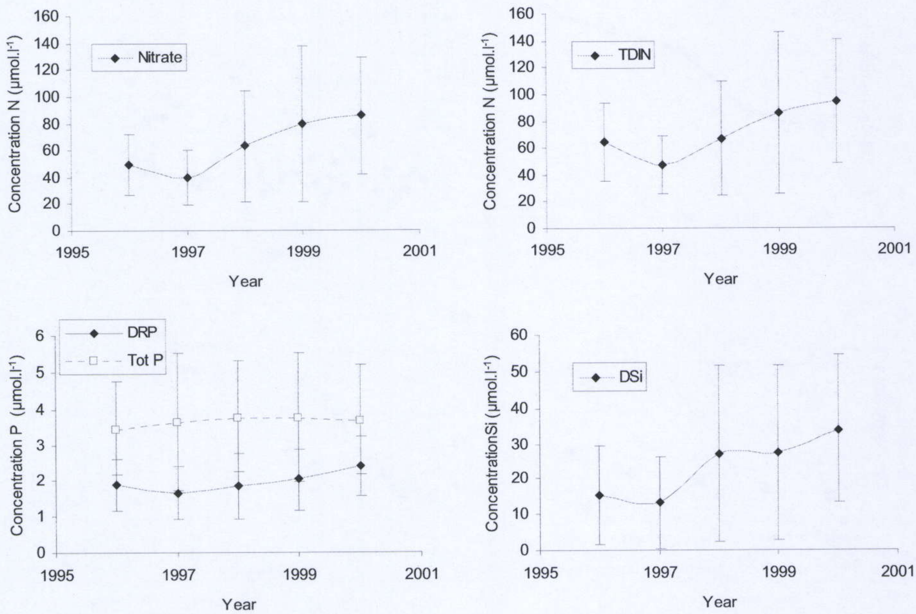

Fig. 4.3: Yearly averaged TotP, DRP-, DSi-, NO_3^-- and TDIN concentrations at Vlissingen (1997-2000), DRP = dissolved reactive phosphorous, TDIN = total dissolved inorganic nitrogen

In contrast to nutrient concentrations, discharged loads of nutrients generally increased throughout the study period. Total discharged loads of DRP, totP (Fig. 4.4a), nitrate, TDIN (Fig. 4.4b), dissolved silica (Fig. 4.4c) and chloride (Fig. 4.4d) showed clear increasing trends over the study period in the freshwater zone. Ammonia loads remained more or less constant (Fig. 4.4b). The relative proportion of nitrate in the total nitrogen load increased steadily. Similar results were observed at Antwerp and in the Rupel (not shown). However, totP loads did not increase in Antwerp. TotP loadings here were lower than the sum of Rupel and upstream freshwater totP loads. In the Rupel, totP loads only increased in 2000. At Vlissingen, total discharged load of totP, DRP (Fig. 4.4e), TDIN and nitrate (Fig. 4.4f) showed no real consistent trend. Discharged loads of silica nearly doubled (Fig. 4.4g). Ammonia loads dropped to near zero over the same period (Fig. 4.4e). Discharged nitrogen, silica and phosphorus loads were much higher at Vlissingen than upstream at Dendermonde.

Table 4.1: Average winter- and summer concentrations (all µmol L^{-1}, except oxygen) of oxygen (mg L^{-1}), nitrate, ammonia, TDIN, totN, DRP, totP and Si at Dendermonde, Antwerp, Vlissingen and in the Rupel. Comparison for the periods 1996-1997 and 1999-2000 and procentual difference. [ ] = concentration, n = number of measurements, p = significance value of Wilcoxon Rank Sum test. Bold = significant difference (p<0.05) between period 1996 for this parameter

	summer						winter					
parameter	summer 96-97		summer 99-00				winter 96-97		winter 99-00			
Dendermonde	[ ]	n	[ ]	n	%	p	[ ]	n	[ ]	n	%	p
O_2 (mg.l^{-1})	**0,35**	**8**	**1,57**	**8**	**349**	**0,02**	**5,41**	**5**	**6,87**	**5**	**27**	**0,03**
NO_3^-	306	8	292	8	-5	0,40	346	5	445	5	28	**<0,01**
NH_4^+	154	8	127	8	-18	0,64	422	5	154	5	-64	**<0,01**
TDIN	492	8	443	8	-10	0,21	781	5	611	5	-22	**<0,01**
totN	651	8	569	8	-13	0,09	902	5	694	5	-23	**<0,01**
DRP	23	8	20	8	-14	0,29	21	5	12	5	-42	**<0,01**
totP	47	8	34	8	-28	0,05	43	5	21	5	-52	**<0,01**
Si	94	7	131	8	39	0,42	223	2	233	5	4	**
Antwerp												
O_2 (mg.l^{-1})	1,24	8	1,01	8	-19	0,49	4,12	6	5,59	6	36	0,11
NO_3^-	241	8	286	8	19	0,10	291	6	356	6	22	0,11
NH_4^+	74	8	53	8	-29	0,67	368	6	149	6	-60	**<0,01**
TDIN	329	8	359	8	9	0,12	662	6	513	6	-23	**<0,01**
totN	429	8	443	8	3	0,49	733	6	569	6	-22	**<0,01**
DRP	9	8	8	8	-11	0,37	8	6	5	6	-35	**0,02**
totP	17	8	14	8	-21	0,06	18	6	9	6	-50	**<0,01**
Si	**50**	**7**	**121**	**8**	**140**	**0,04**	222	3	221	6	-1	**
Rupel												
O_2 (mg.l^{-1})	1,04	8	1,05	8	1	0,83	2,03	2	5,09	6	151	**
NO_3^-	131	8	154	8	17	0,83	221	2	266	6	20	**
NH_4^+	244	8	206	8	-16	0,49	375	2	169	6	-55	**
TDIN	395	8	389	8	-2	0,83	607	2	445	6	-27	**
totN	527	8	510	8	-3	0,60	671	2	506	6	-25	**
DRP	14	8	11	8	-23	0,14	8	2	6	6	-26	**
totP	34	8	21	8	-37	0,14	18	2	9	6	-51	**
Si	**125**	**7**	**203**	**8**	**63**	**0,02**	234	2	233	6	0	**
Vlissingen												
O_2 (mg.l^{-1})	7,62	8	7,16	8	-6	0,40	10,36	3	9,67	6	-7	**
NO_3^-	30	8	47	8	57	0,06	68	3	139	6	104	**
NH_4^+	7,5	8	5,3	8	-29	0,92	22	3	8	6	-64	**
TDIN	39	8	54	8	38	0,07	92	3	150	6	63	**
totN	**	**	**	**	**	**	**	**	**	**	**	**
DRP	1,7	8	1,9	8	12	0,46	1,8	3	2,8	6	56	**
totP	2,9	8	2,9	8	0	0,83	4,7	3	4,5	6	-4	**
Si	**5,1**	**8**	**10**	**8**	**96**	**0,02**	36	3	57	6	58	**

4.3.3 Discharge dependence of concentrations

Discharge was an important causal factor in observed nutrient concentration variability throughout our study period. In winter, oxygen-, TDIN-, totN-, totP- and ammonia-concentrations were linearly dependent on discharge in Dendermonde, Antwerp and the Rupel (Table 4.2). For oxygen, this relationship was positive; the other variables were negatively related to discharge. DRP was negatively related to discharge in Dendermonde and Antwerp, but not in the Rupel. Dissolved silica was totally independent of discharge in winter. For totN, TDIN, ammonia and DRP, linear relationships were not observed in summer, in contrast to winter (Table 4.2). Dissolved silica was positively linearly dependent of freshwater discharge at Antwerp and Dendermonde in summer (Table 4.2).

Table 4.2: Discharge dependence (total monthly discharges) of monthly concentrations of oxygen, nitrate, ammonia, TDIN, totN, DRP, totP and Si at Dendermonde, Antwerp and in the Rupel for winter (up) and summer (down) (least-squares linear regression, data were log-transformed for normalization). +/- indicates a positive respectively a negative relation, bold underlined=significant relationship (p<0.05)

	winter											
	Rupel				Dendermonde				Antwerp			
parameter	p	+/-	R^2	F	p	+/-	R^2	F	p	+/-	R^2	F
O_2	**0,007**	+	**0,57**	**12**	**0,005**	+	**0,56**	**13**	**0,007**	+	**0,50**	**11**
NO_3^-	0,056	+	0,35	5	**0,005**	+	**0,53**	**12**	0,480	+	0,04	1
NH_4^+	**0,008**	-	**0,56**	**12**	**0,001**	-	**0,61**	**17**	**0,020**	-	**0,37**	**7**
TDIN	**0,032**	-	**0,42**	**6**	**0,029**	-	**0,36**	**6**	**0,002**	-	**0,57**	**16**
totN	**0,004**	-	**0,63**	**15**	**0,001**	-	**0,62**	**18**	**0,001**	-	**0,63**	**21**
DRP	0,101	-	0,27	3	**0,006**	-	**0,51**	**12**	**0,030**	-	**0,34**	**6**
totP	**0,002**	-	**0,66**	**18**	**0,002**	-	**0,62**	**18**	**0,021**	-	**0,37**	**7**
Si	0,096	-	0,28	4	0,630	-	0,03	0	0,570	-	0,03	0

	summer											
	Rupel				Dendermonde				Antwerp			
parameter	p	+/-	R^2	F	p	+/-	R^2	F	p	+/-	R^2	F
O_2	**0,017**	+	**0,28**	**7**	0,070	+	0,18	4	0,510	-	0,02	1
NO_3^-	0,053	+	0,19	4	**0,023**	-	**0,26**	**6**	0,950	+	0	0
NH_4^+	0,17	-	0,10	2	0,053	+	0,19	4	0,160	+	0,11	2
TDIN	0,62	-	0,01	0	0,620	+	0,01	0	0,230	+	0,08	2
totN	0,54	-	0,02	0	0,410	-	0,04	1	0,290	+	0,06	1
DRP	0,16	-	0,11	2	0,600	-	0,02	0	0,910	-	0,08	0
totP	0,22	-	0,08	2	0,270	-	0,07	1	0,920	-	0,01	0
Si	0,57	+	0,02	0	**0,006**	+	**0,37**	**10**	**0,019**	+	**0,28**	**7**

The relation between discharge and DSi-, ammonia- and nitrate- concentrations in the tidal freshwater was further studied in the periods October-March (low biological activity) and April-September (high biological activity) (Fig. 4.5). The distinction between low and high biological activity in the chosen periods was ecologically relevant. The repective periods showed low and high chlorophyll-a concentrations respectively throughout the estuary (Van Damme *et al.*, 2005) DSi-, ammonia- and nitrate-concentrations showed opposite relations with discharge over the five-year study period in the respective periods. Chloride shows the same relationship with discharge in both periods: higher discharges lead to lower chloride concentrations in the freshwater.

4.4 Discussion

4.4.1 Fluxes in the freshwater and brackish zone

Based on a compilation of the scattered data of water quality of the Schelde estuary in the period 1965-1995, Van Damme *et al.* (1995) showed that water quality was worst during the 1970's when large parts of the brackish and fresh part of the estuary were anoxic. Investments in both industrial and urban wastewater treatment reduced organic loadings which resulted in increasing oxygen conditions since 1980 from ca. 3 mg L^{-1} to 5 mg L^{-1} in 1995 (year averaged values) near the Dutch-Belgian boarder. At the same sampling point, ammonia-concentrations decreased since 1980 from ca. 214 µmol L^{-1} to 71 µmol L^{-1}, while nitrate-concentrations increased (ca. 214 µmol L^{-1} to 357 µmol L^{-1}). DRP-concentrations clearly decreased since the early 1980's from ca. 20 µmol L^{-1} to 7 µmol L^{-1}.

A further improvement of the water quality, based on concentrations, between 1996 and 2000, is clear in winter, both in the freshwater and brackish zone. TDIN-, totN-, DRP- and NH_4^+-concentrations dropped, while oxygen-concentrations rose. Discharge seems an important causal factor in the latest concentration drops. Dilution in higher water volumes has been observed to have a positive impact on nutrient and pollutant concentrations in the upper Clyde estuary and the river Wear (Scotland) (Curran & Robertson, 1991; Neal *et al.*, 2000).

The hypothesis of dilution with higher freshwater discharges and rainfall could be further supported by the chloride dilution patterns with higher discharge. Freshwater bodies receiving chloride mainly from precipitation differ, according to Gibbs (1970), from freshwater bodies receiving chloride from soil erosion. The difference is made according to total salt concentration and the ratio of Cl to the sum of Cl and HCO_3. With an average chloride concentration of 83 ppm (5 year average 1996-2000, Schelde river upstream Gent, beyond tidal influence) the chloride supply to the freshwater Schelde would, according to this division, not be rainwater dominated but erosion dominated. Non-point sources could probably include both run-off from industry and agriculture in the upstream region and run-off from roads treated against snow and ice as well as soil erosion. Rainfall dilutes chloride concentration in freshwater bodies receiving chloride mainly from erosion, as was observed over the study period.

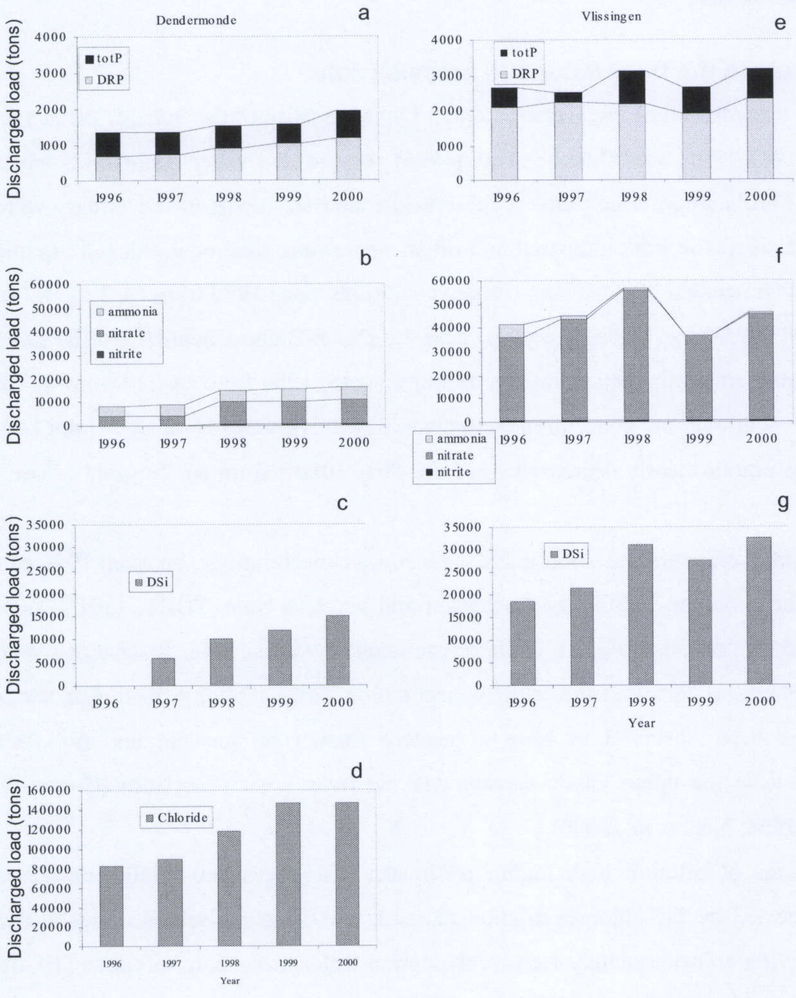

Fig. 4.4: Yearly total discharged loads at Dendermonde (a-d) and Vlissingen (e-f): a),e) DRP and totP; b),f) TDIN, nitrate, ammonia, nitrite; c),g) silica; d) chloride

The strongest indication for increasing non-point surface run-off input is the observation that, along with increased discharges, an increased load of eroded material is imported to the Schelde estuary (Fig. 4.6). Over 50 % of this suspended matter originates from land erosion (source: AWZ). Higher rainfall induces a higher diffuse input of materials to the estuary.

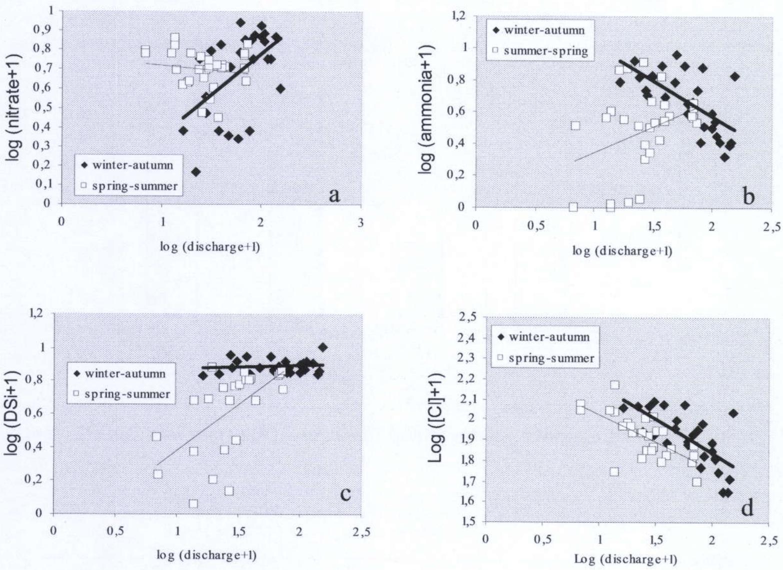

Fig. 4.5: Relation (least-squares linear regression) between total monthly discharge and monthly nutrient concentrations in spring-summer (April-September) and autumn-winter (October-March) at Dendermonde. a) nitrate (summer-spring p=0.40, R^2=0.03; winter-autumn p=0.003, R^2=0.29) b) ammonia (summer-spring p=0.06, R^2 = 0.13, winter-autumn p=0.0001, R^2=0.44) c) silica (summer-spring p=0.0007, R^2=0.39, winter-autumn p=0.53, R^2=0.02) d) chloride (summer-spring p=0.00003, R^2=0.47, winter-autumn p=0.00002, R^2=0.51)

Increased surface run-off of sediments induced increasing non-point input of nutrients. Nutrient loss from agricultural lands by rainfall land erosion can be estimated from knowledge of soil loss (Hargrave & Shaykewich, 1997). Higher inputs of nutrients to the estuary from diffuse sources explain the strong increase of nutrient loadings in the upper estuary. Increasing nitrogen discharges at Antwerp and agriculture N-loss (as calculated by VMM, Flemish Environmental Agency) from agricultural soil over Flanders show similar patterns (Fig. 4.7). The absence of increased loadings for ammonia, with little diffuse input origins, in winter, supports the origin from diffuse input sources. The change in relative proportion of ammonia and nitrate can be explained by rising oxygen concentrations with higher discharges, resulting in more intense nitrification and a decrease in denitrification, an anaerobic process (Seitzinger, 1988; Billen & Garnier, 1997).

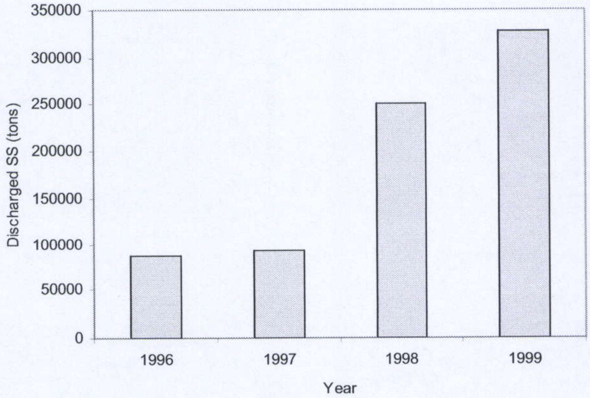

Fig. 4.6: Total discharged suspended solids (SS) by the Schelde (downstream Rupel). Yearly totals. (Taverniers 1999)

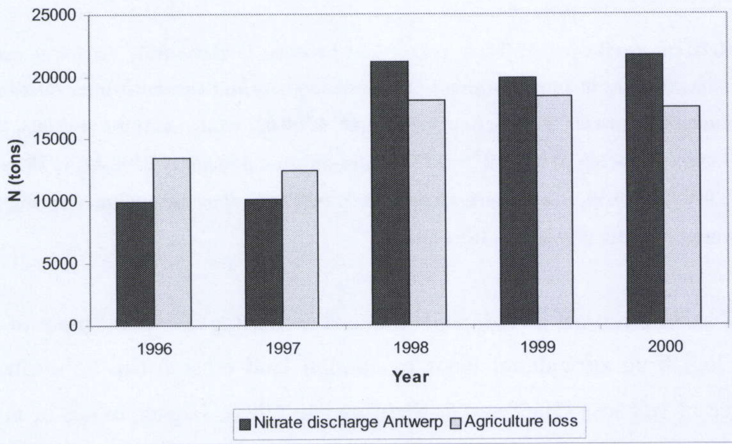

Fig. 4.7: Yearly total discharged nitrate loads at Antwerp vs. total yearly estimated agriculture loss of nitrogen in Flanders Schelde Basin (source VMM, Flemish Environmental Agency, Model Sentwa 4.06)

The increasing discharges of total P in the freshwater estuary apparently do not result in increasing discharges farther downstream in the brackish zone. This could be explained by retention and sedimentation of P within the turbidity maximum, at the freshwater-saltwater interface (Wollast, 1982; Zwolsman, 1994). This could also explain the less clear trend of totP in the Rupel, situated near the turbidity maximum. This hypothesis is supported by the observation that totP loadings at Antwerp are lower than the sum of Rupel and freshwater estuarine loadings.

The impact of respiration and nitrification, processes that increase in efficiency with higher temperatures, on the organic matter and nitrate load, was lowered due to lowered residence times in the freshwater, and less oxygen was used. In summer, high oxygen conditions only occurred at peak-discharges in the freshwater zone. Higher loads of ammonium and organic material were transferred to the downstream regions (Antwerp) due to lower residence times and further processed in the brackish zone by respiration and nitrification, which causes oxygen conditions to remain very low downstream of the freshwater zone. The prolongation of the ammonium removal distance with higher discharges was observed earlier in the Alaska tundra (Vörösmarty & Peterson, 2000). The significant negative relation between discharge and nitrate concentrations (less ammonia is nitrified to nitrate at high discharges) in summer and spring in the fresh water supports this hypothesis. In winter on the other hand, when nitrification and respiration are less intense than in summer, oxygen concentrations increase concurrently with increasing discharge. As a result, nitrification was enhanced in winter at higher discharges. Balls *et al.* (1996) observed a comparable relation between oxygen and discharge in the Forth estuary. All these effects of increasing discharge on ammonia and nitrate concentrations in the periods April-September (higher temperature, nitrification more efficient) and October-March (low temperature, nitrification less efficient) in the freshwater in the end resulted in decreasing seasonal concentration variability. The secondary effects of increasing discharge on nutrient concentrations through increasing oxygen concentration, can add to observed dilution effects. Higher oxygen conditions result in less DRP due to binding reactions with suspended matter (Krom & Berner, 1980; Froelich, 1988).

The biogeochemistry of dissolved silica (DSi) is totally different from that of other nutrients. Silica plays an important role in coastal eutrophication problems (Schelske *et al.*, 1983; Lancelot *et al.*, 1987; Smayda, 1990; Smayda, 1997). In contrast to other nutrients, no important anthropogenic input of silica exists. Dissolved silica (DSi) originates from biogeochemical reactions which set free dissolved silica from alkali and aluminum silicate minerals (Hutchinson, 1957; Correll *et al.*, 2000). In the period October-March, silica concentration is totally independent of discharge conditions. Seasonal variability in DSi is caused by uptake by diatom communities in spring and summer, which results in lower DSi-concentrations. However, with highest discharge conditions, summer and spring concentrations equal winter concentrations in the freshwater Schelde estuary. Freshwater diatom blooms are negatively influenced by higher discharge conditions, and complete diatom communities are "flushed" away by peak discharges. Extreme runoff events were already shown to cause flushing of the entire freshwater reach, whereby the estuarine phytoplankton community is replaced with one of riverine origin, not adapted to growth conditions within the tidal area (Muylaert *et al.*, 2001). With the flushing of plankton, no DSi uptake takes place, which causes summer-spring concentrations to approach winter-autumn concentrations. In parallel with the influence of discharge on nitrate and ammonia concentrations, rising discharge conditions result in the diminution of seasonal differences in silica concentrations. Farther downstream, in Antwerp and at the Rupel, these effects are still manifest. At Antwerp, silica concentrations have more than doubled over the study period.

4.4.2 Fluxes to the coastal zone

Increasing water discharges have multiple effects on the nutrient status of coastal waters near Vlissingen. With higher discharges, the estuarine plume expands farther into the coastal waters. As a result, salinity has decreased at Vlissingen over the five-year study period (Fig. 4.8). Due to conservative mixing with seawater, nutrient concentrations in the Westerschelde decrease when moving towards saltier water (Ouboter *et al.*, 1998). This explains the rising concentrations of Si, DRP, NO_3 and TDIN near Vlissingen from 1996 to 2000.

Discharged silica loads at the mouth of the estuary have increased along with increasing silica discharges at Antwerp and Dendermonde. This load could have further increased due to decreasing salinity and increasing suspended matter in the Westerschelde, which could both have reduced diatom growth in the Westerschelde.

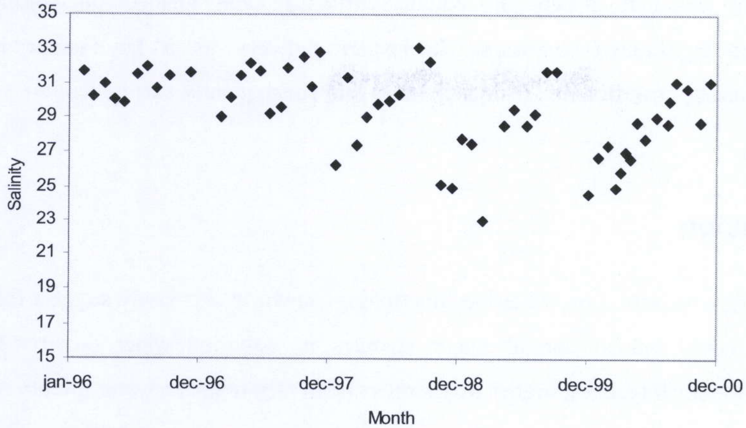

Fig. 4.8: Monthly salinity at Vlissingen (1996-2000)

In contrast to DSi loads near the mouth and nitrate, totP and DRP loads upstream, nitrate, totP and DRP discharges did not increase at Vlissingen. As mentioned earlier, P-retention occurs in the high turbidity zone, which could explain the absence of any trend in total P discharges downstream the turbidity maximum. The absence of any trend in NO_3-discharge to the North Sea, despite massive increases upstream, is not so readily explained and a challenge for future research. Furthermore, nitrate-, TDIN-, DRP-, totP- and silica discharges are much higher near the mouth of the estuary than at Antwerp. A big part of these increased loadings probably results from the influx from the channel Gent-Terneuzen (which flows into the estuary near Terneuzen, Fig. 4.1) and other lateral inputs of nutrients and the degradation of organic matter, flushed through by higher discharges.

Similar results and predictions for the pivotal role climate and hydrology can play in determining the nutrient fluxes to coastal ecosystems have been obtained in other systems across the world. The balance between storage of nitrate in the terrestrial ecosystem and leaching of the nitrate was recently shown to be dependent on hydrology and climate in a long-term study in the Mississippi-basin (Donner *et al.*, 2002). In the Hudson estuary (USA), effects of residence times on primary production have been reported (Howarth *et al.*, 2000). During periods of low freshwater discharge, a combination of longer residence time and deepening of the photic zone, led to increasing susceptibility of this system to eutrophication. Scavia *et al.* (2002)

summarised the potential effects of climate variability and change on coastal ecosystems and highlighted increasing freshwater delivery as a key factor in determining estuarine stratification, residence times and consequently eutrophication.

4.5 Conclusion

The effects of flow variation on estuarine functioning shown in this study suggest that global change could induce several major changes in estuarine water quality. In freshwater and brackish reaches, higher discharges apparently improve water quality by diluting nutrient concentrations and a positive effect on oxygen concentrations. This masks a problem of increasing total loadings of nutrients. The effect of increasing discharge on ammonia, nitrate and Si-concentrations is opposite in spring and summer than in autumn and winter. Future global change could flatten out the seasonal cycles for these nutrients. Although increasing loads observed upstream were not unambiguously visible near the mouth of the estuary in this study, it is clear that higher discharges of nutrients in the upper estuary, caused by increasing non-point input, could pose a major problem to governments trying to reduce nutrient inputs to estuarine coastal regions. For example, in the 1990s, the Flemish government strongly increased efforts to reduce waste input to the brackish and fresh area (Fig. 4.9). These efforts have mainly concentrated on point sources of nutrient pollution. The vast amounts of money invested in point-pollution reduction did not result in decreasing total discharges of N to coastal waters, due to the changing hydrological conditions. In contrast, total N-discharges even increased. In the Seine estuary (France) and the Schelde, it was predicted that reduced organic C input to estuaries would result in increasing discharges of N to coastal waters due to a decrease in denitrification (Soetaert & Herman, 1995; Billen & Garnier, 1997). Increasing freshwater discharge and surface run-off will only add to this problem. The importance of reducing non-point nutrient input to the estuary concurrently with the reduction of point-pollution, was clearly pointed out in Chesapeake Bay (USA) (Boesch *et al.*, 2001).

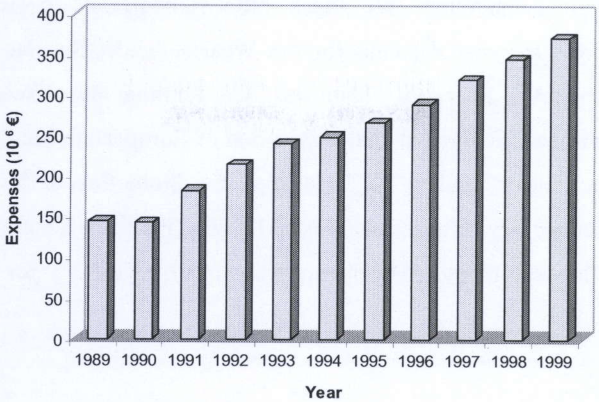

Fig. 4.9: Expenses made by Flemish governmental institutes to reduce point source pollution to surface waters (1996-2000) Source: VMM, Flemish Environmental Society

In this context of global change, measures to reduce diffuse inputs from mainly agricultural sources are more urgent than ever. The European directive on the control of nitrates requires the creation of nitrate-vulnerable zones. In these zones, both wetland restoration and changes in agricultural practices must be implemented (Ducrotoy *et al.*, 2000). Riparian vegetation can significantly reduce non-point nutrient flows to surface waters (Lowrance *et al.*, 1985; Correll *et al.*, 1992). Furthermore, creating more wetlands and thus giving more space to the water, could result in higher water residence times. This could prove to be the solution to the problem of the flushing of entire diatom communities from estuarine freshwater reaches and reduce the flattening out of seasonal cycles.

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