2. Carbon and nitrogen cycling in the Scheldt estuary: the major players, long-term changes and an integrated view

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Abstract

The Scheldt estuary is a highly heterotrophic, nutrient-rich, turbid, tidal estuary in a densely populated area (Belgium/The Netherlands). Here we present the results (1) on the long-term changes in nutrient loadings and transformations within the estuary and (2) on nitrogen cycling rate measurements obtained with isotopic tracers. Moreover, we have developed and applied novel techniques that allow direct linking of process rates to the identity and biomass of the organisms involved. Monitoring data and process studies have been used in numerical models to integrate the various biogeochemical cycles and to advance our understanding of the evolving estuarine filter function of the Scheldt estuary.

i. Introduction

Estuaries are the main transition zones between fresh-water and marine ecosystems. Before entering into the sea, rivers collect nutrients, organic matter and suspended particles from their catchments. The combination of high concentrations of nutrients and particles or colored dissolved organic carbon often causes primary producers in rivers and inner estuaries to be light rather than nutrient limited (Boschker et al., 2005). Estuaries are well known to modify and attenuate carbon and nitrogen transfer from rivers to the coastal sea. The efficiency of this estuarine filter influences the functioning of downstream ecosystems (continental shelves) and this filter function has therefore been studied in a number of estuarine systems. Most of these studies rely on concentration measurements and mass-balance approaches to quantify carbon and nitrogen losses. The most advanced studies on the estuarine filter function are based on state-of-the-art modeling tools to improve budgets based on sparse datasets or include some flux and transformation measurements. While these mass-balance oriented studies provide quantitative data on the retention efficiency of carbon and nutrient, they provide little if any mechanistic understanding, nor information on the organisms and mechanisms involved. For instance, the estuarine residence time has been identified as a key parameter determining the removal efficiency of P, N and Si, independent on the actual form in which N enters estuaries (particulate or dissolved organic nitrogen, ammonium, nitrate, nitrite, etc).

During the Flemish-Dutch co-operation for sea research, the universities of Brussels (VUB) and Antwerpen (UA) and the Centre for Estuarine and Marine Ecology of the Netherlands Institute of Ecology (NIOO-CEME) joined forces to study in detail the carbon and nitrogen cycling in the Scheldt estuary.

ii. Aim

The overall objectives were (1) to elucidate the links between carbon and nitrogen cycling, (2) to link the identity of organisms with their activity, (3) to integrate various biogeochemical processes via isotope labeling and numerical modeling, (4) and to reconstruct long-term changes in nutrient cycling.

iii. Scheldt estuary

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 estuary is a broad (from ~500 m near Antwerp to ~6 km near Vlissingen), relatively shallow (10 m mean depth), and rather short (100 km) funnel-shaped, macrotidal estuary with a medium average freshwater discharge of 104 m^3. s^{-1} and a water residence time of 2 to 3 months depending on river flow. The tidal Scheldt is shallow generally well-mixed, but turbid because of high suspended matter concentrations maintained by tidal mixing. As a consequence the photic zone is shallow and primary production is light-limited in this nutrient-rich system. The Scheldt is a highly heterotrophic system characterized by oxygen undersaturation and carbon dioxide supersaturation and high rates of respiration and bacterial secondary production (Boschker et al., 2005).
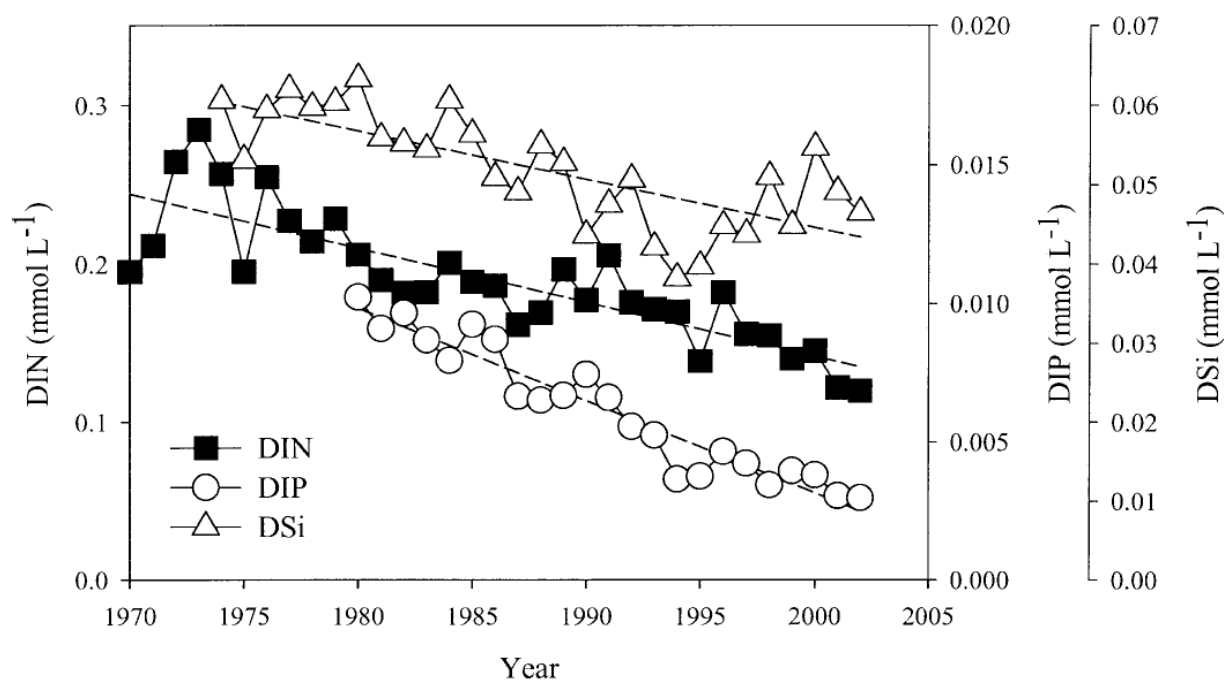
Fig. E-2.1: Long-term changes in dissolved inorganic nitrogen, phosphate and silicate concentrations in the Scheldt estuary (Soetaert et al., 2006)

iv. Long-term changes in Scheldt estuary

During the Anthropocene and in particular during the last 5 decades, human activity has caused major changes in the riverine loads of suspended matter, organic matter and nutrients with dramatic consequences for some ecosystem properties. Moreover, global change may also have affected processes and organisms within the estuary. During the last 30 years large changes in the phytoplankton phenology were observed, with a general trend towards an earlier occurrence of the phytoplankton bloom, which seemed to be related to global warming (Kromkamp & van Engeland, 2010). The Scheldt estuary is one of the most studied estuarine systems and we assembled all available data to generate and exploit a database covering nutrients, oxygen and other monitoring data for the last 5 decades (Soetaert et al., 2006). 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 mmol L-1 y^{-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 % y^{-1}), DIN (1.7 % y^{-1}), and DIP (5.4 % y^{-1}), the N: P and Si : P ratios more than doubled from 1980 to 2002 (Fig. D-3.1). The Si :N ratio varied from 0.2 to 0.4 and was positively correlated with river discharge. The Scheldt estuary 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. The release of P from sediments probably accounted for the additional DIP. 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.
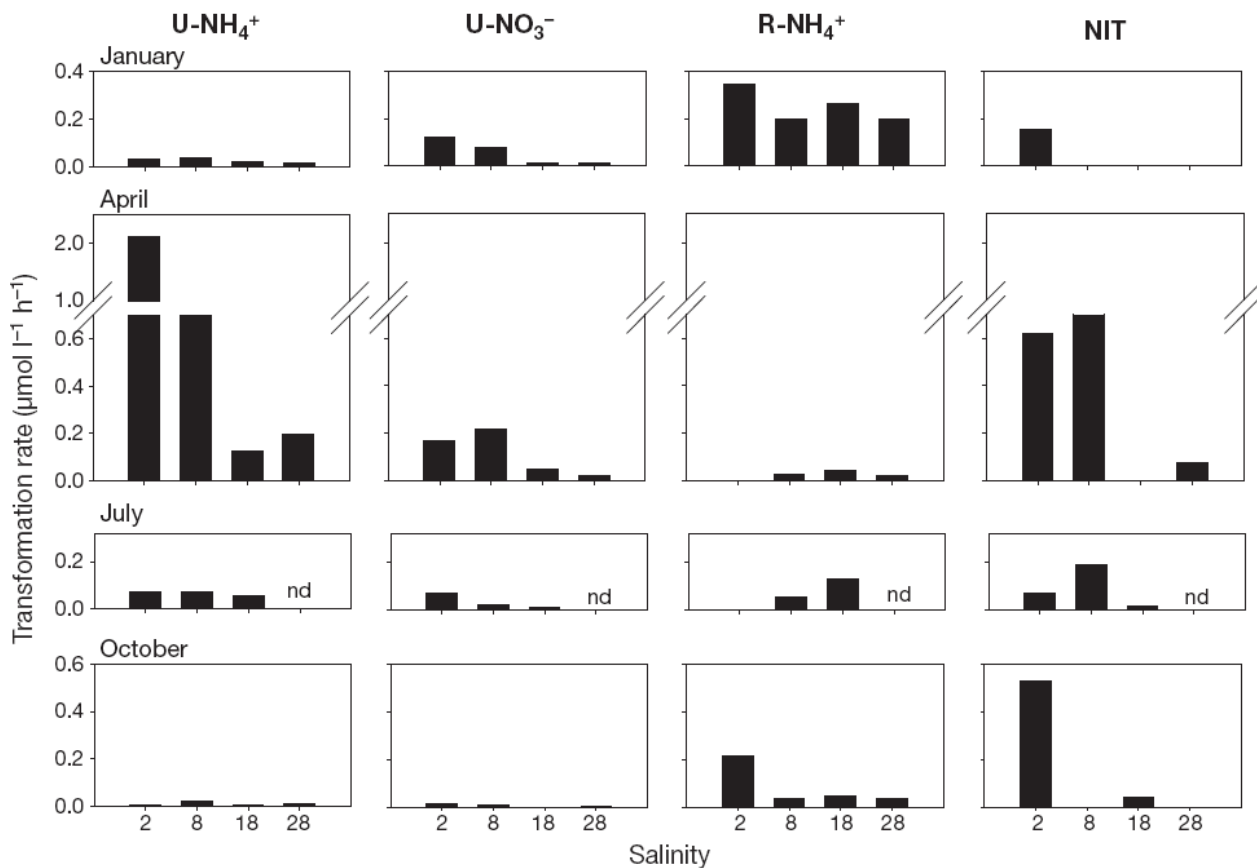
Fig. E-2.2: *Nitrogen transformation rates at the 4 salinity stations in the Scheldt estuary: ammonium and nitrate uptake (U-NH$_4$+and U-NO$_3$–), ammonification (R-NH$_4$+) and nitrification (NIT). nd: not done (Brion et al., 2008)*

v. Nitrogen cycling in Scheldt estuary

However, this apparent conservative behavior of nitrate in the Scheldt estuary in terms of mass balance budgets should not be considered evidence that nitrate turnover is limited. It simply means that nitrate production (regeneration from sediments and nitrification) and nitrate consumption (denitrification and nitrate assimilation) are balanced. To investigate in detail the turnover of nitrogen in the Scheldt estuary we studied sedimentary nitrogen cycling and water column ammonium regeneration, nitrification and uptake of ammonium, nitrate, nitrite, urea and amino acids using ^{15}N as a deliberate tracer (Andersson et al., 2006a, 2006b; Brion et al., 2008). Nitrogen exchange with lateral ecosystems, e.g. tidal fresh-water marshes, have been the subject of another project (see Struyf et al. this volume). Ammonium oxidation by nitrifiers (Archaea and Bacteria) and ammonium uptake by algae and bacteria were of similar magnitude, with nitrification dominating during winter and assimilation processes during the spring bloom. Urea

and amino acids constituted up to 43 and 29 % of total nitrogen uptake, respectively, and were of similar importance as inorganic substrates. Through the use of dual-labelled substrates we revealed that amino-acid nitrogen was consumed year-round, while amino-acid carbon was not assimilated during summer. Nitrification was studied in multiple ways: from the transfer of ^{15}N from ammonium to nitrate, from the dark incorporation of ^{13}C and/or ^{14}C into organic matter with and without nitrification inhibitors (N-serve and sodium chlorate) and from oxygen consumption with or without nitrification inhibitors (Andersson et al., 2006a; Gazeau et al., 2005). Our study revealed that nitrifier activity (as measured with ^{15}N technique) and growth (^{14}C incubation) can be uncoupled, complicating the common use of N:C conversion factors. Moreover, nitrification has been identified one of the most important biogeochemical processes in the upper Scheldt, contributing not only to ammonium consumption, but also to carbon fixation, oxygen consumption (Gazeau et al., 2005) and acidification (Hofmann et al., 2009).


vi. Activity-Identity Linking

Through the combination of biomarkers, organic molecules specific to certain groups of organisms, and stable isotopes, it is possible to link the identity, biomass and activity of organisms (Boschker and Middelburg, 2002). We studied planktonic community structure and isotopic composition using compound-specific ^{13}C analysis of phospholipid-derived fatty acids (PLFA) along the Scheldt estuary during a spring bloom (Boschker et al., 2005). Concentrations of algal PLFA and pigments and microscopic identifications of dominant phytoplankton revealed the same trend: a mixed community of green algae and diatoms dominated the freshwater phytoplankton and there was a major diatom bloom at intermediate salinities (Dijkman and Kromkamp, 2006). Bacterial biomass (also based on PLFA) was much lower for the diatom bloom in the lower estuary than in the net heterotrophic upper estuary. Carbon isotopic ratios of a diatom biomarker were mainly related to changes in ^{13}C values of dissolved inorganic carbon. A green algal marker was much more depleted in ^{13}C than the diatom markers, suggesting that these two main phytoplankton groups use a different inorganic carbon source or carbon dioxide fixation mechanism. In the lower, marine side of the estuary, isotope ratios of bacterial and algal PLFA were similar, suggesting a coupling between primary production and bacterial consumption of organic matter. In the upper estuary carbon isotope signatures of dissolved organic carbon (DOC), particulate organic carbon, and bacterial biomass were similar and significantly enriched relative to those of diatoms and green algae, pointing to allochthonous subsidies as an important carbon source for bacteria. The contribution of algae to zooplankton diets as estimated from isotope ratios averaged 41 % and 75 % respectively. Mesozooplankton relies primarily on grazing on phytoplankton and direct consumption of particulate organic matter and appears to receive little of its carbon from DOC via bacteria (Van den Meersche et al., 2009).

Tracer techniques have shown to provide accurate estimates of the transfer from the dissolved to the particulate phase. However, they do not provide any direct information on the organism involved. We have explored stable-isotope labeling of PLFAs as a technique to study group-specific primary production of phytoplankton, as many algal groups possess a specific PLFA composition. After developing and testing the new method (Dijkman et al., 2009), we have investigated the group-specific primary production of a number of phytoplankton groups, including diatoms, green algae, cryptophytes and the combined group of dinoflaggelates/ haptophytes in the Scheldt estuary. Group-specific primary production revealed major

differences in contribution of main algal groups. Diatoms, the dominant group along the whole estuary, generally contributed less to the primary production than expected from its standing stock, whereas the dinoflagelates-haptophytes group (mainly consisting of Phaeocystis), was relatively more important in the marine section of the estuary. Our measurement indicated that indicated that estuarine algae are growing at the location –or rather in the water mass- where they are found and are not merely transported from either the freshwater or the marine end. These group-specific primary production measurements will be useful in the next generation of estuarine biogeochemical models.

Integrative models

The joint Flemish-Dutch research program generated a wealth of data: new data on the distrubution of nutrients, particles, organic matter and organisms, a detailed historical reconstruction of nutrients inputs and concentrations and limited data on the linkages between carbon, nitrogen and oxygen cycles and the organisms involved. On the basis of these results we have developed a A new 1-D reactive-transport model of the Scheldt estuary that resolves the major carbon and nitrogen species and oxygen, as well as pH (Hofmann et al., 2008). It is a model based on Occam's razor, i.e. as simple as possible but still able to fit the data well enough to determine the fate and turnover of nutrients entering the estuary and their spatial patterns in the years 2000 to 2004. Nitrification was identified as one of the most important processes consuming comparable amounts of oxygen as respiration and model predicted nitrification rates closely matched measurements. The developed model explicitly resolved the effect of biogeochemical processes on pH. Proton production by nitrification is identified as the principal biological process governing the pH. Its acidifying effect is mainly counteracted by proton consumption due to CO_2 degassing. Overall, CO_2 degassing generates the largest proton turnover in the whole estuary on a yearly basis (Fig. E-2.3; Hofmann et al., 2009).
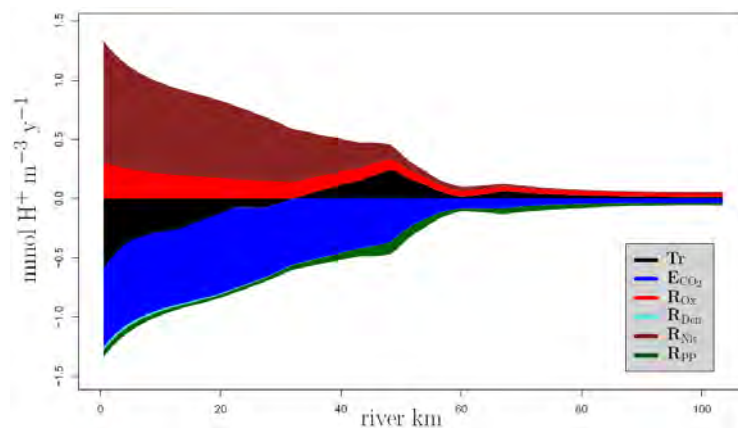
Fig. E-2.3: *The influence of biogeochemical processes on the pH of the Scheldt estuary. Process abbreviations: Tr=advective-dispersive transport, ECO_2=CO_2 degassing, $RO_{x=oxic}$ mineralisation, R_{Den}=denitrification, RNit=nitrification, RPP=primary production.*

vii. Outlook

Future studies will need to focus on a better understanding of the different functional groups in the different biogeochemical processes and ecosystem services. This implies further development

of biogeochemical modeling tools that allow projections of Scheldt ecosystem behavior and properties as a result of climate change (changes in river discharge rates and variability, global warming) and human activity (dredging, nutrient loadings). Moreover, there is also a need to develop new methods that allow enhance taxonomic resolution in activity measurements (e.g. combination of stable isotope labeling with RNA extraction or with NanoSIMS for subcellular isotopic measurements).

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