CHAPTER 2

Nutrient loads to the Belgian Coastal Zone

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2.1 Introduction

Anthropogenic eutrophication in coastal environment results from increased delivery of land-based nutrients considerably enriched in nitrogen (N) and phosphorus (P) compared to silicon (Si). These nutrient inputs strongly modify the nutrient balance N:P:Si of coastal waters with respect to phytoplankton stoechiometry, *i.e.* N:P=16 for marine phytoplankton (Redfield *et al.*, 1963) and N:Si=1 for coastal diatoms (Bzrezinski, 1985). This in turn modifies the composition of the phytoplankton community characterized by a dominance of opportunistic non-siliceous species (*e.g.* Officer & Ryther, 1980; Billen *et al.*, 1991).

Coastal waters are enriched by nutrients delivered by rivers and canals, coastal tributaries, atmospheric deposition, and advection from adjacent areas (Fig. 2.1). River nutrient loads are largely influenced by human activity and depend on the population density in the watershed but also on environmental drivers such as land use and agriculture practices, industrialization, and waste water treatment management (Fig. 2.1). Nutrients are released to surface waters from point sources as domestic and industrial effluents (mainly NH_4^+ and PO_4^{3-}), and diffuse sources through soil leaching and ground water contamination by fertilizers and manure spreading (mainly NO_3^- and $Si(OH)_4$). Once released in the river system, nutrients are involved in physico-chemical and biological processes leading to their transformation, retention or elimination during their transfer along the aquatic continuum (Fig. 2.1; Billen *et al.*, 1991). Atmospheric deposition occurs mostly as N oxide (NO, N_2O, NO_2) originating from industrial and traffic combustion processes and as ammoniac (NH_3) resulting of animal breeding and manure spreading. Once in the atmosphere these gasses are

transformed and transported with the air masses before their wet or dry deposition onto coastal areas (Spokes & Jickells, 2005).

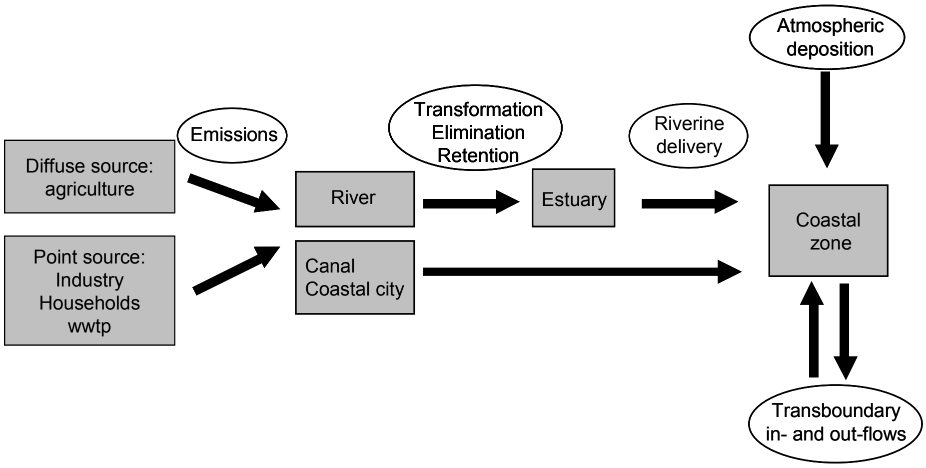

Figure 2.1. Schematic representation of nutrient delivery to coastal water including river, canal and coastal tributaries, atmospheric deposition and transboundary in- and out-flows. Riverine loads of nutrients result from nutrient emissions from point and diffuse sources in the watershed. They can be directly delivered to coastal waters or transformed, retained and/or eliminated during their transfer along the aquatic continuum before reaching the coastal area.

Nutrient enrichment of the Belgian coastal zone (BCZ; Fig. 2.2) results from local riverine inputs of the Scheldt, the IJzer and the coastal tributaries, from atmospheric deposition and from transboundary fluxes brought by the Southwesterly Atlantic waters enriched by the rivers Seine, Somme, Authie and Canche, and Rhine (Lacroix *et al.*, 2004). The relative importance of these different nutrient sources varies depending on change in human activity in the watersheds and on the North Atlantic Oscillation (NAO) which determines the weather conditions over North-western Europe and the hydrological budget of BCZ (Breton *et al.*, 2006).

This chapter synthesizes the information on N, P and Si delivery to the BCZ and resulting enrichment of coastal waters. It compares the present situation with available historical data in order to evaluate their long term changes. Quantitative changes in riverine loads are analysed in relationship with human pressure and biogeochemical transformations within the aquatic continuum. Qualitative changes in nutrients are also considered, in particular changes in the N:P:Si molar ratio determining the limiting element for phytoplankton growth and triggering harmful algal blooms (Billen & Garnier, 1997; 2007).

2.2 Freshwater nutrient loads

2.2.1 The BCZ watershed

The BCZ watershed is here defined as the catchment area of watercourses discharging directly in the BCZ but also indirectly through a significant influence of river plume. As such, the BCZ watershed includes the sub-basins of the IJzer, the coastal tributaries in the northeastern part of Belgium and the Scheldt considered here upstream the Belgian-Dutch border (Fig. 2.2). It covers a total area of 24 010 km^2, distributed in the northwestern France (30%) and Belgium (70%).

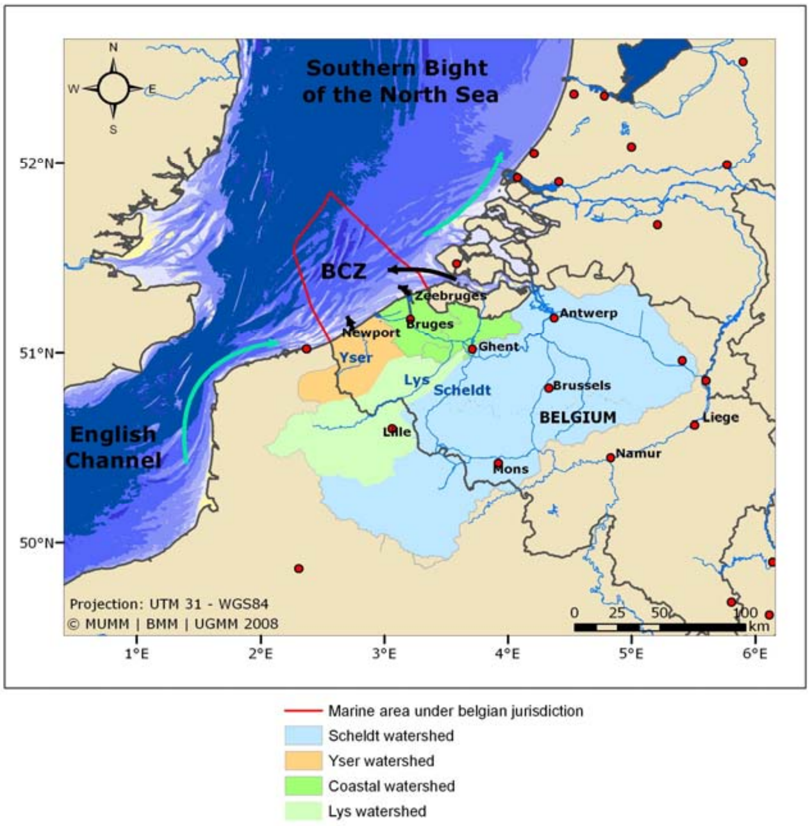

Figure 2.2. The Belgian Coastal Zone (BCZ) in the Southern Bight of the North Sea and its watershed including the Scheldt, the IJzer and the Coastal sub-basins. The Leie watershed is also indicated. Source: Map (MUMM-BMDC, 2008); bathymetry (Maes *et al.*, 2005); hydrology in Belgium and The Netherlands (DGRNE - Scaldit) and BD-CARTO (copyright IGN-PARIS-2000), BD-CARTHAGE (copyright IGN-PARIS-2000), AGENCE DE L'EAU ARTOIS-PICARDIE, DIREN NORD PAS DE CALAIS in France. Arrows indicates the riverine (black) and transboundary (blue) nutrient fluxes.

The river Scheldt is a lowland river, with a total length of 355 km. Its main affluents are the Haine, Dender and Rupel with its confluents the rivers Zenne, Dijle, Grote and Kleine Nete (Fig. 2.3). The course of one of its tributary, the river Leie, has been deviated directly to the sea through several canals (Van Geystellen *et al.*, 1980) so that the Leie sub-basin (4344 km^2) will be here included in the Coast watershed (Fig. 2.2). Contrarily to the tributaries of the Coast and IJzer watersheds which discharge directly freshwater to marine waters, the river Scheldt has a tidal estuary, the Westerschelde, showing large seasonal fluctuations of the freshwater discharge (20-350 $m^3\ s^{-1}$). High water velocities and bottom friction are sufficient to mix efficiently the water column so that little or no vertical stratification of solutes occurs. This estuary is 100 km long. Salt intrusion in the brackish estuary occurs up to Hemiksem, *i.e.* downstream the confluence of the main rivers at about 85 km from the mouth but tidal limits are located more upstream in the main affluents (Fig. 2.3). The residence time of Scheldt freshwater may reach 2 to 3 months during the summer but about 1 month during the high flood period in winter and early spring. The long residence time and the fluctuations of the water composition within the estuary are very favorable conditions for the occurrence of physical, chemical and biological transformations, which may significantly modify the nutrient fluxes to the BCZ.

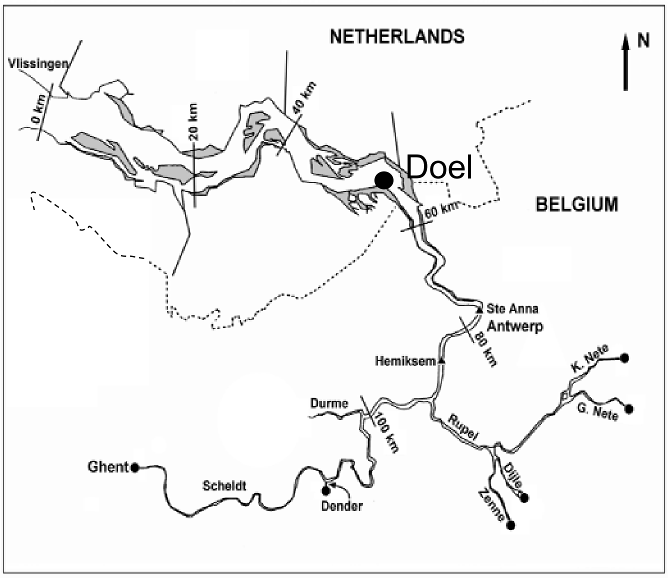

Figure 2.3. The Scheldt estuary. Upstream tidal intrusion occurs up to Hemiksem while the limits of tidal influence are located in the rivers Scheldt, Dender, Zenne, Dijle, Grote Nete and Kleine Nete (solid circles). The location of Doel, at the Belgian-dutch border is also indicated.

The IJzer watershed (1749 km^2) drains the western coastal area of Belgium (Fig. 2.2). Its hydrographic system receives mainly polder effluents. The Coast watershed (1914 km^2; Fig. 2.2) drains the maritime plain in the northeastern part of the BCZ watershed. Its main watercourse consists of canals that mainly receive polder drainage and flow seaward via harbour channels (Gent-Oostend, Leopold, Schipdonk and Gent-Terneuzen canals).

The population density differs considerably between the three river basins with 522, 417 and 227 inhab km^{-2} for the Scheldt, Coast and IJzer watersheds respectively. The higher population density in the Scheldt basin is mainly due to the presence of the large cities Antwerp, Brussels and Ghent (Fig. 2.2). Agricultural practices differ also considerably from one sub-basin to another with very intensive cattle, pig and poultry farming in the IJzer and Coast watersheds. Pig farming is very significant in the IJzer watershed with animal density being eight-fold that of the Scheldt (Rousseau *et al.*, 2004). High population density, intensive agriculture and industrialization (mainly in the northern watershed), make of the Scheldt one of the most heavily polluted rivers in Europe (Billen *et al.*, 2005).

2.2.2 N and P emissions in the BCZ watershed in 2000

2.2.2.1 N and P emissions to surface waters of the Scheldt, IJzer and Coast watersheds

Domestic, industrial and agricultural N and P emissions to surface waters of the Scheldt, IJzer and Coast watersheds were estimated for the year 2000 from data reported in the last exhaustive inventory of human activities and land use by Federal Institutes and by the Regions (see details in Rousseau *et al.*, 2004). Domestic emissions of N and P were calculated on basis of the watershed population, a per capita load of 10 g N and 1.8 g P $inhab^{-1}$ d^{-1} specific for western european countries in the late nineties (Billen *et al.*, 1999; Servais *et al.*, 1999), the wastewater treatment capacity in each watershed and a rate of N and P elimination by wastewater treatment specific to each watershed. Industrial emissions of N and P were estimated based on a census of industry and a specific release rate of N and P to surface waters and to public waste water treatment plants. The transfer of N and P from agricultural sources to surface water was estimated using the semi-empirical model SENTWA (System for the Evaluation of Nutrient Transport to WAter, Ministry of Small Enterprises, Traders and Agriculture). This model is based on reliable statistical data on land use, livestock density, spreading of animal manure and fertilizers taking into account lithology, nutrient species and meteorology. It also calculates N and P fluxes to surface water resulting from atmospheric deposit, direct flow, drainage, groundwater overflow, excess fertilizer or manure use, erosion and run-off.

This detailed census estimated the total N and P emissions to surface waters of the BCZ watershed in 2000 to 65.2 kt N (Fig. 2.4a) and 6.6 kt P (Fig. 2.4c) respectively. The Scheldt watershed was the main source of nutrients, contributing to 69% of N and 73% P of the total emissions. The Coast watershed was responsible for some 20% of N and P discharge while the IJzer

contributed to only 10% of N and 7% of P total emissions. Nutrient sources varied according to the different watersheds. Agriculture was indeed the major source of N (81%) and P (54%) in the IJzer watershed while domestic emissions in the Scheldt watershed are responsible for most N (52%) and P (75%) emissions. The Coast watershed shows an intermediate situation with agriculture as the main source of N (60%) but a major household contribution (52%) to P emissions.

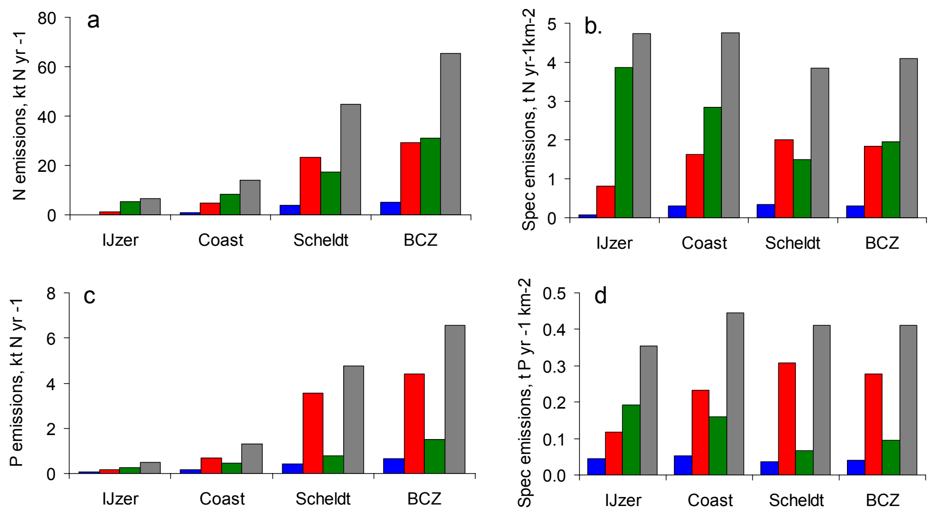

Figure 2.4. N (a) and P (c) emissions and N (b) and P (d) specific emissions to surface water of the IJzer, Coast, Scheldt and BCZ watersheds. Agriculture (green), domestic (red), industry (blue) and Total (grey) nutrient emissions are indicated.

These differences reflect contrasted land use in the three watersheds as shown by the specific emissions of N (Fig. 2.4b) and P (Fig. 2.4d), *i.e.* emissions related to the respective area of each watershed. In the densely populated Scheldt watershed, specific emissions of N and P from domestic activities are dominant. Specific agricultural emissions of N and P dominate all other emissions in the IJzer and Coast catchment basins due to the intensive agricultural practices developed in these watersheds, in particular the cattle, pig and poultry manure production and spreading on fields.

2.2.2.2 N and P loads from IJzer, Coast and Scheldt watersheds

Annual N and P loads for 2000 were estimated at the outlet of each sub-watershed (Fig. 2.5). Scheldt nutrient loads were computed from nutrient concentrations measured at Doel and runoffs available at station Schelle. Nutrient loads from the IJzer and Coast watersheds were estimated from nutrient concentrations and runoffs available at downstream monitoring stations

(see details for calculations and data source in Rousseau *et al.*, 2004). These N and P loads can be considered as the nutrient delivered to the BCZ. In total, some 56.8 kt N (Fig. 2.5a) and 4.4 kt P (Fig. 2.5b) were delivered by the 3 watersheds in 2000 with the Scheldt being by far the major contributor to N and P total loads. Coastal tributaries discharged about one third of N and P loads while the river IJzer contributed to only 5% of both N and P loads.

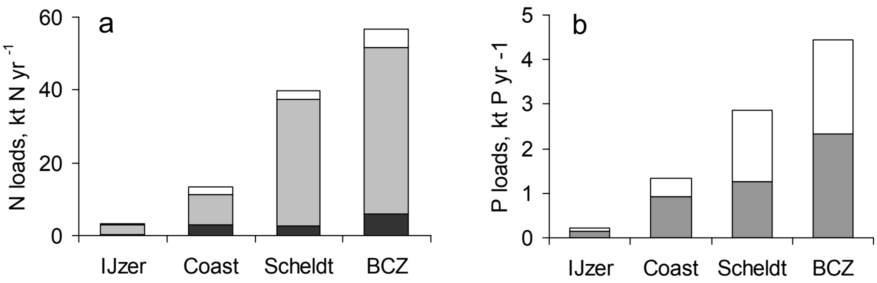

Figure 2.5. N (a) and P (b) riverine loads discharged to the BCZ by the IJzer, Coast and Scheldt watersheds in 2000. N forms represented as NH_4^+ (black), NO_3^-+NO_2^- (grey), Total N – DIN (white) and P forms as PO_4^{3-} (grey), Total P-PO_4^{3-} (white). Data compiled as described in Rousseau *et al.* 2004.

Dissolved inorganic nitrogen (DIN) loads represented a large part (in average 90%) of the N delivered to the BCZ with oxidized N forms (NO_3^-+NO_2^-) contributing to some 80% (Fig. 2.5a). NH_4^+ loads from the IJzer and Coast watersheds were the highest. Globally half of the P riverine load was delivered as PO_4^{3-} but with contrasted situation in the different basins. In the IJzer and Coast watersheds, PO_4^{3-} contributes to about two thirds of P loads but 44% in the Scheldt watershed (Fig. 2.5b).

Comparison between nutrient loads and emissions in 2000 (Table 2.1) indicates that the efficiency of nutrient retention varied among watersheds. Nutrient retention was the highest in the IJzer watershed where half of the N and P emitted to surface waters was retained in the aquatic environment. In contrast, nutrient retention was not significant in the Coast watershed where a very slight P production occurred. In the Scheldt watershed, some 11% of N and 40% of P were retained. Globally, some 13% N and 32% of P emitted in the BCZ watershed are retained in the aquatic continuum. However, as the uncertainty on emissions may be large, retention should be considered with care.

Table 2.1: Nutrient retention in the IJzer, Coast, Scheldt and BCZ watersheds in 2000

kt N yr^{-1}	IJzer	Coast	Scheldt	BCZ
Emissions	6.47	13.94	44.83	65.24
Loads	3.31	13.50	39.94	56.75
Retention (%)	49	3	11	13
kt P yr^{-1}	**IJzer**	**Coast**	**Scheldt**	**BCZ**
Emissions	0.48	1.30	4.77	6.55
Loads	0.23	1.34	2.87	4.44
Retention (%)	52	-3	40	32

2.2.3 Nutrient emissions, transformations and loads in the Scheldt estuary

The link between anthropogenic emissions of nutrients, their riverine loads, their delivery to the coastal waters and the biogeochemical processes leading to their transformation and elimination are the best known for the Scheldt watershed.

2.2.3.1 Changes in nutrient emissions in the Scheldt watershed between 1950 and 2000

Human activities and land use with resulting nutrient emissions to surface- and ground-water of the Scheldt watershed have considerably varied between 1950 and 2000 (Fig. 2.6; Billen *et al.*, 2005). Point sources of nutrients were at their maximum in the seventies when domestic and industrial emissions were discharged without treatment into surface water of the Scheldt and its tributaries. Domestic loading into surface waters increased dramatically between 1950 and 1975 mainly due to the connection of the population, whose rate increased from 15 to 90%, to sewer systems with however a low water treatment capacity at that time (Fig. 2.6a). Secondary waste water treatment was implemented in the Scheldt watershed from the early seventies with a capacity progressively increasing from 1 to 5 M eqinhab between 1970 and 2000 (Fig. 2.6a; van Damme *et al.*, 1995; Billen *et al.*, 2005). Nutrient emissions by industries (mainly chemistry and food) increased considerably following the post-world war development up before being very efficiently reduced (some 90%) by the implementation of waste water treatment plants from the mid-seventies (Fig. 2.6b). Also, the use of polyphosphate-containing detergents for domestic and industrial purposes in the seventies and eighties was responsible for increase of P emissions to rivers. These polyphosphate-containing detergents were progressively ban in the early nineties (Billen *et al.*, 1999; 2001). Agricultural practices, with large-scale use of fertilizers and intensive cattle-farming (Fig. 2.6c), have also considerably evolved over this fifty years

period impacting both point and diffuse nutrient sources (Billen *et al.*, 2005). As an example, Billen *et al.* (2005) estimate that groundwater nitrate concentrations in the aquifers of the Scheldt watershed were increasing from 2 to 10 mg N L^{-1} between 1950 and 2000.

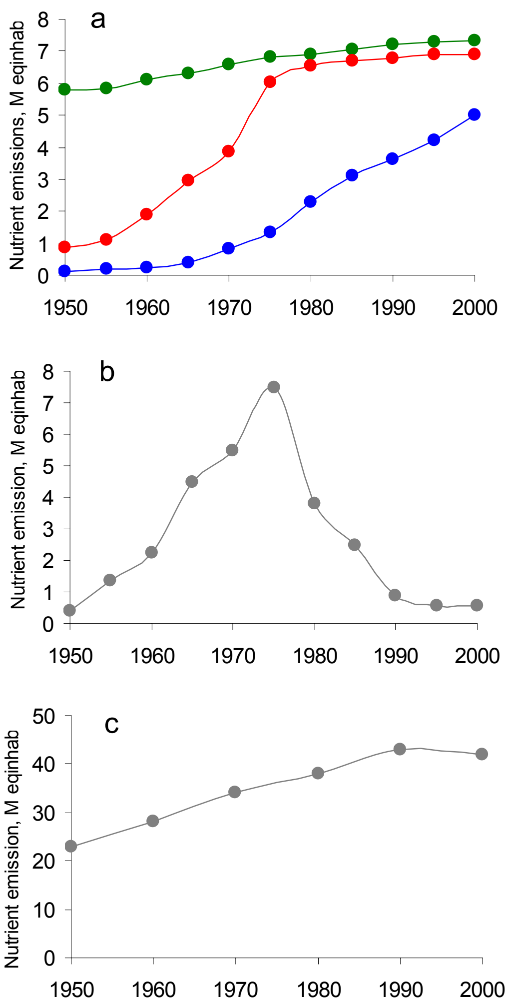

Figure 2.6. Evolution during the period 1950-2000 of nutrient emissions (expressed in terms of M inhabeq) in the Scheldt watershed of domestic loads by the population (green), by population connected to a sewer system (red) and to wastewater treatment plant (blue) (a); net industrial loads (b) and cattle waste (c). Redrawn from Billen *et al.*, 2005.

2.2.3.2 Nutrient filtering capacity of the Scheldt estuary

Once released in the aquatic environment, nutrients undergo biogeochemical transformations which depend on the physico-chemical conditions prevailing along the aquatic continuum. These transformations are especially important in the estuary. By determining light availability in the water column, turbidity is an important factor governing phytoplankton growth. In the uppermost freshwater tidal reaches of the Scheldt estuary where light and residence time are sufficient, summer phytoplankton blooms reaching up to up to 160 µg chl *a* L^{-1} are responsible for significant nutrient removal (Billen *et al.*, 1986, Muylaert *et al.*, 2001). Downstream, in the brackish and salt estuary, phytoplankton blooms occur from April to September but are much less pronounced than in the river due to higher turbidity (Baeyens *et al.*, 1998; Muylaert *et al.*, 2000) except in the most marine part where summer blooms of marine species are recorded.

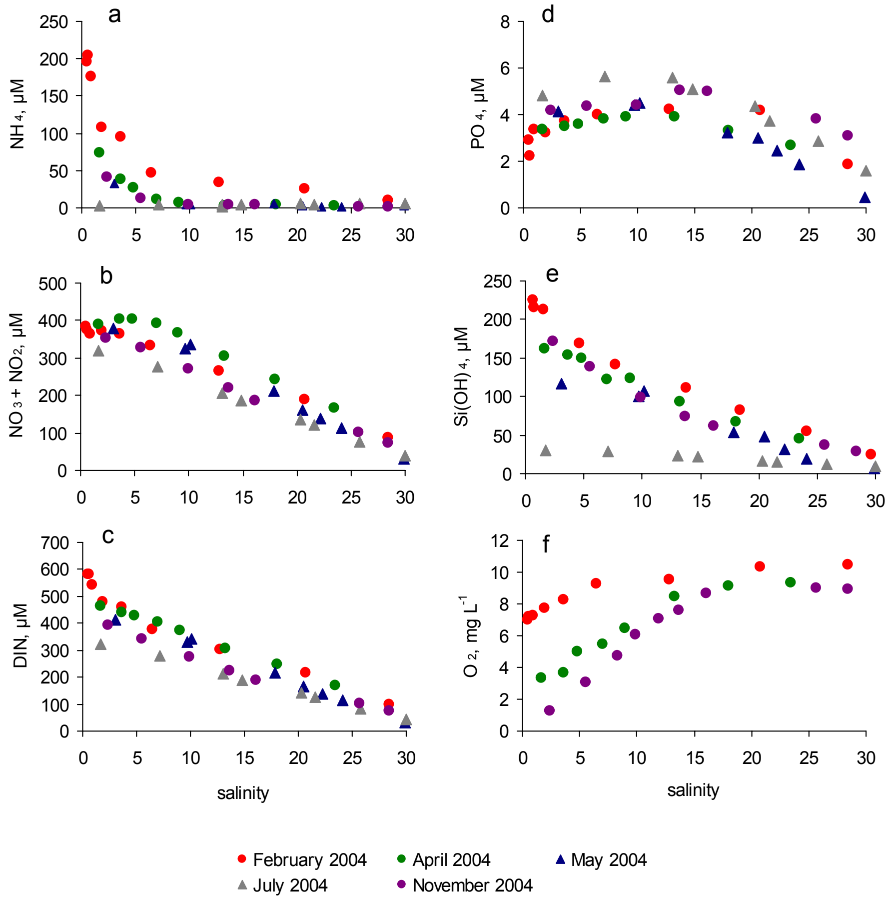

Figure 2.7. Longitudinal profiles of NH_4^+ (a), NO_3^-+NO_2^- (b), DIN (c), PO_4^{3-} (d), $Si(OH)_4$ or DSi (e), and O_2 (f) as a function of salinity at different seasons in 2004 in the brackish Scheldt estuary. Data compiled from MUMM (Monitoring the Belgian Continental Shelf and the Scheldt estuary, dots) and SISCO (Silica retention in the Scheldt continuum and its impact on coastal eutrophication, triangles).

The oxygen status of riverine and estuarine waters, largely dependant on the organic matter load, is another important factor governing the biogeochemical transformations of nutrients. During the seventies, complete oxygen depletion resulting from the aerobic respiration of the organic matter from anthropogenic origin especially in summer months was the rule in many rivers of the Scheldt watershed (Soetaert & Herman, 1995; Billen *et al.*, 2005). From the eighties, the water quality has considerably improved owing to wastewater treatment policies but anoxia is still present in summer in the Rupel (Billen *et al.*, 2005).

Nitrogen biogeochemistry. The major microbiological processes affecting N in aquatic systems are ammonification (production of NH_4^+ by the mineralization of organic matter), nitrification (transformation of NH_4^+ into NO_3^-) and denitrification (elimination of NO_3^- in anaerobic zones through its transformation into gaseous N_2). They are particularly significant in both the freshwater and brackish Scheldt estuary (van Damme *et al.*, 1995; Herman & Heip, 1999; Soetaert *et al.*, 2006; van der Zee *et al.*, 2007; Brion *et al.*, 2008). In the freshwater estuary, mass balance calculations of N fluxes measured in the productive period of 2003 (May-September) showed that nitrification dominated the most upper part of the freshwater estuary (420 t of N-NH_4^+ converted to N-NO_3^-) while the more downstream section was dominated by ammonification with a net production of 42 t N-NH_4^+ and denitrification with a net consumption of 270 t N-NO_3^- (van der Zee *et al.*, 2007). Globally, the freshwater estuary acts as a sink for N (180 t N or 10% of incoming N). In the brackish estuary, the occurrence of nitrification is visible on the longitudinal profiles of N species, showing a significant decrease of NH_4^+ (Fig. 2.7a) concomitant to a NO_3^-+NO_2^- increase particularly evident in April (Fig. 2.7b) and resulting in conservative DIN profiles (Fig. 2.7c). Additionally, the importance of ammonification and nitrification processes was demonstrated by direct process measurements (Table 2.2). Nitrification has considerably intensified in the Scheldt as a result of the implementation of secondary waste water treatment in the mid-seventies and subsequent improvement of the oxygenation status of the Scheldt tributaries and estuary (Billen *et al.*, 2005; Soetaert *et al.*, 2006). This intensification is coupled to an upstream migration of the nitrification key site from the mid-estuary in the seventies to its freshwater part since the nineties (Soetaert & Herman, 1995; Soetaert *et al.*, 2006). Reversely, the water quality improvement negatively impacts the importance of denitrification. During the seventies and eighties, this process was responsible for the complete elimination of NO_3^- in the upper Scheldt estuary under summer anoxic conditions (Billen *et al.*, 2005). The reduction of riparian denitrification due to agricultural drainage also contributes to the decrease of NO_3^- elimination in the watershed (Billen *et al.*, 2005). In the late seventies, riparian and in-stream denitrification was indeed responsible for the elimination of some 65% (48 kt N yr^{-1}) of the total N loading to the Scheldt river system while 25 years later, some 50% (35 kt N yr^{-1}) of N emissions were eliminated (Billen *et al.,* 2005). Above salinity 10 in the brackish estuary, dilution is the main process affecting N dynamics as shown by the conservative behaviour of NH_4^+, NO_3^-+NO_2^- and DIN (Fig. 2.7a-c). Their concentrations vary however seasonally with lower values during summer. The NH_4^+ decrease is particularly significant with complete depletion of this nutrient during summer (Fig. 2.7a).

Table 2.2. Daily N fluxes associated with pelagic ammonification and nitrification in the Scheldt estuary between Rupelmonde and Breskens in 2003 (Brion *et al.*, 2008)

tN d^{-1}	Ammonification	Nitrification
January	215	30
April	25	150
July	140	20
October	40	40

Phosphorus biogeochemistry. The P biogeochemistry is complex and displays a strong seasonal variability. P retention due to sorptive removal of PO_4^{3-} on suspended iron hydroxides in oxygenated water with further aggregation and precipitation onto the bottom sediments and planktonic algal uptake, is very efficient in the freshwater part of the Scheldt estuary (Zwolman, 1994; Billen *et al.*, 2005). Mass balance calculations of P fluxes measured from March 2003 to February 2004 estimates that some 0.45 kt P-PO_4^{3-} and 0.57 ktP-TP corresponding respectively to 53% of PO_4^{3-} and 25% of TP entering the Scheldt affluents at the tidal limits, were retained in the freshwater tidal estuary (Van der Zee *et al.*, 2007). Under the low oxygen conditions prevailing at the fresh-brackish interface during spring and summer, increase of PO_4^{3-} concentrations has been attributed to the remobilization from reducing fluvial sediments (Zwolman, 1994). In the brackish estuary, a production of PO_4^{3-} is observed along year in the salinity range 0-15 before it is conservatively diluted up to marine waters (Fig. 2.7d). This source would result from the desorption of PO_4^{3-} from iron hydroxides due to lower stability of iron-bound P when pH increase along the salinity gradient (Zwolman, 1994). This production can be significant, acting as an important source of PO_4^{3-} to the BCZ where this nutrient can be limiting for phytoplankton growth in spring (Van der Zee & Chou 2005; Lancelot *et al.*, 2005; Gypens *et al.*, 2007). As an example, Van der Zee *et al.* (2007) estimated that in May 2004, about 51% of the PO_4^{3-} flux exported to the coastal marine waters originated from PO_4^{3-} desorption and would correspond to 75% of the PO_4^{3-} retained in the freshwater tidal estuary. Over the period 1990-2005, the maximum PO_4^{3-} concentrations in the Scheldt profile decrease from 15 µM in 1992 to about 5 µM in 2005. Both increasing PO_4^{3-} retention due to precipitation in the re-oxygenated Scheldt estuary (Zwolman 1994; Van Damme *et al.*, 1995; Van der Zee *et al.*, 2007) and decreasing P emissions could have contributed to this significant decrease of PO_4^{3-} concentrations.

Silicon biogeochemistry. The main process affecting Si dynamics in the Scheldt is its retention due to diatom uptake and sedimentation. While not important in the river, Si uptake by diatoms might be significant in the upper freshwater and marine Scheldt estuary in summer (Fig. 2.7e; Muylaert *et al.*, 2005; Chou & Wollast, 2006; Lionard *et al.*, 2008). These blooms can be responsible for the retention of one third of the riverine dissolved silicate (DSi or $Si(OH)_4$; Carbonell *et al.*, in prep). From October to April, DSi behaves as a conservative element in the brackish Scheldt estuary with concentrations of some 250 µM at the

freshwater end-member (Fig. 2.7e). The nowadays situation with both freshwater and estuarine diatom blooms consuming DSi contrasts with that reported in the late sixties when these only occur in the brackish estuary depleting DSi around salinity 20. The lack of diatom blooms in the freshwater estuary was due to the prevailing high turbidity preventing diatom growth at that time (Wollast & De Broeu, 1971).

2.2.3.3 Long-term changes in the Scheldt N, P and Si loads to the BCZ

Quantitative trends. Long-term trends of nutrient loads integrate changes in both nutrient emissions in the Scheldt watershed (section 2.3.1) and their biogeochemical transformations along the aquatic continuum (section 2.3.2). Scheldt N, P and Si loads were estimated at station Doel, at the Belgian-Dutch border in the brackish estuary (Fig. 2.3) from which nutrients behave nearly conservatively up to the coastal zone. Nutrient loads were calculated as described in Rousseau *et al.* (2004) based on available nutrient concentrations (source: RIKZ, http://www.waterbase.nl) and Scheldt runoff at Schelle (source: AWZ, Administratie Waterwegen en Zeewezen of the Ministry of Flemish Community) available for the period 1965-2005.

N, P and Si loads show marked variations during this period each however with a different timing and amplitude (Fig. 2.8). Nutrients originating mainly from point source as NH_4^+ (Fig. 2.8a) and PO_4^{3-} (Fig. 2.8f) show a marked decreasing long term trend in their loads. However nutrients of diffuse origin are mainly modulated by fluctuations of the Scheldt runoff (NO_3^-+NO_2^- ; Fig. 2.8 b,h; r=0.88 and DSi; Fig. 2.8 e,h; r=0.69).

After a two-fold increase between 1966 and the early seventies resulting from the increasing rate of sewage collection and industrial activity with a low capacity of waste water treatment, NH_4^+ loads decrease by some 93% from the early seventies up to 2005 (Fig. 2.8a). This drop is explained by nutrient retention during waste water treatment and the intensification of estuarine nitrification resulting from the net improvement of the oxygenation of the Scheldt river system following the implementation of secondary waste water treatment (sections 2.3.1 & 2.3.2). The decline of PO_4^{3-} loads over the same period shows a two-step trend, being first sharp between 1966 and 1983 and then more gradual up to reaching in 2005 lower levels than those prevailing in the early seventies (0.6 kt P; Fig. 2.8f). Such a decrease is also visible in the Tot P loads which drop by some 86% between 1974 and 2005 (Fig. 2.8g). The considerable increase of P Scheldt loads observed in the seventies has been related to the intensive domestic and industrial use of polyphosphate-containing detergents (Billen *et al.*, 1999; 2001). Their further decrease during the last twenty years is explained by the progressive ban of PO_4^{3-} from detergents, the increased wastewater treatment capacity implemented in the early eighties but also higher P retention due to the co-precipitation of PO_4^{3-} with Fe(oxy)hydroxydes in the re-oxygenated freshwater tidal Scheldt estuary (Zwolman 1994; Billen *et al.*, 2001; Van der Zee *et al.* 2007; sections 2.3.1 & 2.3.2).

Despite the fluctuations related to hydrological conditions, NO_3^-+NO_2^- loads show a global increase since the mid-seventies (Fig. 2.8b) reflecting not only the evolution of diffuse sources of nitrate through leaching of agricultural soils

but also the improvement of the oxygen status of the river, which reduced denitrification but increased the nitrification of the ammonium load (Billen *et al.*, 2005). Altogether this was caused by the intensification of agricultural practices, in particular the large-scale use of fertilizers and the intensive cattle-farming (Fig. 2.6) but also enhanced nitrification and decreasing denitrification due to a better oxygenation of Scheldt tributaries and estuary (section 2.3.2; Billen *et al.* 2005). As a result of NH_4^+ and NO_3^-+NO_2^- load fluctuations, DIN (Fig. 2.8c) and Tot N (Fig. 2.8d) loads show a slight decreasing trend from the early eighties up to 2005. The contribution of NO_3^-+NO_2^- and NH_4^+ to DIN loads was however completely reversed with NH_4^+ representing 60% in 1976 but less than 10% in 2005. DSi loads decreased by about 26% between 1975 and 2005 (Fig. 2.8e) explained by a higher diatom uptake in the upstream courses of the drainage network (Chou & Wollast, 2006).

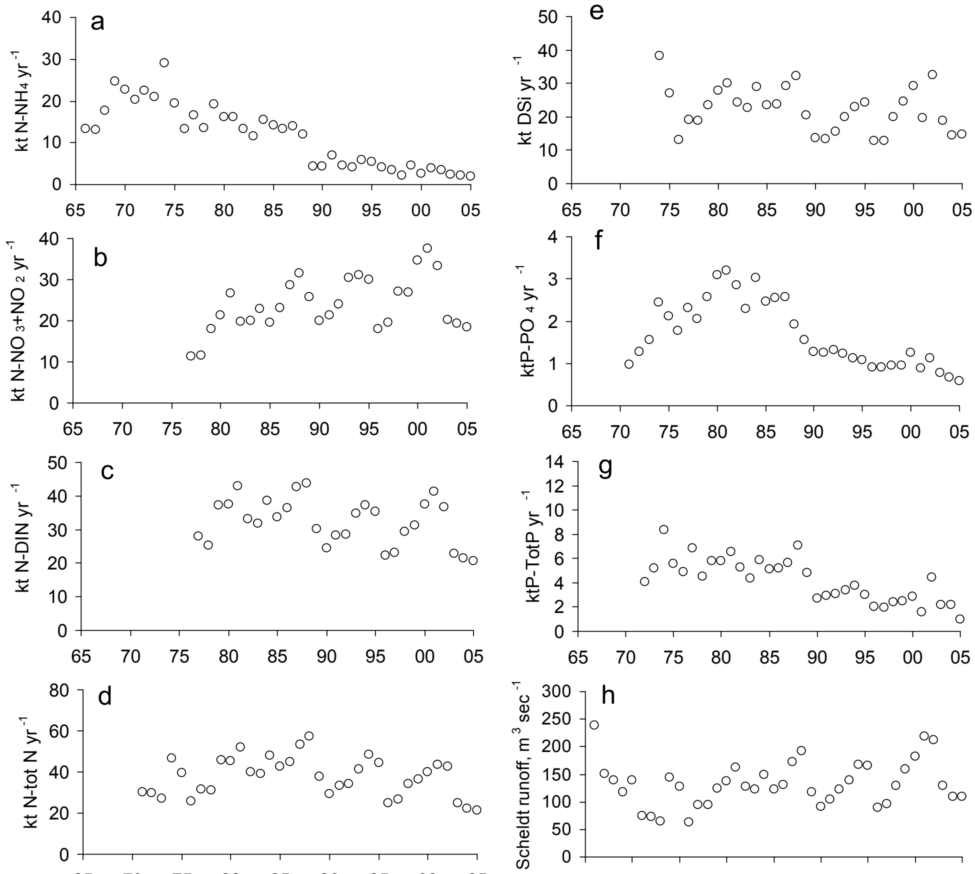

Figure 2.8. Inter-annual variations between 1966 and 2005 of Scheldt loads of NH_4^+ (a); NO_3^-+NO_2^- (b); DIN (c); Tot N (d); DSi (e); PO_4^{3-} (f); Total P (g) and mean yearly runoff (h). Loads were calculated based on nutrient concentration data at Schaar van ouden Doel from www.waterbase.nl courtesy of RIZA and Scheldt runoff available at Schelle (Courtesy of Administratie Waterwegen en Zeewegen).

Qualitative trends. The long-term changes observed in the annual Scheldt loads modify substantially the N:P:Si balance of nutrients discharged to the BCZ since the three last decades (Fig. 2.9). Major shifts occurred in the late eighties when the molar TN:TP ratio increased from values close to the Redfield's ratio in the 1970-1990 period to values higher than 30 in the present-day (Fig. 2.9a). This shift is much more pronounced for the DIN: PO_4^{3-} ratio, which amounted 30 in the mid-seventies and increased by more than a factor 2 (Fig. 2.9a). This shift, stressing a dramatic excess of N over P, is mainly caused by the significant reduction of PO_4^{3-} (Fig. 2.8f) compared to DIN loads (Fig. 2.8c; Soetaert *et al.*, 2006). Compared to the N:Si stoechiometry of diatoms, N largely exceeds Si (DIN:DSi ~ 3) since the mid-70's (Fig. 2.9b). This excess is exacerbated in the 1990's although slightly relieved during the last years. Molar ratios of DSi:PO_4^{3-} present value close to 10 from mid-70's up to mid-80's, lower than the diatom Si:P (*i.e.* 16) indicating a deficit of DSi for diatom growth. This situation reversed in the late eighties when DSi: PO_4^{3-} ratios increase up to 25 indicating at that time a potential PO_4^{3-} limitation for diatom growth (Fig. 2.9c).

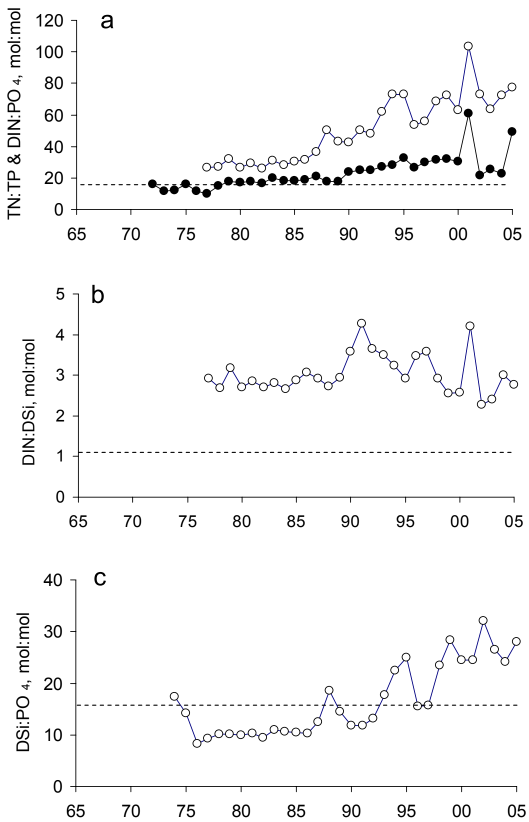

Figure 2.9. Interannual variations (1972-2005) of Scheldt load molar ratios DIN:PO_4^{3-} (open dots) and TN:TP (filled dots) (a); DIN:DSi (b); DSi:PO_4^{3-} (c) compared to phytoplankton N:P (Redfield *et al.*, 1963) and diatom N:Si and Si:P (Brzezinski, 1985) stoechiometry (hatched lines).

2.3 Atmospheric nitrogen deposition

The tropospheric environment of the North Sea and more particularly of the Southern Bight of the North Sea is surrounded by industrialised countries which are important sources of atmospheric nitrogen. Atmospheric inputs are delivered to surface waters through dry deposition of gases and aerosol particles and in wet deposition. Nitrogen deposition is influenced by wind speed and direction, wave size and frequency, and precipitation with the highest deposition occurring during strong winds, high and frequent waves and abundant precipitation events during winter and summer storms (Spokes & Jickells, 2005 and references therein).

2.3.1 Emissions of gaseous nitrogen by adjacent countries of BCZ

BCZ, as adjacent coastal areas, is submitted to reactive N gasses originating from Belgium, France, Germany, the Netherlands and the United Kingdom, but also from the intense ship traffic occurring in the North Sea and adjacent Atlantic Ocean (OSPAR, 2005). These N emissions to the atmosphere have been estimated to some 3 216 kt N yr^{-1} in 2001 among which 51% as NO_x (Fig. 2.10a) and 49% as NH_y (Fig. 2.10b). Emissions of NO_x have decreased by some 35% between 1990 and 2001, especially in France, Germany and UK (Fig. 2.10a). NH_y emissions also decreased in the same period but to a smaller extent (12%; Fig. 2.10b).

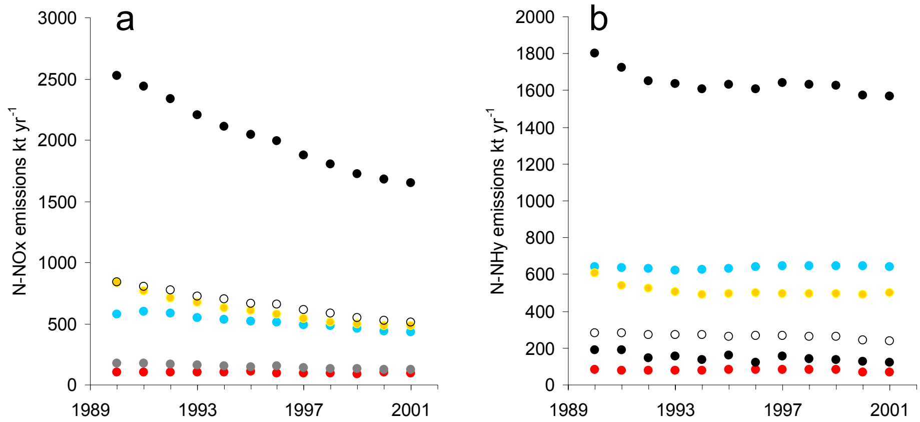

Figure 2.10. Inter-annual variation of annual N emission as N-NO_x (a) and N-NH_y (b) in Belgium (red), France (blue), Germany (yellow), The Netherlands (grey), the United Kingdom (white) and total (black). Source: OSPAR data (OSPAR, 2005).

2.3.2 Atmospheric deposition of N and P into BCZ

N deposition to the BCZ has been quantified using the Unified EMEP model simulating atmospheric transport and deposition of acidifying and euthrophying compounds in Europe (Simpson *et al.*, 2003; OSPAR, 2005). Results indicate

little variations in N deposition between 1991 and 2001 (Fig. 2.11) amounting in average to 1 t N $km^{-2}yr^{-1}$ from which 55% as NO_x and 45% as NH_y. This result is in very good agreement with the value estimated by Rousseau *et al.* (2004) based on literature data on measurements and/or modelling available for the Southern North Sea (Nelissen & Stefels, 1988; Rendell *et al.*, 1993). This synthesis estimates a specific N deposition flux varying between 0.96 and 1.04 t N km^{-2} yr^{-1}. N deposition into BCZ is therefore estimated for the BCZ superficy (3600 km^2) to 3.6 kt N yr^{-1}, corresponding to 0.1 % of the total N emissions by bordering countries of the Southern Bight of the North Sea.

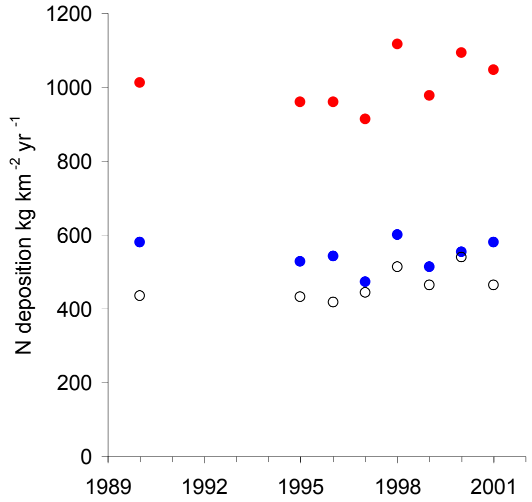

Figure 2.11. Inter-annual variation of annual N deposition (NO_x in white, NH_y in blue, total in red) in BCZ. Source : OSPAR data (OSPAR, 2005).

N emissions originating from France and UK, located upstream BCZ with respect to dominant winds, contributed to 46 % of N deposition in BCZ, Belgium and the Netherlands to 27% and the rest (26%) from ship traffic and other bordering countries such as Germany (OSPAR, 2005).

2.4 Transboundary fluxes

Transboundary nutrient fluxes between BCZ and the adjacent marine areas of France and the Netherlands are those associated with the Southwesterly Atlantic water fluxes enriched by the nutrients brought by the rivers Seine, Somme, Authie and Canche, and Rhine (Lacroix *et al.*, 2004; Fig. 1.2 in Ruddick and Lacroix, 2008). It is commonly admitted that residual currents flow parallel to the coast and that lateral advective fluxes are negligible. The water inflow from the Channel into the Southern North sea is highly variable and

depends on the wind regime with stronger inflow driven by dominant southwesterly winds themselves related to NAO (Breton *et al.*, 2006; Ruddick & Lacroix, 2008). Quantifying nutrient exchange between BCZ and adjacent areas is therefore very complex and requires modeling.

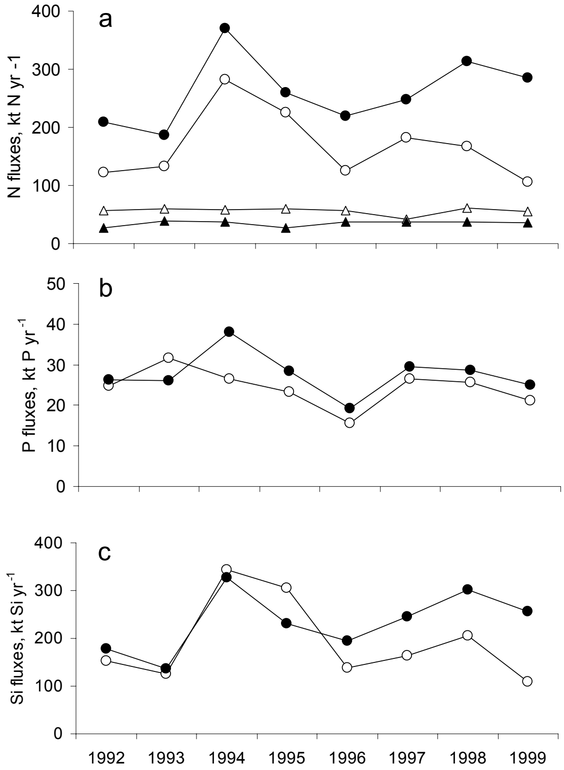

Figure 2.12. Transboundary fluxes of NO_3^-+NO_2^- (dots) and NH_4^+ (triangles) (a); PO_4^{3-} (b) and DSi (c) across the southwestern (Open symbols) and northeastern (filled symbols) borders of BCZ.

Estimations of transboundary fluxes of NO_3^-+NO_2^-, NH_4^+, PO_4^{3-} and DSi were calculated on a monthly basis for the period 1992-1999 as the product of modeled water fluxes and nutrient concentrations measured along the BCZ southwestern (French-Belgian) and northeastern (Belgian-Dutch) bordering transects (see details in Rousseau *et al.*, 2004). The Southwesterly Atlantic water fluxes across the BCZ were calculated using a vertically integrated, 2D

"shallow water wave equation" model (J. Ozer, unpublished). These calculations show that the annual nutrient fluxes across the southwestern and northeastern borders of BCZ are highly variable from one year to another (Fig. 2.12). These fluxes are one order of magnitude higher than the Scheldt nutrient loads (section 2.3.3). The significant fluxes of 1994 correspond to a particularly high intrusion of the Southwesterly Atlantic water into BCZ due to dominant southwesterly winds related to high NAO (Breton *et al.*, 2006).

On an annual basis, there is a net export of NO_3^-+NO_2^- from the BCZ to the North (Fig. 2.12). This is also generally the case for PO_4^{3-} and DSi although some years retention of these nutrients occurs in the BCZ. On the contrary, BCZ acts as a sink for NH_4^+ (Fig. 2.12).

2.5 Nutrient enrichment of BCZ

2.5.1 Spatial distribution of winter nutrients

Nutrient enrichment of BCZ results from the nutrient loads associated to freshwater discharges, atmospheric deposition and Southwesterly Atlantic water inflow (see sections 2.2-2.4). The contribution of these nutrient sources varies with meteorological and hydrological conditions (Breton *et al.*, 2006) resulting in a strong variability of the spatial distribution of nutrient concentrations (Rousseau *et al.*, 2004). High nutrient concentrations associated to low salinity field on BCZ are prevalent when the Scheldt plume spreading is high and the Southwesterly Atlantic water intrusion is moderate. In contrast, a weak extent of the Scheldt plume associated to a large intrusion of Atlantic water into BCZ under persistent strong southwesterly winds result in higher salinities and lower nutrient concentrations.

The enrichment of BCZ is illustrated by the distribution of nutrients and salinity in winter 2003 (Fig. 2.13). As shown by salinity distribution, the Scheldt plume extended on the Southeastern part of BCZ (Fig. 2.13a). Nutrients show a clear gradient from the Scheldt mouth to offshore with higher concentrations close to river and canal mouths indicating the major role of the Scheldt as nutrient source in BCZ but also local effects of the IJzer and coastal tributaries. DIN concentrations (mostly as NO_2^-+NO_3^-) higher than 80 µM are recorded nearby the Scheldt mouth and along the coast decreasing progressively to the northwest where concentrations between 10 and 20 µM, *i.e.* higher than the signature of Atlantic waters (8 µM), are still measured (Fig. 2.13b-d). More than half of the southern BCZ area is characterized by PO_4^{3-} concentrations higher than 1 µM with maximum PO_4^{3-} concentrations (1.5-2 µM) offshore Zeebrugge and Ostend harbours (Fig. 2.13f). The distribution of DSi is similar with concentrations higher than 20 µM prevailing over half of the southern BCZ area (Fig. 2.13e).

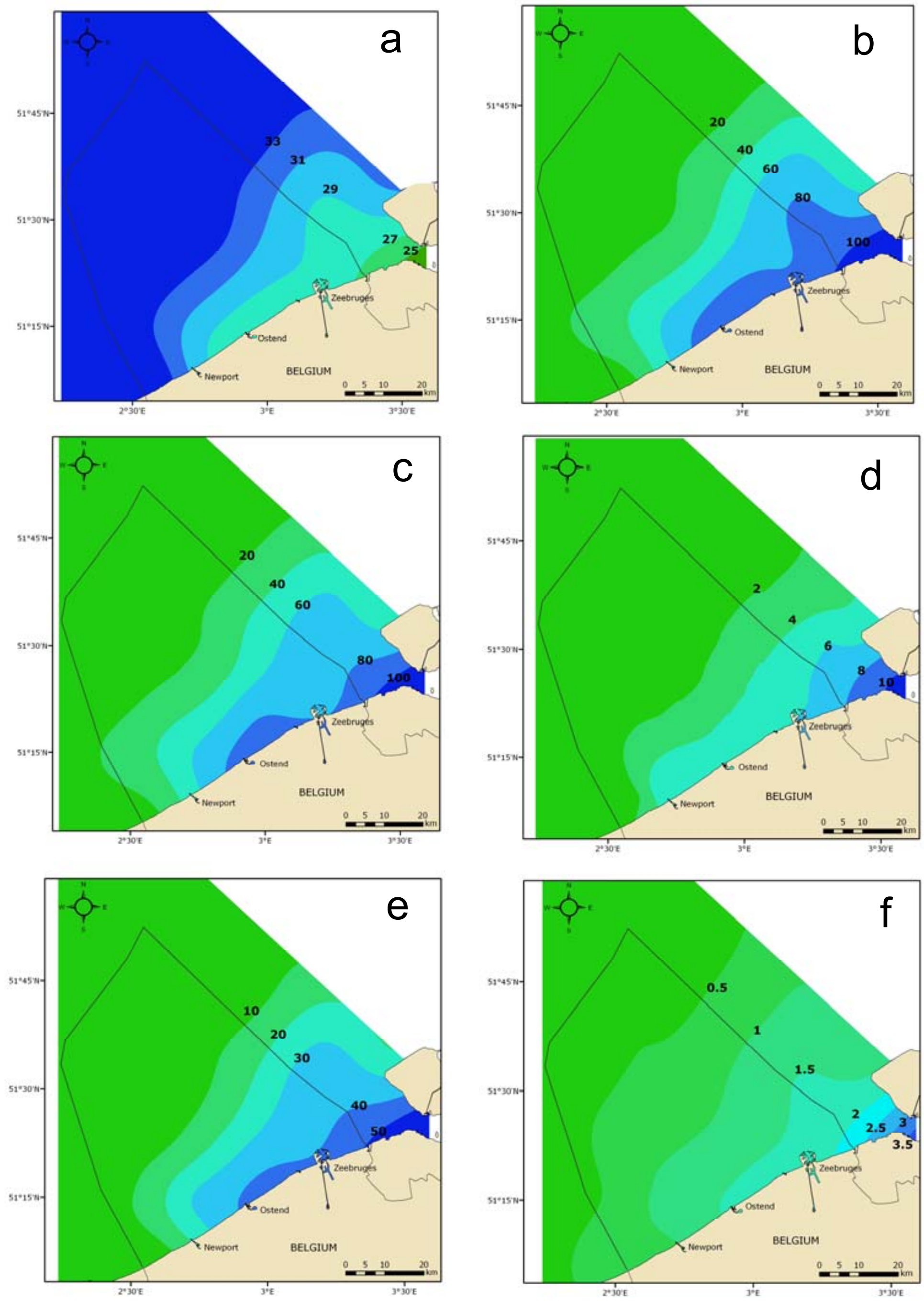

Figure 2.13. Spatial distribution of salinity (a); DIN (b); NO_3^-+NO_2^- (c), NH_4^+ (d), DSi (e) and PO_4^{3-} (f) concentrations (µM) in January 2003 in BCZ.

2.5.2 Long term changes in the enrichment of the BCZ

The average enrichment of the BCZ and its long term evolution were estimated using winter nutrient concentrations and salinity available for the period 1974-2005. In order to encompass hydrological variability, the average nutrient enrichment was computed as the nutrient concentration interpolated at the BCZ salinity of 33.5 as described in Rousseau *et al.* (2004). Both NH_4^+ (Fig. 2.14a) and PO_4^{3-} (Fig. 2.14c) concentrations decrease markedly during this three decade period, reaching values respectively lower than 1.5 and 1 µM in 2005. Such a trend is not observed for NO_3^-+NO_2^- (Fig. 2.14b) and DSi (Fig. 2.14d) in spite of high fluctuations. A long term average of 12 and 27 µM Si and N respectively is calculated. The contribution of NO_3^-+NO_2^- to inorganic N is significant and increases from 90% in the seventies to 95-97% in 2000-2005 (Fig. 2.14a,b). As a result, DIN concentrations do not show significant changes during the 1974-2005 period (not show). These long term changes in the global nutrient enrichment of BCZ reflect the evolution of Scheldt nutrient loads (Fig. 2.8). This is particularly evident for point source NH_4^+ and PO_4^{3-} whose decrease at sea corresponds to the marked drop in Scheldt loads during the late eighties (Fig. 2.8). The PO_4^{3-} decrease is however much less pronounced at sea than in the Scheldt estuary.due to the larger P inputs by inflowing Southwestern Atlantic waters (Lancelot *et al.*, 2005; 2007).

As a result of PO_4^{3-} winter concentration decrease, the N:P:Si balance of winter nutrients is significantly modified over the 1974-2005 period when compared to nutrient requirements of coastal phytoplankton (Redfield *et al.*, 1963) and diatoms (Brzezinski, 1985). Both N:P (Fig. 2.14e) and Si:P (Fig. 2.14g) winter molar ratios show a marked shift in the mid-eighties. The former evolves from values closed to Redfield ratio during the 1972-1985 period to high N excess conditions after the mid-1980's, with a most significant change during the nineties when it increased from 20 to more than 35 (Fig. 2.14e). The evolution of Si:P clearly indicates that the coastal ecosystem evolved from a Si limitation between 1974 and 1990 to a much balanced situation in terms of Si and PO_4^{3-} availability (Fig. 2.14g). N:Si molar ratios fluctuating between 2 and 5 indicates that DIN availability largely exceeded the Si requirement of diatom during the whole period (Fig. 2.14f).

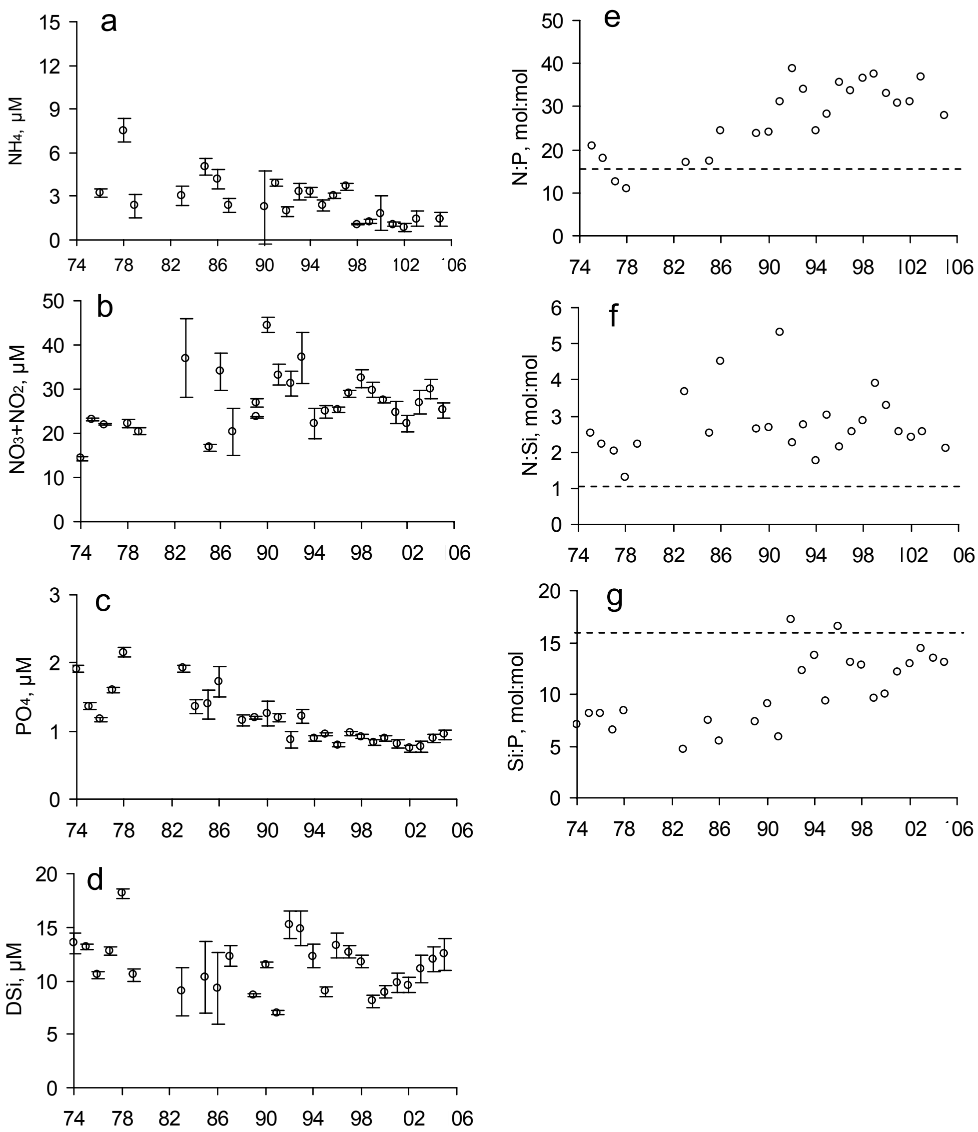

Figure 2.14. 1974-2005 evolution in BCZ of NH_4 (a), NO_3+NO_2 (b), PO_4 (c) and DSi (d) average concentrations and N:P (e), N:Si (f), Si:P (g) winter molar ratios. Hatched line indicates phytoplankton N:P (Redfield *et al.*, 1963) and diatom N:Si and Si:P (Brzezinski, 1985) stoichiometry.

2.6 Conclusions and perspectives

Nutrient enrichment of the BCZ, at the base of eutrophication problems, results from local riverine inputs of the Scheldt, the IJzer and the coastal tributaries, from atmospheric nutrient and from transboundary fluxes brought by the river-enriched Southwesterly Atlantic waters (Lacroix *et al.*, 2004).

2.6.1 Nutrient emissions and loads

The major nutrient loads to the BCZ are the river-enriched transboundary fluxes which are submitted to important interannual fluctuations. These fluxes are in average one order of magnitude larger than riverine and coastal tributary loads while atmospheric deposition is of minor importance.

Emissions of nutrients in the BCZ watershed are strongly correlated to economic development and environmental policy. As illustrated for the Scheldt basin, nutrient emissions varied considerably between 1950 and 2000. Development of demography and economic needs following the WW-II period has resulted in the increase of point and diffuse sources of N and P due to untreated sewage effluents and intensification of agriculture. From the 70’s on, ecological considerations were translated in more restrictive environmental policy rules that resulted in a progressive reduction of nutrient point sources thanks to the implementation of waste water treatment and the banishment of polyphosphate-containing detergents. However, agricultural practices, with large-scale use of fertilizers and intensive cattle-farming proved to be, politically, much more difficult to control and diffuse nutrient sources continued to increase until the 2000’s. Nutrient loads to the BCZ partly reflect this economical and environmental evolution but are also strongly dependant on complex biogeochemical transformations occurring in the watershed. For example, although N point sources decreased since the 70’s, N loads did not significantly decrease probably because of the still important diffuse sources and the restoration of better oxygen levels in streams, reducing the self purification (denitrification) of the N load. On the contrary, phosphorus loads strongly decreased since the 70’s as a direct result of reduced emissions combined to increased in-stream retention processes thanks to higher oxygen levels. The link between nutrient emissions and loads to the BCZ is thus complex to understand and to predict. Comprehensive tools such as mathematical models describing the complex ecological interactions between the nutrients and the environment are needed to predict such changes. Their development and implementation should be considered as priority research field in the future (see Lancelot *et al.*, 2008).

2.6.2 Nutrient budget in the BCZ

An annual budget of inorganic nutrients in the BCZ has been established based on estimations of riverine inputs (section 2.2, Rousseau *et al.*, 2004), atmospheric deposition (section 2.3) and transboundary fluxes (section 2.4). This budget has been established as an average for the period 1990-2000.

Table 2.3. Average annual N and P budgets in the BCZ for the period 1990-2000. Average riverine loads have been estimated from Rousseau *et al.* (2004). OUT-IN represents the difference between nutrient inputs and outputs.

kt N yr^{-1}	BCZ
Loads from the BCZ watershed	43
Loads from atmosphere (DIN only)	3.5
Net loads to Northeastern area (DIN only)	72
OUT-IN	+ 25.5

kt P yr^{-1}	BCZ
Loads from the BCZ watershed	2.7
Net loads to Northeastern area	4.5
OUT-IN	+ 1.8

The difference between nutrient inputs (riverine loads, atmospheric deposition) and outputs (net average export of DIN and P for the period; section 2.4), OUT-IN, indicates a net average annual export of both DIN and P (Table 2.3). This suggests the existence of an important nutrient source within the BCZ. The DIN and P source could well originate from organic matter mineralization processes occurring in both the water column and/or sediments. Organic forms of nutrients are not considered in this budget which is limited to inorganic forms of N and P. Data on organic nutrients are hardly available so that their significance is not currently quantifiable. According to Brion *et al.* (2008), organic N could represent between 30% (winter) and 90% (summer) of the total N pool in Channel waters, and between 20% (winter) and 40% (summer) in Scheldt plume waters. Additionally, Cornell *et al.* (1995) reports DON concentrations in rainwater over the sea twice as high as the DIN concentrations. Diaconu (2008) showed that NH_4^+ regeneration rates through the mineralization of organic matter were intensive in the water column of the Southern Bight of the North Sea, and more or less equalled inorganic N uptake on an annual scale. A nutrient budget established on basis of both inorganic and organic nutrients would thus lead to different conclusions. Lancelot *et al.* (2005) have estimated a global N and P annual budget, including organic nutrient forms, for the BCZ area under influence of the Scheldt (1500 km^2) based on simulations with the ecological MIRO model of nutrient uptake and remineralization. These authors concluded that nowadays this area retained annually 2 and 4% of the respective total N and total P inputs to the BCZ. Nitrogen transformations in the BCZ are suggested to decrease inorganic and organic N forms flowing out of the area by respectively 3 and 1 %, respectively, compared to inflows. Altogether the model

calculates an increased export of NH_4 and PO_4 towards the North Sea (Dutch coastal zone).

Owing to their presumed importance in the BCZ, measurements of organic nutrient pools and dynamics in the BCZ constitute then a priority for future research. Accordingly organic nutrient concentration measurements should be included in future monitoring programmes.

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