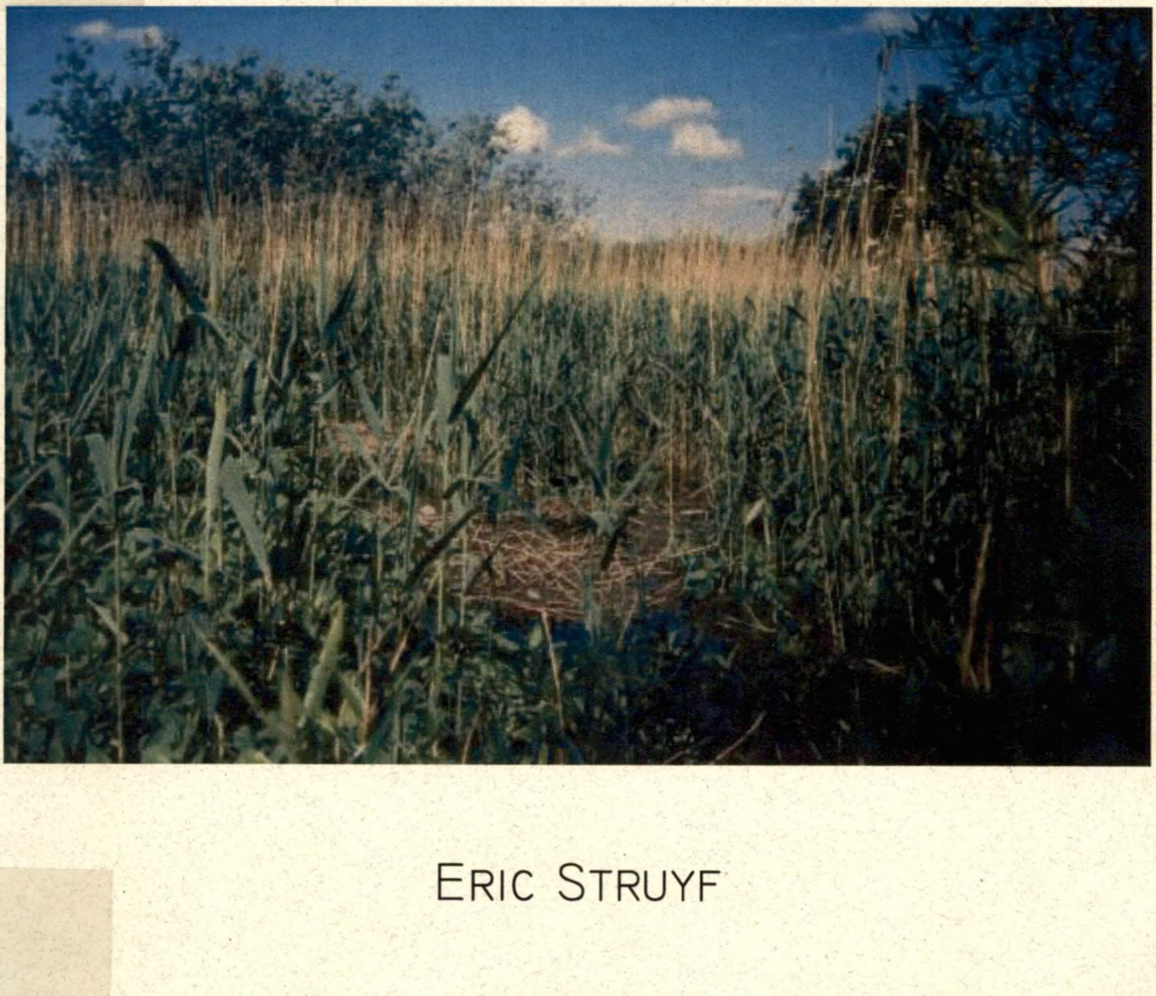
THE ROLE OF FRESHWATER MARSHES IN ESTUARINE SILICA CYCLING

(SCHELDT ESTUARY)



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The role of freshwater marshes in estuarine silica cycling (Scheldt estuary)

De rol van zoetwaterschorren in de estuariene siliciumcyclus (Schelde-estuarium)

Proefschrift voorgedragen tot het behalen
van de graad van Doctor in de Wetenschappen
verdedigd door Eric Struyf

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Promotor: Prof. Dr. Patrick Meire
Co-promotor: Prof. Dr. Jack Middelburg

Dankwoord

Maart 2000. De beslissing was genomen: mijn licentiaatsthesis zou handelen over de standaardisatie van estuariene waterkwaliteitsdata, verzameld langsheen de Schelde. Na een jaar gevuld met dertienuursmetingen, pH-experimenten en sondeperikelen (niet voor niets genoot onze sonde de bijnaam “de worst”), had ik er blijkbaar lang niet genoeg van en besloot ik nog wat verder te blijven vertoeven in het getijdengebied, met een lichte interne verplaatsing naar de schorren en siliciumcyclering.

Silicium en schorren: veel mensen keken raar op bij de combinatie. Soms werd zelfs gefluisterd dat enkel een fan van bedenkelijke B-films zich met een dergelijk onderzoek zou bezighouden... Wat er ook van zij: het zijn 4 boeiende onderzoeksjaren geworden, en het uiteindelijke resultaat is er mede gekomen dankzij de hulp van een pak mensen, die ik hier dan ook wil bedanken.

Ik had deze weg nooit ingeslagen zonder Stefan: niet alleen leerde hij me als begeleider van mijn licentiaatsthesis de kneepjes van het estuariene vak; hij was het ook die voor het eerst silicium uit schorren zag sijpelen, en daarmee de basis leverde voor dit doctoraatsonderzoek. Stefan, bedankt voor de fantastische samenwerking gedurende de afgelopen 5 jaren, het is echt plezant geweest.
Mijn promotor, Patrick, zag soms tot zijn ontzetting hoe ik de onstilbare drang voelde om collega’s in levensbedreigende situaties te brengen: alle ijskoude Ardennenriviertjes, verraderlijke voetbalvelden en droppings ten spijt, bleef hij me samen met mijn co-promotor Jack steeds bijstaan bij het uitwerken van deze thesis. Patrick en Jack, bedankt!
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Chapter 1

Introduction

1.1 Si and coastal eutrophication

Estuaries are the transitional zones between land-based ecosystems and the ocean. Although shallow marine areas occupy less than 8 % of the planet's surface, they account for about 25 % of the biological production (Mann 1988; Glantz 1992). As such, they have both a huge ecological and economical importance, as they support a wide biodiversity of both species and communities. The complexity of estuarine ecosystems results in a high vulnerability to global change and direct anthropogenic pressures. Expansion of agricultural activities, increasing freshwater demand, reservoir construction, urbanization and industrialization and concurrent release of chemical compounds (nutrients and toxicants) have all had a severe impact on the coastal zone throughout the world in recent decades (Kondratyev & Pozdnyakov 1996). Sea-level rise, increasing discharges and temperature increase as a result of human induced climate change can further worsen the situation.

In contrast to N and P, which are delivered in large amounts to the surface waters by agriculture and urban waste water, the anthropogenic input of Si to estuarine systems has always been negligible. While in most major rivers worldwide the concentrations of N and P have at least doubled as a result of human pollution, the DSi concentrations have remained similar (Meybeck 1982; Justic et al. 1995). The change in the ratio of N, P and Si concentrations (through human interference) controls the species composition of the coastal and estuarine phytoplankton community. Diatom communities have been identified as the main energetic source for estuarine and coastal food chains (Peterson & Howarth 1987; Sullivan & Moncreiff 1990). Diatoms require about equal amounts of N and Si. Generally, they have a competitive advantage over flagellates, because diatoms have a higher photosynthetic capacity and lower maintenance energy requirements (Billen et al. 1991).

The high human input of P and N to estuaries can lead to Si limitation of the diatom communities, and induce a succession of the diatom dominated phytoplankton community to a community dominated by non-diatom species (e.g. *Phaeocystis* sp., *Gonyaulax* sp., *Chrysochromulina* sp.), which are less available to the higher trophic levels (Schelske et al. 1983; Smayda 1997). Apart from this negative effect on estuarine and coastal foodwebs, enhanced non-diatom phytoplankton production can have several other negative consequences including increased water turbidity, anoxic conditions and appearance of toxic algal blooms (Gazeau et al. 2004).

Eutrophication problems have been reported in aquatic systems worldwide (Conley et al. 1993). The biogeochemical cycling of N and P in estuarine systems, in intertidal wetlands, sediments and the pelagic environment, has been studied and reviewed intensively in recent decades (e.g. Howarth et al. 1996; Nixon et al. 1996). Tidal marshes have been reported to play a major role in N and P retention (Cai et al. 2000; Li et al. 2003) and to provide a major reactive surface, which may result in increased N speciation capacity (Dame et al. 1996; Merrill and Cornwell 2000). Salt marshes have a high capability of removing N from highly nutrified estuarine waters (Howes et al. 1996). In general, one could state that tidal marshes import inorganic N and P, while exporting both nutrients in high-energy, organic form and, as a result, support secondary production in adjacent estuarine waters (Teal & Howes 2000).

However, compared to our knowledge concerning N and P processing, transport and cycling of Si in the aquatic continuum is significantly less known. Si research has mainly been focused on the oceanic silica cycle, given the important role diatoms play as the major primary producers in the oceanic environment (Officer and Ryther 1980) and the potential of BSi burial as a paleoproductivity indicator (Ragueneau et al. 2000). Yet, research of the biogeochemical cycling of Si in transitional waters is essential, not only to understand the eutrophication events in the estuaries themselves, but also given the important role of rivers in balancing the marine Si budget (see below: "the global Si cycle").

1.2 The global Si cycle

The earth's crust consists for 28 % of silicon (Cotton & Wilkinson 1966). Si occurs most often combined with oxygen as SiO_2 (quartz) in rocks and minerals (Iler 1979). Atmospheric transport of particulate Si is small compared to dissolved fluxes from weathering (Fig. 1.1). It is however of importance for the deep ocean, where the contribution of river materials is reduced substantially (Buat-Menard & Chesselet 1979). The weathering and erosion of crust materials however provides the single largest continuous supply of dissolved silicon, H_4SiO_4 (DSi, commonly referred to as "silicate"), to rivers, estuaries and ultimately the ocean (Fig. 1.1). This chemical weathering of lithogenic Si results in enhanced removal of carbon dioxide from the atmosphere, through the dissolution of soil carbon into HCO_3^-. On geological timescales, this CO_2 transfer is an important control on atmospheric CO_2, and as a result on global climate.

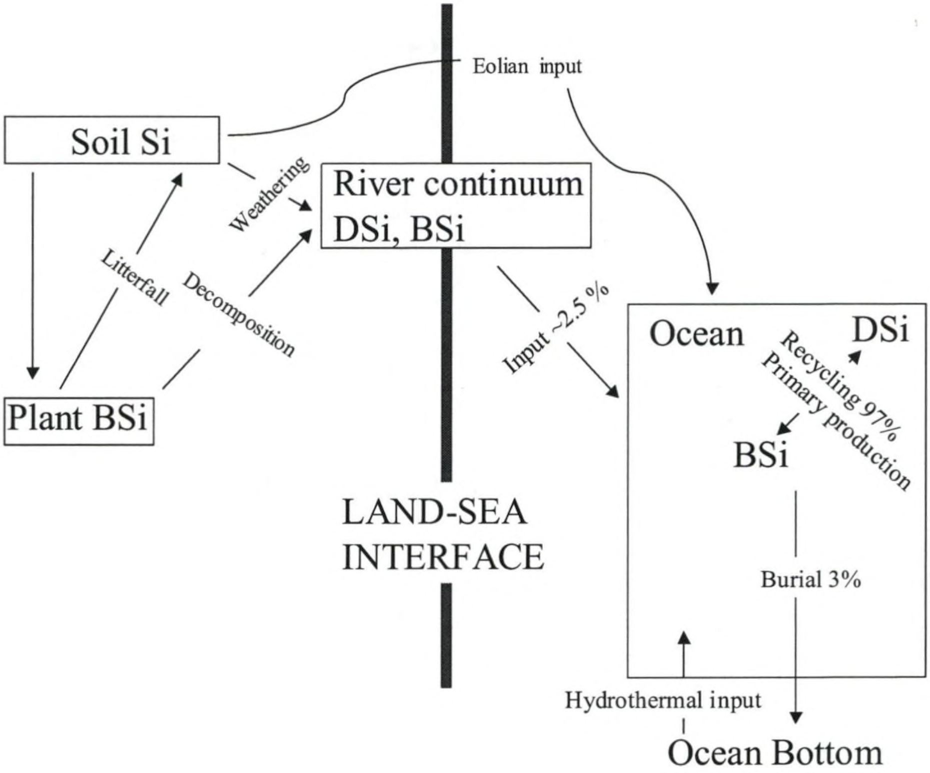

Figure 1.1 The global cycling of Si. Left from the land-sea interface is the terrestrial component, to the right is the oceanic cycle.

Not all DSi is transported to the oceans directly after weathering. In solution, the dissolved silica concentrations are controlled by processes such as precipitation, biological removal and recycling. Uptake in biota can significantly alter the DSi fluxes which ultimately reach the ocean.

Silicon is a major biogenic element. Some organisms (the most important being diatoms or *Bacillariophyta*) have an absolute requirement for Si, to build up structural elements of hydrated, amorphous silica, known as biogenic silica or opal (BSi, SiO_2NH_2O). BSi is however not only limited to diatoms. BSi is a heterogenous collection of different components (Conley 1998). Plants take up DSi along with water, and vegetation is a major reservoir of BSi in the global cycling of Si. The global average of Si content in plant tissue is between 1-3% of the total dry weight (Conley 2002). Once absorbed by the plant, BSi is stored in the plant tissue in siliceous bodies known as plant phytoliths. Conley (2002) estimated the annual worldwide production of BSi accumulated in plants as phytoliths to range between 60-200 Tmole Si year^{-1}, as opposed to an oceanic gross production of BSi of 240 Tmole Si year^{-1} and annual inputs of DSi in the ocean around 5 Tmole Si year^{-1} (Tréguer et al. 1995). This was the first identification of the importance of the terrestrial biogeochemical cycle of BSi, which was previously considered insignificant compared to the oceanic BSi fixation.

Many plant scientists still consider plant DSi uptake as a by-product of water assimilation (Epstein 1999). It is often not considered an essential element or a plant nutrient. This is mainly the result of a limited definition of essential: although most plants (except *Equisetaceae*) will grow in a Si-deprived growth medium, the addition of Si can bless the plant with several competitive advantages over Si-deprived individuals. Enhancement of growth and yield, increased shoot rigidity, promotion of photosynthesis, resistance to disease, herbivores, metal toxicity, salinity and drought stress and protection against temperature extremes are among the roles of Si in plant life (Epstein 2001).

BSi is an important source of DSi in the global biogeochemical cycling of Si, especially on biological timescales. The dissolution rate of BSi is much higher than the dissolution rate of lithogenic Si, considered inert at biological timescales (10^{-11}-10^{-12} mol m^{-2} s^{-1}, Van Cappellen 2003). Hence, efficient recycling of BSi to DSi occurs within terrestrial and marine ecosystems. In deciduous, coniferous and bamboo forest ecosystems, the fixation of Si in biomass is yearly balanced by an equal amount of BSi deposited in litterfall (Bartoli 1983, Meunier et al. 1997).

In ocean waters, 75 % of settling BSi is recycled in the upper 1000 m of the water column (Tréguer et al. 1995). After reaching the ocean bottom, BSi is still subject to dissolution to marine porewaters and diffusive efflux as DSi. Only 3 % of the ocean BSi production is ultimately buried in the bottom sediments (Van Cappellen 2003). On timescales shorter than 1000 years, the ocean floor is therefore only a minor sink for Si. With the passing of time however, the cumulative losses become significant. Hydrothermal sources and eolian transport partially balance these losses, but the chemical weathering and concurrent transport of DSi and BSi through estuaries, is the single largest source of Si for the ocean, and essential to balance the permanent deposition of BSi in bottom sediments (Conley 1997). A thorough knowledge of transport, processing and retention of Si in the estuarine environment is therefore essential in understanding the global cycle of Si.

1.3 Estuarine Si cycling

Land-derived materials transported though estuaries are significantly processed in the estuarine environment. For all three major nutrients, N, P and Si, an estuarine cycle exists. The nutrients are subject to intense transformation, retention and recycling during their journey to the coastal waters. As for the other nutrients, uptake by phytoplankton communities and consequent uptake in higher organisms and interactions with the particulate phase significantly alter the Si speciation in estuarine environments (Figure 1.2).

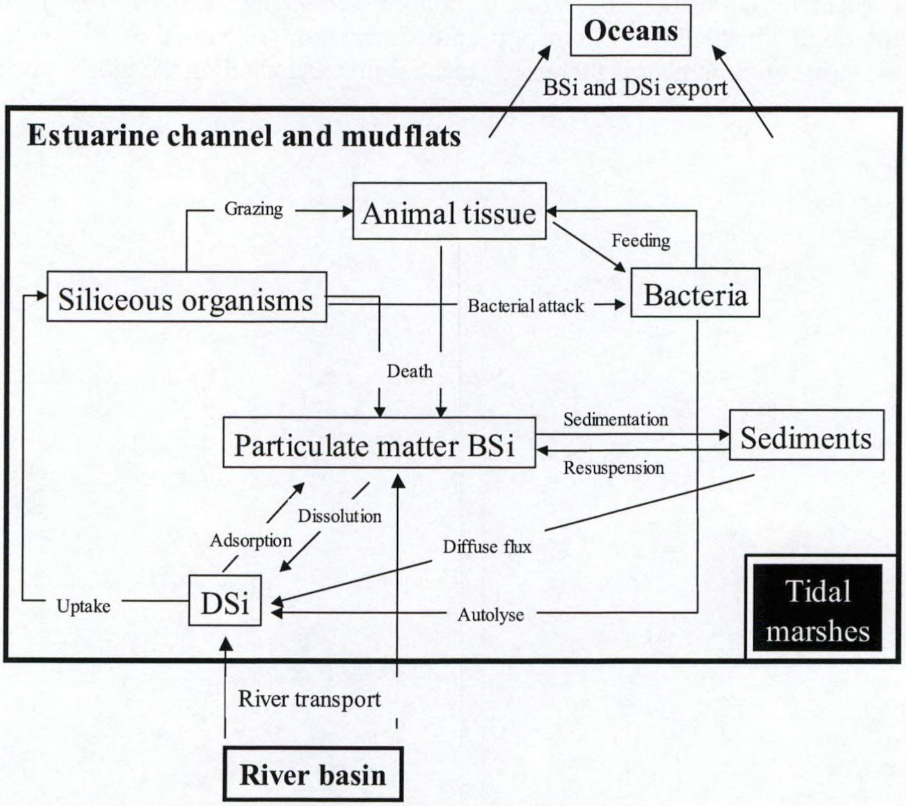

Figure 1.2 The estuarine Si cycle (partially after Aston 1980). Estuaries receive BSi and DSi from the river basin, and after internal cycling and recycling, Si is eventually transported to the oceans. The role of tidal marshes in the estuarine Si cycling has always remained something of an enigma.

The DSi concentration which enters the tidal estuary at the interface with the non-tidal river, has been reported to be positively influenced by increasing discharge (Uncles et al. 2003), through increased weathering of soil Si in precipitation run-off. However, high discharge can also negatively influence the DSi concentration, through exhaustion of the easily soluble Si and through dilution effects (Rendell et al. 1997). The typical average concentration of DSi carried in rivers to the ocean is 150 μmol.L^{-1} (4 mg.L^{-1}); for BSi this concentration is 28 μmol.L^{-1} (0.8 mg.L^{-1}) (Conley 1997).

Once in the estuary, DSi is subject to seasonal uptake by diatom communities, both benthic and pelagic (Wollast & De Broeu 1971; Sharp et al. 1982; Clark et al. 1992) In winter and autumn, when there is no uptake, DSi behaves conservatively, and DSi concentrations decrease linearly along the salt gradient. During diatom blooms in summer and spring, uptake by diatoms results in an increase of BSi concentrations, and DSi can deviate from conservative behaviour, because of this uptake at the one hand, and the decay of diatom communities at the saltwater-freshwater interface on the other hand. Burial of diatoms can enhance the BSi content of the estuarine sediments, and consequent dissolution results in fluxes of DSi from the sediments to the water column (Asmus et al. 2000).

The uptake of DSi by diatoms in the freshwater part of estuaries has been shown to be dependent on discharge (Muylaert et al. 2001; Struyf et al. 2004). Freshwater estuarine diatom blooms are negatively influenced by high discharge conditions, and entire diatom communities can be flushed away by peak discharges. The estuarine diatom community can even be replaced by a community of riverine origin, unadapted to the tidal environment. With the flushing of diatom communities, no uptake of DSi takes place and summer concentrations of DSi can approach winter concentrations. Increasing discharge through global change could result in the flattening out of the seasonal cycle of Si in the upper estuary.

It is a striking fact that up to this date, almost all research on the estuarine silica cycle has focused on processes in the estuarine channel and, to a lesser degree, on processing in intertidal mudflats (see below). As of yet, the processing of Si in tidal marshes has remained something of an enigma, a black hole in our knowledge of the Si cycle (Fig. 1.2); very little is known about both the processes within the tidal marsh environment and the exchange between the nearby coastal waters and the marsh ecosystem. Below, the sparse knowledge about Si in the intertidal environment has been bundled.

1.4 Si in tidal marshes

Research on Si processing and retention in estuaries has mainly been focused on subtidal benthic sediments and uptake and recycling by pelagic diatom communities (e.g. Yamada & D'Elia 1984; Muylaert et al. 2001). Tidal wetlands have been mostly neglected in the study of coastal Si cycling. The BSi content of tidal saltwater marsh plants has been studied quite intensively (e.g. Sangster 1982; Eleuterius & Lanning 1987; De Bakker et al. 1999; De Boer 2000), but these studies were plant ecology oriented, and not directly linked to marsh functioning in the Si cycle. On tidal mudflats, which in contrast to marshes flood every tidal cycle, benthic fluxes of DSi have been studied in systems worldwide (Feuillet-Girard et al. 1997; Mortimer et al. 1998; Mortimer et al. 1999; Asmus et al. 2000). Both import and export of DSi from the mudflats and subtidal benthic sediments have been reported, but mean rates were directed towards the water, out of the sediment. Mean reported efflux rates were between 63 and 617 µmol m^{-2} h^{-1} (Asmus et al. 2000). The flux rate was enhanced by temperature, salinity (Yamada & D'Elia 1984) and bioturbation (Gehlen et al. 1995). The import flux was attributed to uptake by benthic diatoms.

Recent research on a mesohaline tidal marsh in North Carolina (USA), has highlighted the large capacity of tidal wetlands to store Si, primarily as amorphous BSi in vegetation and in sediment, through the burial of aquatic diatoms and phytoliths from higher plants (Norris & Hackney 1999). The high availability of BSi for dissolution results in high DSi concentrations in marsh porewater, compared to adjacent estuarine waters (Hackney et al. 2000). In 1997, considerable export of DSi was observed from a freshwater marsh along the Scheldt estuary to nearby estuarine waters, during a limited survey of 3 tidal cycles conducted in spring and summer (Van Damme et al. 1998). The ability of tidal marshes to enhance and sequester internal cycling of both biogenic and dissolved Si, was hypothesised to provide an alternate, complementary explanation for the observed relationship between tidal marsh production and secondary production of economically valuable fish and invertebrates in coastal waters (Hackney et al. 2000), through the stimulation of production of estuarine diatoms. Enhanced Si recycling could add to alternate explanations for the observed link between tidal marshes and secondary production.

The uptake of tidal marsh plants in the detrital food chain (Teal 1962; Odum & De la Cruz 1967) or marshes providing structural habitat for feeding (Turner 1977; Boesch and Turner 1984; Sullivan & Currin 2000) have been argued as possible explanations. However, the limited research on Si retention and processing in tidal marshes has prevented the verification of this hypothesis.

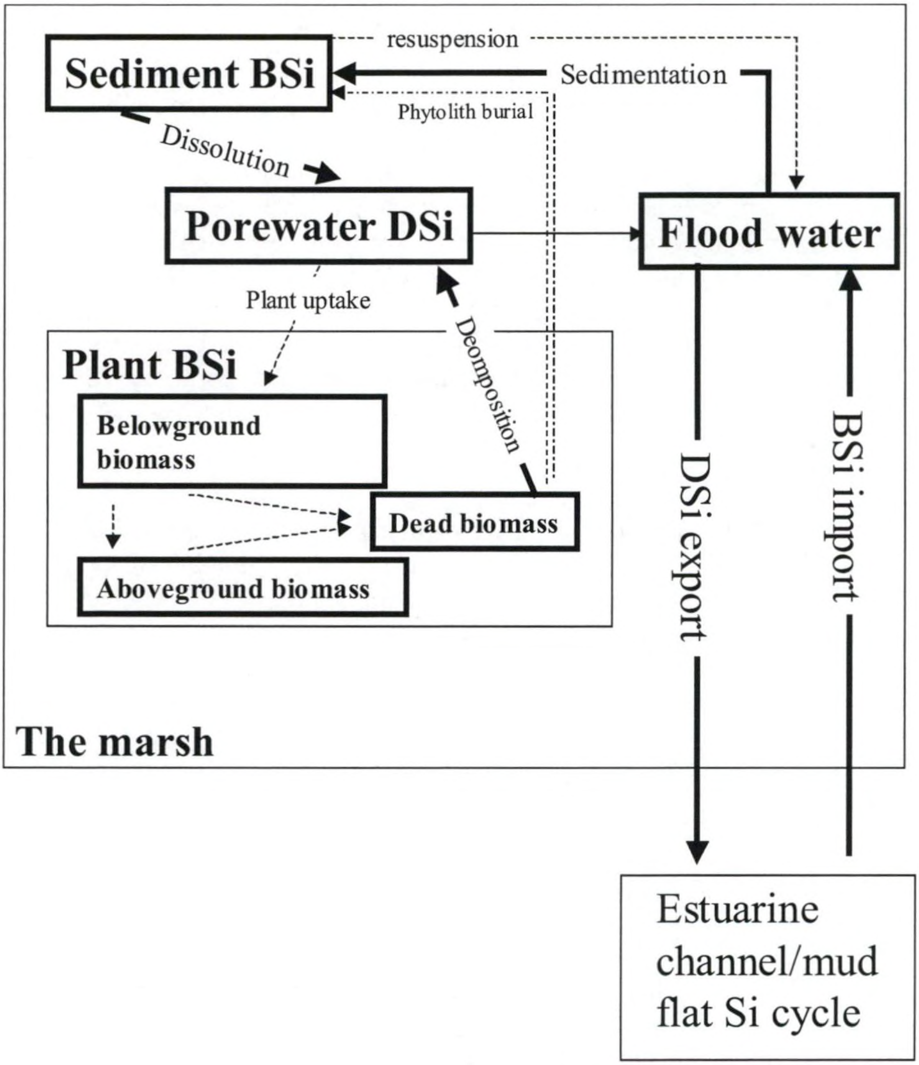

Figure 1.3 The hypothesised cycling of Si in marshes. BSi is imported into the marsh, while DSi is exported. Plant and sediment BSi are both recycled to DSi, which enriches the porewater DSi-concentrations, and enhances the export of DSi from the marsh.

1.5 This thesis

The aim of this thesis was to gain insight into the role freshwater marshes play in the estuarine Si cycle and to understand the internal marsh processes that underlie the considerable export of DSi observed from a freshwater marsh along the Scheldt in 1997. Fig. 1.3 shows the studied stocks and fluxes of both BSi and DSi and the proposed marsh Si cycling scheme.

It was hypothesised that the high retention capacity of marsh sediments and vegetation for BSi enhanced internal recycling of DSi in the marsh. Entrainment of marsh porewater in tidal floodwater, low in DSi concentration, was hypothesised to enrich the tidal ebb water with DSi, resulting in a net export of DSi from tidal freshwater marshes. The second hypothesis was that similar processes could take place in all tidal marshes, regardless of their position along the salinity gradient. Combined hypotheses imply that marshes would act oppositely in estuarine Si cycling compared to N and P cycling, importing organic BSi and exporting inorganic DSi. In the N and P cycle, marshes generally import inorganic nutrients and export organic forms.

In chapter 2, the retention capacity of marsh vegetation and sediments for BSi was quantified during a year-long two-monthly monitoring campaign. All the major plant species were sampled for changes in BSi content during the growing season, and the upper 30 cm of sediment in all vegetation types was sampled concurrently for BSi in 4 depth layers. DSi in marsh pore water was sampled similarly at three depths in the upper 30 cm of marsh sediment.

Fluxes between the freshwater marsh and nearby coastal waters were studied in chapter 3 and 4. To quantify the exchange of BSi and DSi between the freshwater marsh habitat and the adjacent estuarine waters, 6 whole tidal cycle mass-balances were conducted at different seasons and compared to mass-balances of DSi conducted in 1997. A small marsh area was isolated completely for this purpose, in such a way that water only entered through one single creek, which allowed for accurate water and Si balances. Whole tidal cycle mass-balances of BSi and DSi were further conducted on a saltwater marsh to compare exchange fluxes with those observed at the freshwater marsh to verify the hypothesis tidal marshes in general could contribute to Si cycling and retention in estuaries.

In chapter 5, the contribution of suspended matter associated BSi to marsh BSi retention and DSi recycling capacity was quantified. BSi-import on sediment traps was incorporated in a zero-dimensional time-stepping model of sedimentation on freshwater tidal marshes (Temmerman et al. 2003). Modelled results were used to reconstruct the BSi depth gradient observed in the sediment, and the Si retention and recycling capacity of marsh sediments was quantified, through the complete evolution from a young and rapidly rising marsh to a marsh in equilibrium with mean high water level.

Ex situ decomposition experiments allowed to quantify the BSi dissolution rate from litter of *Phragmites australis*, the common reed, in chapter 6. Antibiotics were used to examine bacterial influence on DSi dissolution from the litter. *In situ* litterbag experiments allowed to estimate the contribution of the litter layer to marsh DSi recycling capacity. The litter layer was sampled in winter and summer to quantify the stock of litter BSi.

1.6 Si in the Scheldt estuary

The catchment of the river Scheldt is situated in Northwest France, the west of Belgium and the Southwest Netherlands (Fig. 1.4). The Scheldt river becomes a tidal estuary in Gent, 160 km from the mouth. The Scheldt estuary has been subject to major anthropogenic stress. Its 21,863 km^2 drainage basin is inhabited by more than 10 million individuals. As a result, the estuary has a long history of extensive anthropogenic pollution (De Pauw 1971; Bakker & Heerebout 1971; Wollast 1988; Baeyens 1998). It is known as extremely eutrophic and receives large inputs of nutrients from non-point as well as point sources (Heip 1988). The major tributaries to the Scheldt, 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.

A large freshwater tidal area characterizes the Scheldt. This is approximately situated between Gent and Temse. The total surface area of freshwater marshes along the Scheldt is approximately 450 ha on a total of 3000 ha of tidal marshes. The total area of tidal mudflats is approximately 9000 ha. The Westerscheldt (downstream km 50) in the Netherlands is the saltwater part of the estuary.

The water quality of the Scheldt estuary has been frequently monitored since the early 1970^{ies}. Most of this early research and monitoring was focused on the brackish and marine estuary, and the freshwater part was often neglected in monitoring campaigns. Since the 1970^{ies}, the DSi concentrations in the Belgian brackish part of the Scheldt estuary have decreased slightly until 1990, from 0.2 mmol L^{-1} (5.6 mg Si L^{-1}) to 0.11 mmol L^{-1} (3 mg Si L^{-1}) (Soetaert et al. 2005). This decrease is attributed to recovery of oxygenation in the brackish estuary, resulting from the first implemented nutrient reduction measures. Prior to this oxygenation recovery, frequent anaerobic conditions inhibited diatom growth. The anaerobic water was characterized by a black color, resulting in extremely light limited conditions.

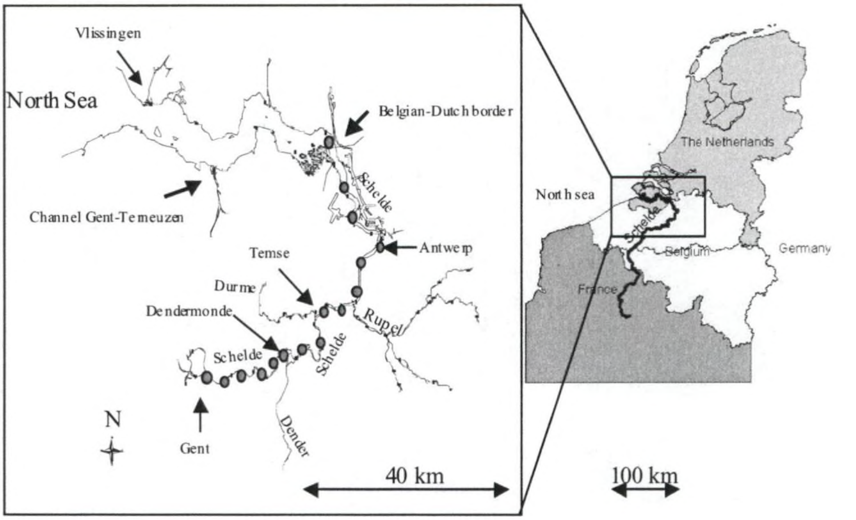

Figure 1.4 The Scheldt estuary and the major tributaries and cities. In grey circles on the left map, monitoring spots are indicated of the monthly DSi monitoring campaign along the Zeescheldt.

Since 1996, a monthly monitoring has been installed along the complete length of the Belgian Scheldt estuary, including the freshwater part (Fig. 1.5). In most years since 1996, a seasonal trend in DSi concentration was clearly visible, with low concentrations in summer and high concentrations in winter. However, in the early 21st century, years were characterized by flattened out seasonal cycles. This is attributed to the high discharge conditions. In years with high discharge, summer DSi concentrations approach winter concentrations, due to the inability of diatom communities to flourish under flushing conditions (Fig. 1.6).

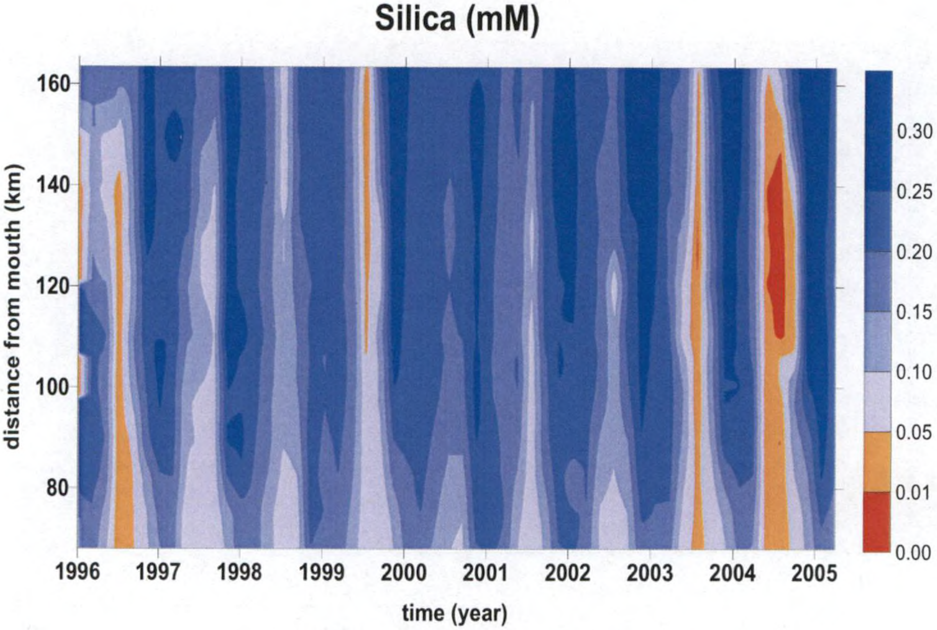

Figure 1.5 The evolution of DSi concentrations in the Belgian Scheldt estuary (vertical axis) for the period 1996-2005 (horizontal axis). Orange and red colors indicate periods of low Si concentrations (< 50 μM). A concentration beneath 5 μM indicates limited possibility for diatom DSi uptake.

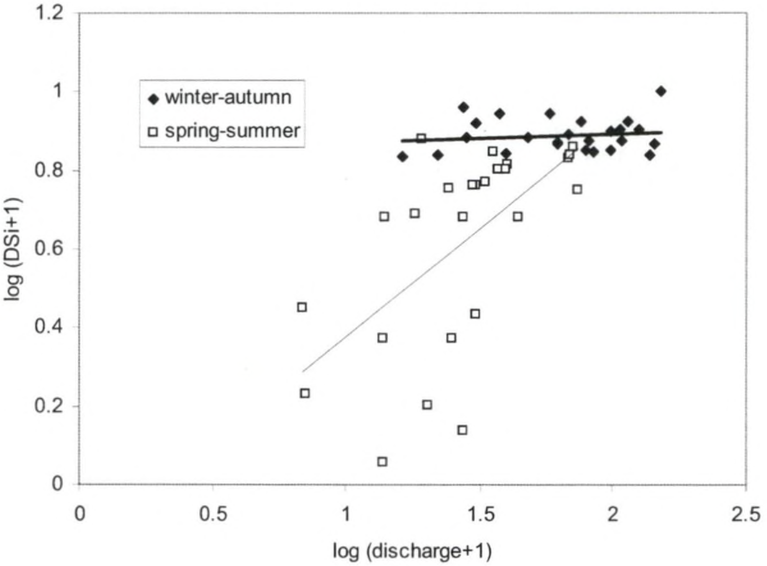

Figure 1.6 The monthly DSi concentrations in the freshwater Scheldt estuary near Dendermonde vs. monthly averaged discharge at Dendermonde. Discharge ($m^3 s^{-1}$) and DSi-concentration (mg Si L^{-1}) were log-normalized. Data were split for winter-autumn (October-March) and summer-spring (April-September). Data are for the period 1996-2000, from the monthly Scheldt monitoring campaign (figure taken from Struyf et al. 2004).

In years with low discharge, summer concentrations of DSi in the upper Scheldt estuary can drop below 10 µmol L^{-1} (Fig. 1.5). Fisher et al. (1988) indicated that DSi concentrations below 5 µmol L^{-1} are indicative for situations where Si becomes limiting for the phytoplankton community. Under these conditions, the conservative decrease of the DSi concentration downstream through mixing with seawater can result in even lower DSi concentrations in the lower parts of the Scheldt estuary.

The stoichiometric ratio of N, P and Si has been frequently used to indicate the potential occurrence of either nutrient limitation for phytoplankton growth. Limitation occurs whenever the proportion deviates substantially from the balanced ratio required for optimal plant growth (N: Si: P ratio = 16:16:1) (Redfield 1958). The general agreement is that N:P ratio's higher than 20-30 indicate P limitation relative to N, while N:P ratio's below 10 indicate N limitation. Nitrogen was never limiting in the Belgian Scheldt estuary over the past decade (Fig 1.7). Si limitation and concurrent negative ecological effects occur when Si:N < 1 and Si:P < 3 (Justic et al. 1995).

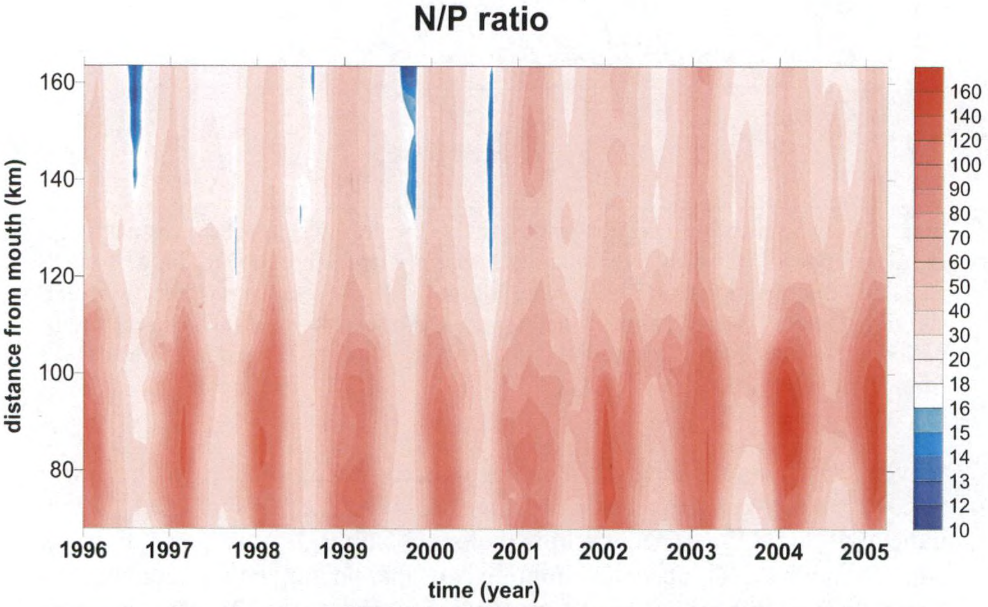

Figure 1.7 The molar N/P ratio in the Belgian Scheldt estuary over the past 10 years.

The Si:N ratio in the Belgian Scheldt estuary was always lower than 1 during the past decade (Fig. 1.8), while the Si:P ratio was frequently lower than 3 during summer and spring (Fig 1.9). There is a clear imbalance in the stoichiometric ratio of nutrients in the Belgian Scheldt, and Si is frequently the growth limiting nutrient.

The estuaries adjacent to the North Sea, among which the Scheldt estuary, are light limited, and impact of imbalanced stoichiometric ratio's on ecological functioning may be limited in upper estuarine zones. Nevertheless, the eventual transport of nutrients to the marine estuary and coastal zone, where light is not limiting any more (lower suspended solids), is affected by both water discharge and nutrient concentrations in the upper estuary. The imbalance of the delivered nutrients and the restricted nature of the North Sea have led to increasing Si-limitation induced eutrophication events (Ducrotoy et al. 2000), with algal blooms of *Phaeocystis* sp., *Chrysochromulina* sp. and the toxic *Gonyaulax* sp.

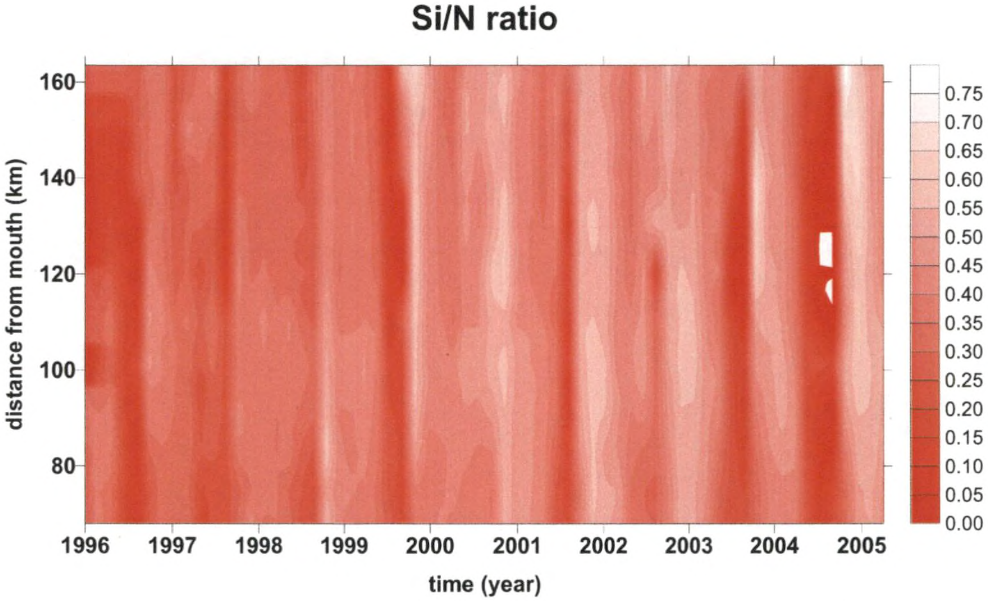

Figure 1.8 The molar Si/N ratio in the Scheldt estuary over the past 10 years.

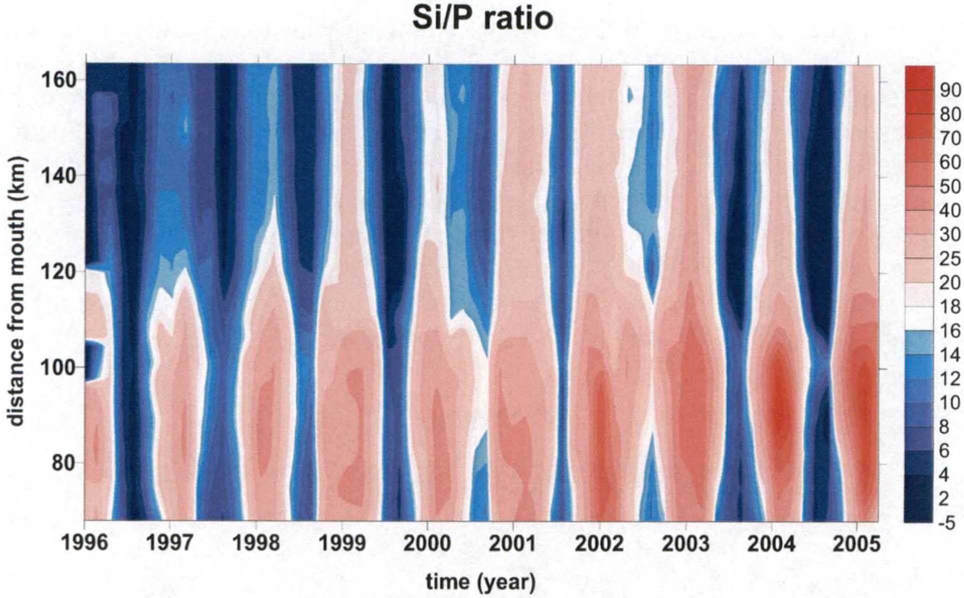

Figure 1.9 The molar Si/P ratio in the Belgian Scheldt estuary over the past 10 years.

1.7 The Tielrode study area

Research was conducted at three study sites. Here, a brief and general description of the most important study site, the Tielrode freshwater marsh, is provided. Research specific details will be provided in the respective chapters, as well as the description of the other study sites: a saltwater marsh in France (Carmel Polder) and the freshwater Notelaar marsh (Scheldt estuary).

The Tielrode freshwater marsh was the main study site: the retention capacity of freshwater marsh vegetation, sediment and porewater for Si (chapter 2), freshwater marsh whole tidal cycle exchange studies (chapter 3,4) and litterbag experiments (chapter 6) were all conducted here.

The Tielrode marsh is situated near the confluence of the small tributary Durme and the Scheldt (Fig. 1.4). In total, the surface area of the Tielrode freshwater marsh area is 10 ha. Only a small part of the total marsh area was used as study site: a 3500 m^2 area located in the most northern part of the marsh Fig. 1.10 - 1.12). To the east, the study site was bordered by a winter dike, which borders the controlled inundation area of Tielrode. To the west and the north, it was flanked by a former summer dike. It was completely flooded only at the highest 26% of the tides. The tidal amplitude at Tielrode in the estuarine channel averages 5.5 m.

The topography and the vegetation were both mapped in detail (Fig. 1.10 and Fig. 1.11). The vegetation was characterized by all the major vegetation types typical for the freshwater Scheldt estuary: pure *Phragmites australis* (common reed) stands and *Phragmites australis* dominated stands with tall-herb intrusion at the lower patches; stands dominated by tall-herbs (*Impatiens glandulifera, Urtica dioica, Epilobium hirsutum*) and *Salix* sp. dominated vegetation were found at higher elevations. The vegetation cover was very dense, with *Phragmites australis* and *Impatiens glandulifera* growing up to exceptional heights of 4 m. A digital terrain model was constructed using geographic information systems (GIS) and a detailed field mapping of the topography.

The isolated nature of the study site (mostly bordered by dikes) made it ideal for mass-balance studies. Water only enters at high water through one creek. Prior to arriving into the study area, the tidal water has travelled a considerable distance (~1 km), from the main river through tidal marsh creeks.

A sampling platform was constructed over the creek at the entrance into the study site. Underneath the sampling platform, the creek profile was measured accurately. To the east and the west of the bridge, the southern boundary of the study site was isolated artificially from the rest of the marsh with wooden screens of 1 m height (Fig 1.12), dug 20-30 cm into the sediment, to prevent water from entering the marsh next to the creek. Only the 4.5 m span of the entrance creek was not screened off. Instead a flume channel was constructed by placing 3 meter long screens along the creek. Groundwater input into the marsh was negligible as the marsh surface was several meters above the ground level of the neighbouring embanked controlled inundation area.

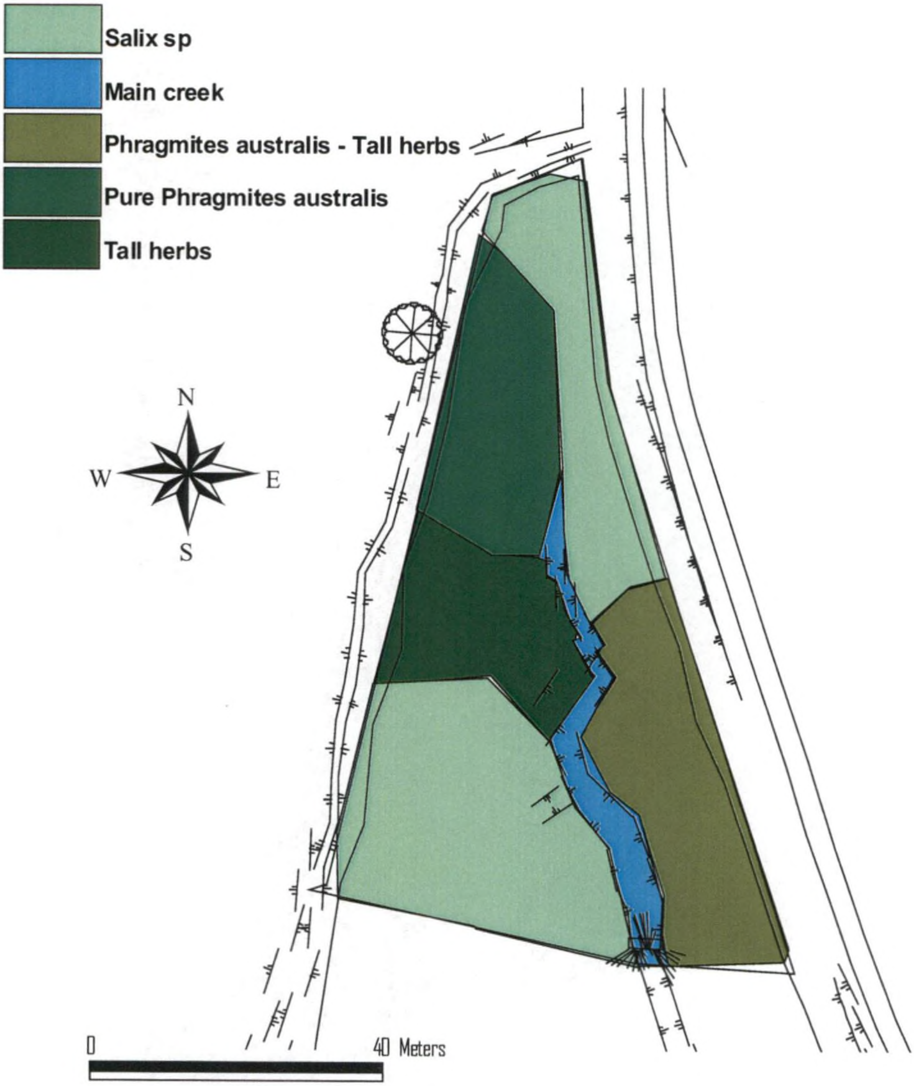

Figure 1.10 Vegetation in the Tielrode study area.

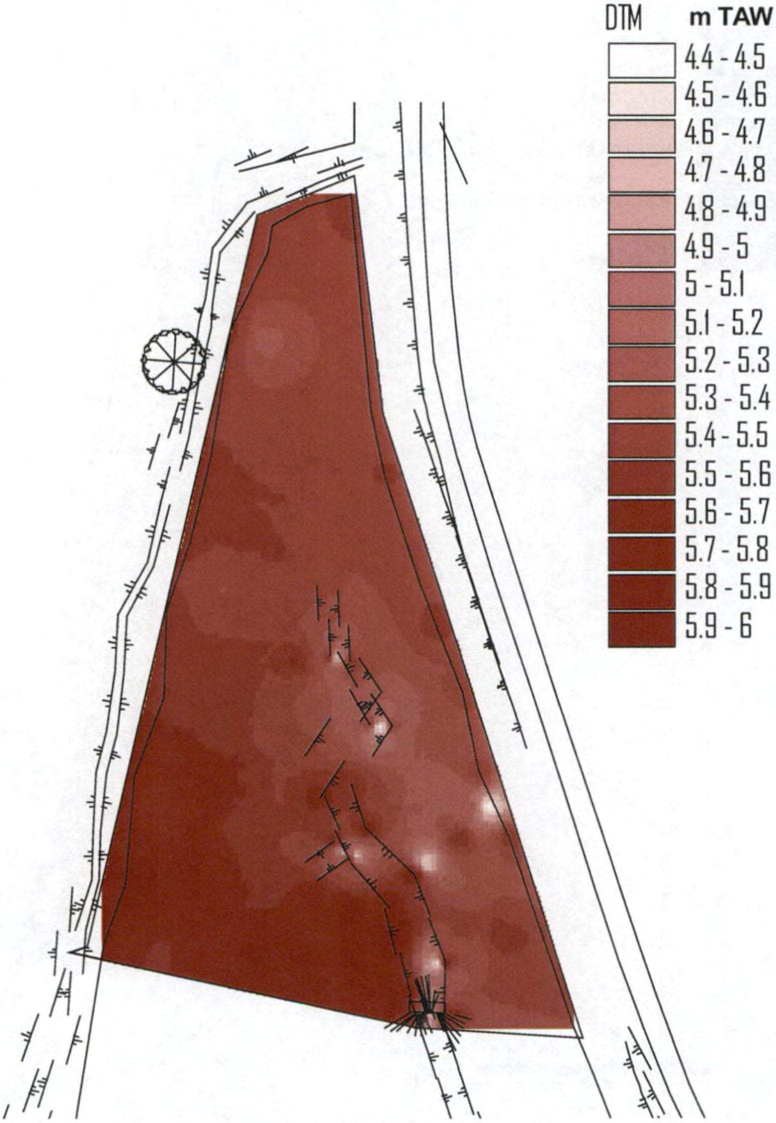

Figure 1.11 Digital terrain model for the Tielrode study area. Surface heights are in m TAW, the Belgian national tidal reference level (approximately height over mean low sea level).

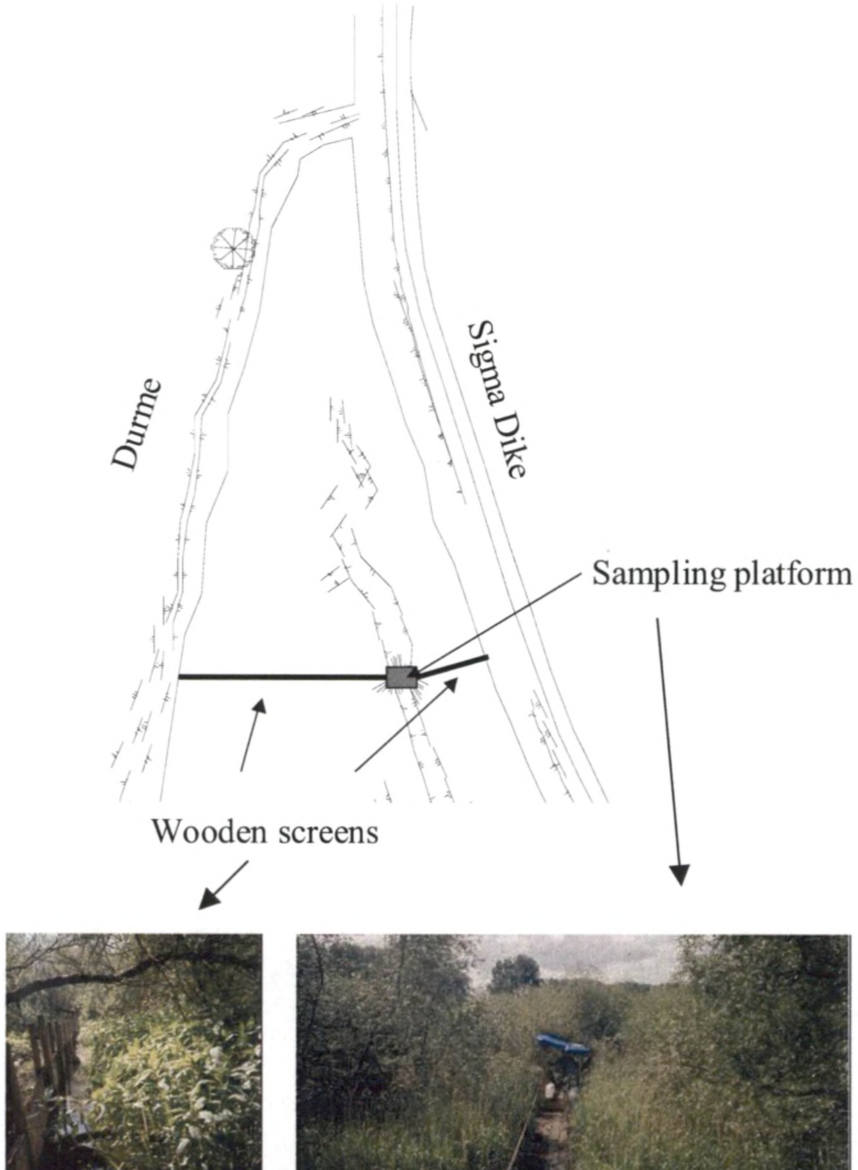

Figure 1.12 The isolated nature of the Tielrode study site, and the wooden screens used to screen of the southern border. Location of the sampling platform above the entrance creek.

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Chapter 2

Biogenic silica in freshwater marsh sediments and vegetation (Scheldt estuary, Belgium)

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(Marine Ecology Progress Series, in press)

2.1 Abstract

Up to this date, silicon cycling in freshwater intertidal marshes has mostly been neglected in estuarine ecosystem research. However, tidal marshes can store large amounts of biogenic silica (BSi) in vegetation and sediment. BSi content of the typical freshwater marsh plants *Phragmites australis*, *Impatiens glandulifera*, *Urtica dioica*, *Epilobium hirsutum* and *Salix* sp. was analysed year round. All herbaceous species accumulated silica in their tissue during their life cycle. *P. australis* contained most BSi (accumulation from 6 to 55 mg g^{-1}). Dead standing *P. australis* shoots had the largest BSi content (up to 72.2 mg g^{-1}). *U. dioica* (< 11.1 mg g^{-1}), *I. glandulifera* (< 1.1 mg g^{-1}), *E. hirsutum* (< 1.2 mg g^{-1}) and *Salix* sp. (< 1.9 mg g^{-1}) had much lower BSi content. Underground biomass (< 6 mg g^{-1}), except for *P. australis* rhizomes (< 15 mg g^{-1}) contained low amounts of BSi. Sediment BSi decreased from the surface (9-10 mg g^{-1}) towards deeper layers (5-7 mg g^{-1}). There was no seasonal variation in sediment BSi. Porewater dissolved Si was highest in summer (ca. 600 μM) and lowest in winter (ca. 400 μM). *P. australis* vegetation (aboveground and roots) contained up to 140 g m^{-2} BSi, while the sediment upper 30 cm accumulated up to 1500 g m^{-2} BSi, making sediment the largest BSi reservoir in the marsh. We can conclude that *P. australis* wetlands could be an essential, yet overlooked sink for BSi in the biogeochemical cycling of Si.

2.2 Introduction

Coastal zones and shallow marine areas are among the most productive systems in the world (Mann 1988; Glantz 1992) and represent the main fishery grounds on Earth (Postma & Zijlstra 1988; Sherman et al. 1991). The amount of dissolved silica (DSi) that is transported to coastal waters through estuaries is essential for the occurrence of eutrophication events in the coastal zone. In contrast to N and P, with large human inputs through river basins, anthropogenic input of Si to estuarine systems is negligible. In summer and spring, DSi in estuarine and coastal waters is taken up by diatom communities, for which DSi is an essential nutrient. High anthropogenic inputs of N and P can induce DSi limitation of diatom communities and subsequent succession to a non-diatom phytoplankton community (Schelske et al. 1983; Lancelot 1995; Smayda 1997; Billen et al. 2001). This can negatively influence the structure of coastal foodwebs, as diatoms are the most important energetic source in estuarine food chains (Peterson & Howarth 1987; Sullivan & Moncreiff 1990).

Recently, intertidal habitats have been indicated as important Si stocks and processors in the estuarine ecosystem. In North Carolina, a study of silica in mesohaline marsh sediments, vegetation and porewater clearly revealed these intertidal habitats as huge reservoirs of silica (Norris & Hackney 1999). Moreover, it was shown how a freshwater marsh (Scheldt estuary, Belgium) acted as an important DSi recycler in the estuarine environment (Chapter 3 and 4).

Marshes have a high DSi recycling capacity because they act as efficient biogenic silica traps, concentrating Si at levels above those found in nearby estuarine waters (Hackney et al. 2000). BSi in marsh ecosystems is mainly stored in plants and sediments. DSi taken up by marsh plants from the porewater is stored as amorphous silicon dioxide in plant phytoliths. It is accumulated during the plant life cycle and only released to the environment after the plant decays. Silicon uptake can positively influence plant growth and development, providing rigidity to plant structures and enhancing resistance to abiotic and biotic stresses, such as toxic metal accumulation and herbivory (Epstein 1994). The role of Si in cell walls is similar to that of lignin, but it is energetically cheaper to incorporate Si (Raven 1983).

BSi in sediments is mainly attributable to plant phytoliths and diatom shells, deposited on the sediment at flood tide along with suspended matter. BSi dissolution occurs when porewater comes into contact with the sediment BSi in between tidal flooding events, resulting in high porewater DSi concentrations in marshes.

Despite the importance of Si processing in tidal marshes, very few studies have focused on tidal marsh Si cycling and storage. The silica content of sediment, porewater and vegetation in freshwater marshes has never been studied in detail. Recent estimates of the terrestrial BSi cycle have shown that BSi in vegetation plays an essential role in global Si mass balances. Further quantification of Si in complete ecosystems is needed, especially from grassland ecosystems, to quantify the role of the terrestrial cycle in the global biogeochemical cycle of Si and in the transport of Si to the ocean through rivers (Conley 2002; Meunier 2003).

The aim of this study was to determine the BSi and DSi content of vegetation, sediment and porewater in a *Phragmites australis* dominated freshwater marsh. Most studies on the ecology of *Phragmites australis* dominated freshwater marsh systems have focused on C- or N-cycling (Meyerson et al. 2000, Soetaert et al. 2004). *P. australis* has a big potential as a nutrient sink, because of its high productivity and dense clonal growth, and because dead culms can remain standing for two or more years before collapsing. We performed a year long, two-monthly study of silica content in porewater, sediment and vegetation, in order to gain a complete image of the amounts of Si stored in the freshwater marsh ecosystem and to explore the seasonal variability in Si storage.

2.3 Materials and methods

Sampling

All sampling was done in the Tielrode freshwater marsh (site description in 1.6)

Vegetation

Aboveground vegetation samples were taken two-monthly from June 2002 until May 2003 for 4 target herbaceous species (*Epilobium hirsutum, Phragmites australis, Urtica dioica and Impatiens glandulifera*) and for *Salix* sp. shrubs. All sampled vegetation was dead in January and March. *I. glandulifera*, *E. hirsutum* and *U. dioica* (January only) were sampled as decomposing litter during these months. *P. australis* was sampled as both dead standing reed and decomposing litter during winter. *Salix* sp. leafs were sampled when available (June, September and November). *Salix* sp. twigs were sampled in September, November, January and March. All individual plant samples were transported to the laboratory immediately after sampling. Half of the sampled individuals for the most abundant species in the marsh (*P. australis*, *U. dioica* and *I. glandulifera*) were separated in leafs and shoots directly upon arrival in the laboratory.

Underground biomass was sampled in January, March, May, July and October 2003 in the upper 30 cm of the marsh sediment from 8 sediment cores (diameter 5 cm), 2 in each vegetation type (chapter 1, Figure 1.10), to ensure analysis of roots of all plant species present. The underground biomass from the 2 cores collected within the same vegetation type was treated as a single mixed sample. Underground biomass was separated in dead and living biomass. *P. australis* rhizomes were analysed separately. In January 2003, no rhizomes were found in the cores. In other months, rhizomes were always found in at least 2 cores. In September 2004, vegetation coverage (individuals per squared meter) was studied in 48 vegetation plots of 1 m^2, 12 in each vegetation type (Table 2.1). Combined with individual plant weights, these data were used for marsh biomass estimates.

Sediments and porewater

In each of the 4 different vegetation types 5 sediment cores were taken at random in September 2002, November 2002, January 2003, March 2003 and May 2003. The sediment cores were sub sampled at four different depths (0-1cm, 1-10 cm, 10-20 cm and 20-30 cm) and pooled per depth per vegetation type. Roots and litter were removed manually from the sediment. Porewater was sampled in January, March, May, July and October 2003. Porewater samples were taken at 12 different sampling points, 3 in each vegetation type (not in tall-herb in July) using Eijkelkamp polymerous rhizons (diameter 2.5 x 1.4 mm). Subsamples were taken at 0-10 cm depth, 10-20 cm and 20-30 cm. Samples were pooled per depth per vegetation type.

	***Salix* vegetation**				
	Number of individuals				
	Imp gla	Epi Hir	Phr aus	Urt dio	Phr aus dead
plot 1	17	0	0	6	0
plot 2	6	0	0	11	0
plot 3	23	0	0	8	0
plot 4	0	0	0	28	0
plot 5	5	0	0	11	0
plot 6	0	0	5	0	0
plot 7	0	0	0	22	0
plot 8	0	0	12	14	0
plot 9	4	0	8	2	7
plot 10	0	0	30	15	0
plot 11	0	20	0	3	0
plot 12	1	10	5	0	0

	***P. australis* with tall-herbs**				
	Number of individuals				
	Imp gla	Epi Hir	Phr aus	Urt dio	Phr aus dead
plot 1	4	0	50	0	6
plot 2	3	0	49	0	9
plot 3	0	0	42	0	3
plot 4	0	0	70	0	3
plot 5	6	0	34	0	18
plot 6	1	0	41	0	12
plot 7	25	0	57	0	9
plot 8	9	0	29	11	2
plot 9	1	0	56	0	13
plot 10	7	0	37	0	9
plot 11	19	0	26	1	19
plot 12	0	6	40	0	3

	Tall-herbs vegetation				
	Number of individuals				
	Imp gla	Epi Hir	Phr aus	Urt dio	Phr aus dead
plot 1	14	0	15	4	0
plot 2	0	25	14	15	6
plot 3	0	10	60	0	0
plot 4	0	30	30	3	0
plot 5	60	0	0	11	0
plot 6	71	0	0	11	0
plot 7	64	0	0	10	0
plot 8	9	0	3	17	5
plot 9	32	0	0	6	0
plot 10	20	2	13	0	0
plot 11	3	13	39	0	0
plot 12	0	6	36	0	0

	Pure *P. australis* vegetation				
	Number of individuals				
	Imp gla	Epi Hir	Phr aus	Urt dio	Phr aus dead
plot 1	0	0	74	0	15
plot 2	0	0	81	0	9
plot 3	0	0	75	0	8
plot 4	0	0	78	0	32
plot 5	0	0	111	0	20
plot 6	0	0	76	0	17
plot 7	0	0	117	0	18
plot 8	0	0	81	0	32
plot 9	0	0	104	0	15
plot 10	0	0	63	0	25
plot 11	0	0	71	0	6
plot 12	0	0	86	0	21

Table 2.1 Number of individuals of the target herbaceaous species in 12 plots (1 m^2) in each vegetation type.

Analysis

After sampling, plant samples were oven-dried for 3 days at 75°C, after which dry weight of individual plants was determined. Subsequently, samples were grinded and sieved over a 300 μm mesh size. To extract biogenic silica, 25 mg of sieved plant material was incubated for 4 hours in 0.1 M Na_2CO_3 (De Master 1981). Sediment was oven-dried for 3 days at 75°C, always within 24 hours after sampling. BSi was extracted from the sediment (25 mg) in a 0.1 M Na_2CO_3 solution at 80°C. Subsamples were taken after 150, 210 and 270 minutes. BSi was calculated by extrapolating the linear line through the three extraction points in a time-extracted silica plot (DeMaster 1981). Dissolved silica was analysed spectrophotometrically on an IRIS ICP (Inductively Coupled Plasmaspectrophotometer).

2.4 Results

Vegetation

Phragmites australis was the biggest plant BSi accumulator (Table 2.2). During the whole growing season silica was accumulated in the plant tissue in a linear way from 6.6 mg g^{-1} in May to 55.0 mg g^{-1} in November ($F_{1,37}$ = 87,89, $R^2 = 0.7037$, $p < 0.00001$) (Fig. 2.1). Shoot length was used as age indicator. In January and March, the shoot length for standing dead shoots and decomposing reed litter on the marsh surface was considered constant at a high level. This level was higher than was observed in any living reed plants. This way, dead plants in Fig. 2.1 are always correctly indicated as being "older" than living plants. Accumulation patterns were similar in leafs and shoots. Shoots contained more BSi than leafs (Wilcoxon signed-rank test, n = 20, $p<0.0001$). Standing dead reed shoots contained most BSi (Table 2.2, Fig. 2.2). They were present during the whole year, and silica content was at similar high levels throughout the year (from 51.1 mg g^{-1} in June 2002 to 72.2 mg g^{-1} in September 2002). The decomposing litter contained about half of the BSi present in the standing dead shoots (Table 2.2, Fig. 2.1). BSi content of the reed litter decreased between January and March (34.7 mg g^{-1} and 25.5 mg g^{-1} respectively).

Impatiens glandulifera (monthly average 0.4 – 2.5 mg g^{-1}), *Urtica dioica* (monthly average 4.2 – 8.6 mg g^{-1}) and *Epilobium hirsutum* (monthly average 0.5 – 2.6 mg g^{-1}) contained less silica than *Phragmites australis* (Table 2.2). During the early growing season, biogenic silica content of *I. glandulifera* was slightly higher than later in the life cycle (Fig. 2.2a). Accumulation of silica in the tissue during the main growing season was less apparent in *I. glandulifera* than in *P. australis*, although highest BSi contents were mostly found in the oldest plants. No significant linear accumulation pattern was found. *I. glandulifera* litter content of BSi (6.8 – 8.0 mg g^{-1}) was one order of magnitude higher than silica content of the living individuals (Fig. 2.2a).

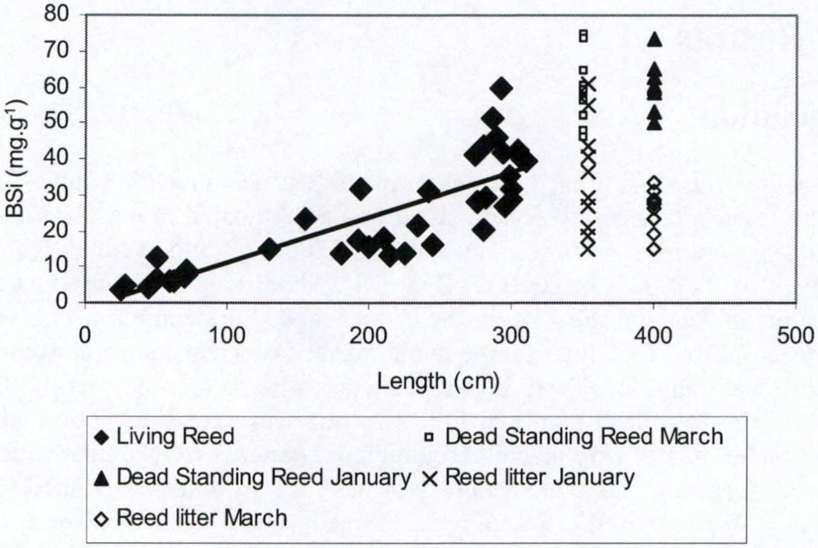

Figure 2.1 BSi-content in the plant tissue of *P. australis* throughout the different stages of its life cycle. Shoot length is used as age indicator. Dead plants and litter have been given an imaginary length higher than any living individuals, to indicate that they are the last stages of the life cycle. Dead plants have not been included in the regression.

The accumulation pattern was very similar for *E. hirsutum* with higher Si contents in the early life cycle and higher BSi contents in the decomposing matter (3.6 – 5.5 mg g^{-1}) (Fig. 2.2b). In contrast to *I. glandulifera*, significant linear accumulation ($F_{1,13}$ = 9.4, R^2 = 0.4196, $p < 0.01$) was observed during the main growing season. *U. dioica* leafs contained more BSi than shoots (Table 2.2, Wilcoxon signed-rank test, n = 20, $p < 0.0001$). Linear accumulation ($F_{1,27}$ = 23.64, R^2 = 0.4668, $p < 0.0001$) during the main growing season pattern was similar to *E. hirsutum* and *P. australis* but the differences between the 3 life cycle stages (early, main and litter) were smaller (Fig. 2.2c). Both *Salix* leafs (0.5 –1.2 mg g^{-1}) and *Salix* twigs (0.4 – 1.9 mg g^{-1}) contained very low amounts of BSi (Table 2.2).

Plant BSi content	**June 2002**			**September 2002**			**November 2002**		
	BSi	SD	NOI (n)	BSi	SD	NOI (n)	BSi	SD	NOI (n)
	mg.g^{-1}	mg.g^{-1}		mg.g^{-1}	mg.g^{-1}		mg.g^{-1}	mg.g^{-1}	
P. australis (entire plant)	16.6	3.4	10	40.6	6.3	10	55.0	14.8	10
P. australis (shoot)	25.4	6.8	5	42.1	6.7	5	49.3	2.9	5
P. australis (leafs)	9.4	2.6	5	26.6	4.5	5	32.1	6.3	5
P. australis (dead standing)	51.1	26.5	10	72.2	14.4	10	51.3	18.9	5
P. australis (litter)	*	*	*	*	*	*	*	*	*
E. hirsutum (entire plant)	0.5	0.2	5	1.5	0.6	5	1.2	0.1	5
I.glandulifera (entire plant)	0.4	0.2	10	2.5	2.0	10	1.1	0.5	10
I. glandulifera (shoot)	0.2	0.1	5	1.1	0.1	5	1.1	0.5	10
I. glandulifera (leafs)	0.3	0.1	5	0.6	0.1	5	*	*	*
U. dioica (entire plant)	4.2	1.5	10	7.7	1.2	10	8.6	1.8	10
U. dioica (shoots)	1.1	0.4	5	4.9	1.4	5	4.8	1.0	5
U. dioica (leafs)	5.4	1.4	5	9.2	1.6	5	11.1	2.8	5
Salix sp. (leafs)	0.5	0.3	5	1.2	0.1	5	1.1	0.4	5
Salix sp. (twigs)	*	*	*	1.9	1.0	5	0.5	0.2	5
	January 2003			**March 2003**			**May 2003**		
	BSi	SD	NOI (n)	BSi	SD	NOI (n)	BSi	SD	NOI (n)
	mg.g^{-1}	mg.g^{-1}		mg.g^{-1}	mg.g^{-1}		mg.g^{-1}	mg.g^{-1}	
P. australis (entire plant)	59.2	9.7	10	60.5	6.3	10	6.7	2.6	10
P. australis (shoot)	59.2	9.7	10	60.5	6.3	10	7.6	2.2	5
P. australis (leafs)	*	*	*	*	*	*	5.0	1.0	5
P. australis (dead standing)	59.2	9.7	10	60.5	6.3	10	*	*	*
P. australis (litter)	34.7	15.4	10	25.5	5.5	10	*	*	*
E. hirsutum (entire plant)	5.5	1.0	5	3.6	1.9	5	2.6	0.5	5
I.glandulifera (entire plant)	6.8	2.8	10	8.0	1.4	10	2.3	1.0	10
I. glandulifera (shoot)	6.8	2.8	10	8.0	1.4	10	2.6	1.6	5
I. glandulifera (leafs)	*	*	*	*	*	*	1.0	0.3	5
U. dioica (entire plant)	8.5	2.3	10	*	*	*	5.2	1.1	10
U. dioica (shoots)	8.5	2.3	10	*	*	*	2.3	0.9	5
U. dioica (leafs)	*	*	*	*	*	*	6.3	0.7	5
Salix sp. (leafs)	*	*	*	*	*	*	*	*	*
Salix sp. (twigs)	0.6	0.1	5	0.4	0.1	5	*	*	*

Table 2.2 BSi content of different plant species in the Tielrode marsh observed throughout the different seasons. NOI = Number of individuals, SD = standard deviation, * = no data.

Dead underground biomass was generally highest in winter (Fig. 2.3b). Living non-rhizome root biomass was mostly highest in summer (Fig. 2.3a). Dead underground biomass was much higher (about ten-fold) than living (non-rhizome) biomass. BSi content of both dead and living (non-rhizome) underground biomass (Fig. 2.3c,d) was between 1 and 5 mg g^{-1}. Generally, lowest values were found in the *Salix* vegetation, and highest values in the *P. australis* vegetation.

The total amount of Si stored in the dead underground biomass was much higher (one order of magnitude) than in the non-rhizomeous living roots. It was highest in winter (Fig. 2.3e,f).

Rhizomes contained more BSi than the other underground biomass (Fig. 2.4). BSi content observed in rhizomes was highest in winter (15 mg g^{-1}) and lowest in late summer and early autumn (8 mg g^{-1}). On a squared meter basis, *P. australis* was the biggest BSi sink in the marsh in all four vegetation types, containing up to 85 g BSi per meter squared in aboveground vegetation (Table 2.3). The other plant species and underground non-rhizomeous biomass were far minor sinks compared to *P. australis* (Table 2.3). Based on a biomass estimate of 2500 g m^{-2} (Schierup 1978; Asaeda & Karunaratne 2000), rhizomes could accumulate on average 30 g m^{-2} BSi.

		vegetation type			
A		Phr aus	Phr aus/Tall herb	Salix	Tall-herb
species	Phr aus	85 +/- 39	45 +/- 22	5 +/- 9	18 +/- 21
	Phr aus ds	11 +/- 7	5 +/- 4	0	0,5 +/- 1,4
	Imp gl	0	0,5 +/- 0,7	0,6 +/- 0,8	1,7 +/- 2,5
	Urt dio	0	0,1 +/- 0,3	0,9 +/- 0,8	0,6 +/- 0,6
	Epi hir	0	0,1 +/- 0,1	0,2 +/- 0,5	0,5 +/- 0,8
	living roots	0,03 +/- 0,02	0,04 +/- 0,02	0,06 +/- 0,07	0,04 +/- 0,02
	dead roots	0,7 +/- 0,5	0,5 +/- 0,2	0,7 +/- 0,3	0,3 +/- 0,3
	rhizoms	30*			

B		sediment	porewater
depth	0-1 cm	64 +/- 23	0,8 +/- 0,1
	1-10 cm	533 +/- 220	
	10-20 cm	511 +/- 183	0,9 +/- 0,1
	20-30 cm	429 +/- 146	0,9 +/- 0,1

Table 2.3 BSi content of the different marsh sinks: (A) BSi content (g m^{-2}) of the target plant species and underground biomass in the different vegetation types, (B) BSi-content (g m^{-2}) of sediment and porewater averaged over the vegetation types. For sediments, calculation was based on a sediment bulk density of 0.74 g cm^{-3} (Van de Moortel & Deckers 1998). ds = dead shoots.

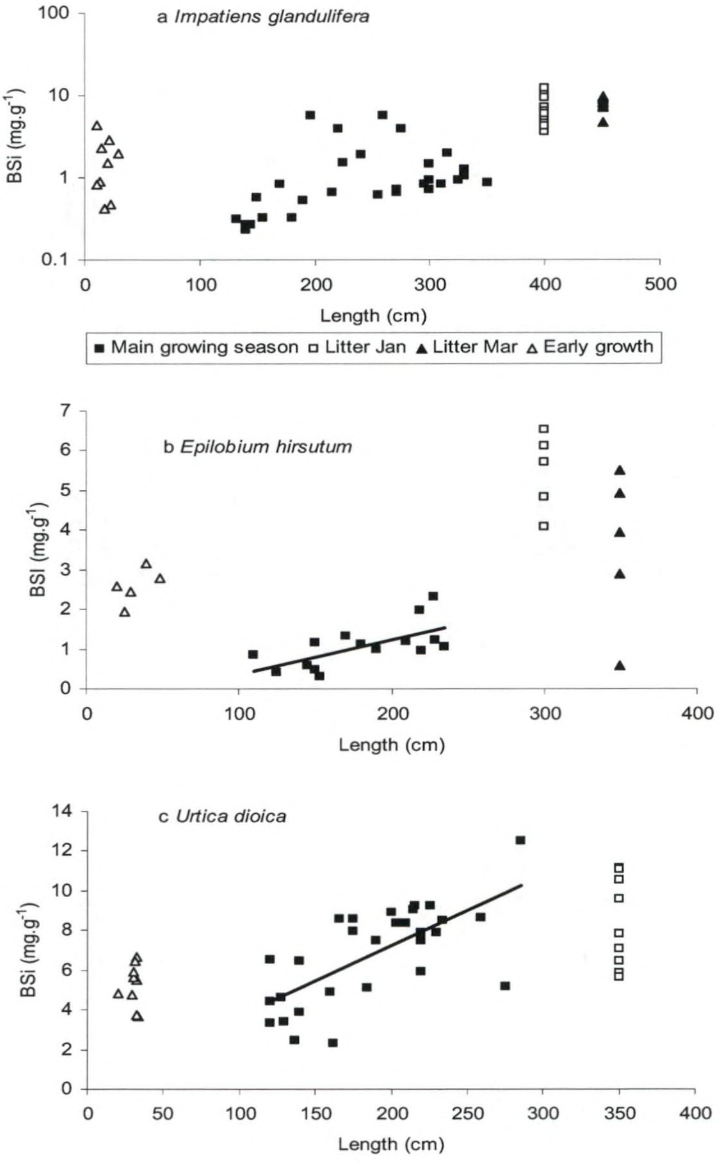

Figure 2.2 BSi content throughout the life cycle in a: *Impatiens glandulifera*, b: *Epilobium hirsutum* and c: *Urtica dioica*. Shoot length is used as age indicator. Litter has been given an imaginary length higher than any living individuals, to indicate that litter is formed in the last life cycle stage. Litter has not been included in the regressions.

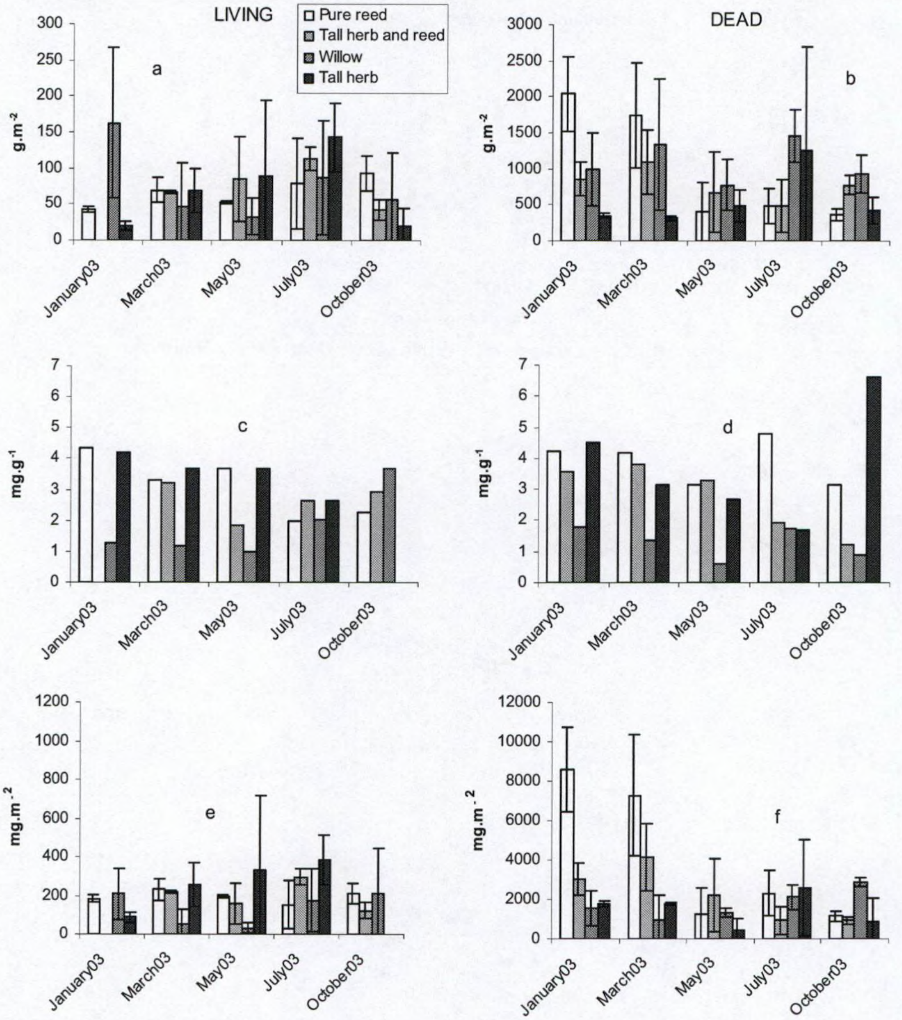

Figure 2.3 Underground biomass (a,b), BSi content in underground biomass (c,d) and BSi per surface unit (e,f) in the upper 30 cm of sediment in 4 different vegetation types (pure reed, mixed tall herb-reed, willow and tall herb) throughout the year 2003. Left (a,c,e) = living biomass, right (b,d,f) = dead biomass.

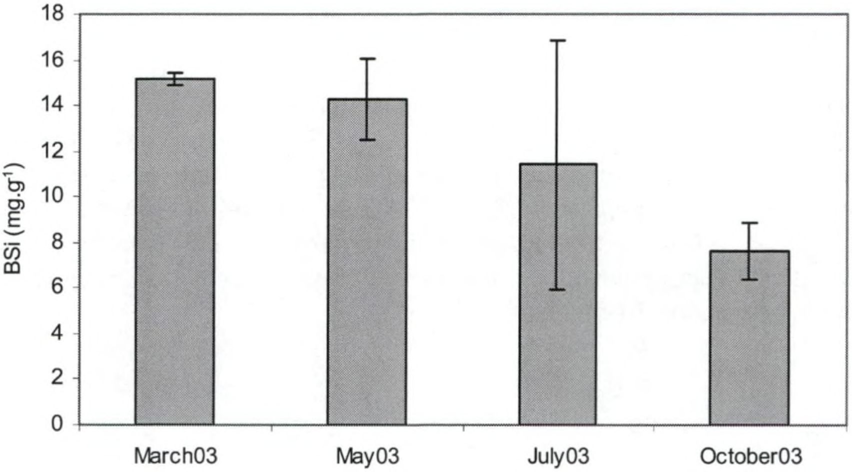

Figure 2.4 BSi content of *Phragmites australis* rhizomes.

Sediment and porewater

BSi content in the sediment in the pure *Phragmites australis* vegetation type was generally higher than in the other vegetation types (Fig. 2.5). The whole marsh averaged BSi content in the marsh sediment (Fig. 2.6) was similar during all monitored months. A two way ANOVA with depth and month as class variables showed a significant depth gradient of sediment BSi content ($F_{3,60} = 10.11$, $p < 0.0001$). Highest BSi content was observed in the upper sediment layers (0-1 cm, 9.5 mg g^{-1}). BSi content gradually decreased in the deeper sediment layers (1-10 cm, 8.7 mg g^{-1}; 10-20 cm, 7.5 mg g^{-1}, 20-30 cm, 6 mg g^{-1}) (Fig. 2.6). BSi in the 20-30 cm layer was about two-third of the BSi content in the upper 10 cm. Only in January 2003, the upper cm of sediment contained less BSi than the deeper layers. No consistent seasonal variation was observed. On a squared meter basis, sediment was the biggest BSi sink in the marsh, containing on a yearly average basis, 1500 g m^{-2} BSi in the top 30 cm (Table 2.3).

Average DSi concentration for all vegetation types in the porewater (Fig. 2.7) was highest in summer (500-600 μM) and lowest in winter (350-410μM). DSi in the porewater gradually increased from January to July. Between July and October, DSi concentrations decreased again. The *P. australis* vegetation had higher porewater DSi concentrations (Fig. 2.7). A three-way ANOVA with depth, time and vegetation type as class variables showed significant seasonal ($F_{4,22} = 20.96, p < 0.000001$) and vegetation type ($F_{3,22} = 13.57, p < 0.0001$) differences in porewater DSi concentration. No significant depth gradient was observed. Porewater contained around 3 g DSi per m^{-2} in the top 30 cm (Table 2.3).

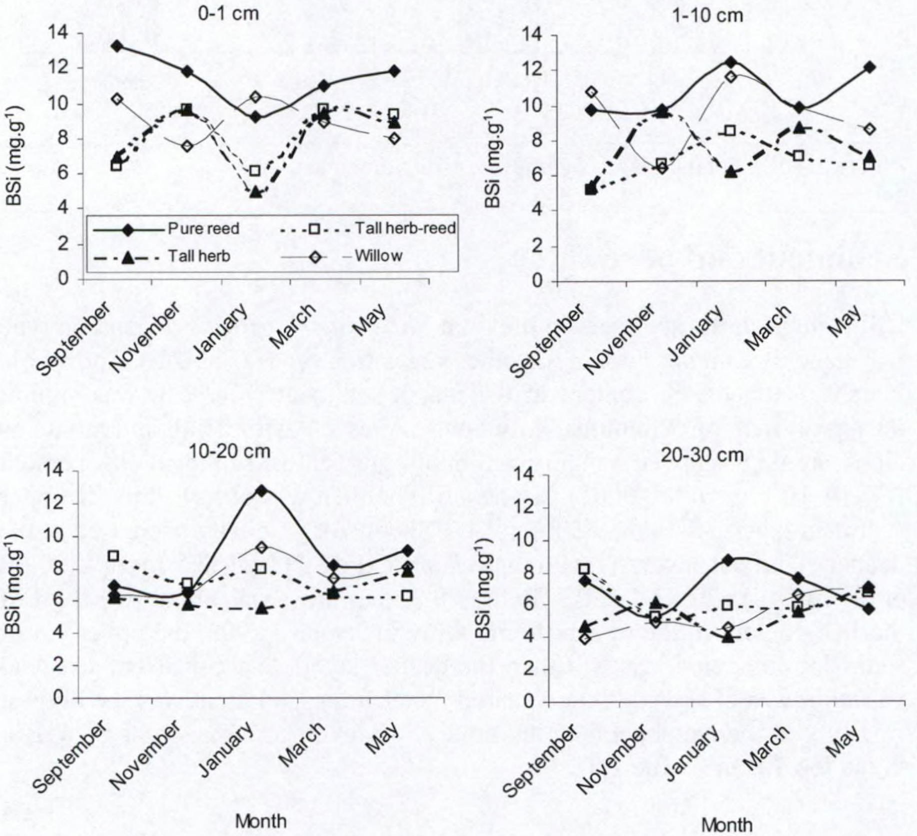

Figure 2.5 BSi concentration in the different sediment layers (0-1 cm, 1-10 cm, 10-20 cm and 20-30 cm) of the marsh throughout the year 2003. Variation observed over the different vegetation types.

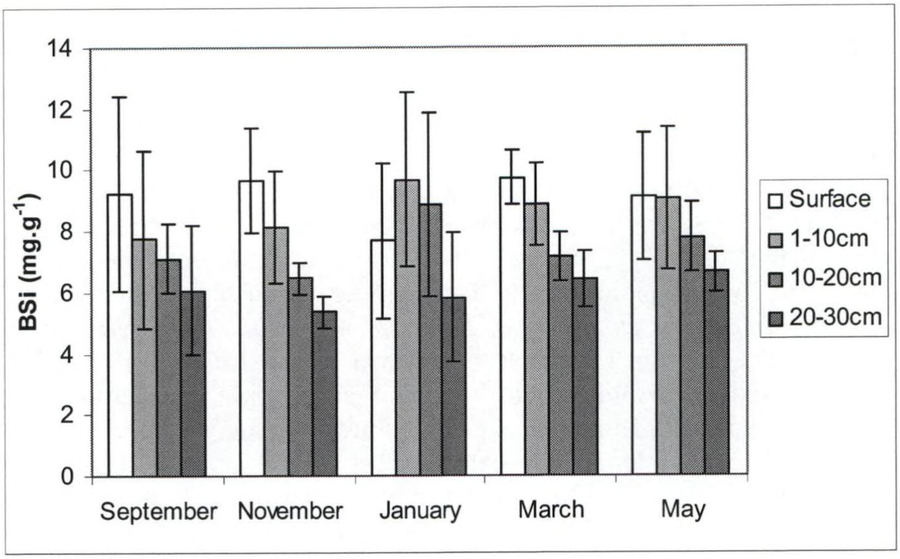

Figure 2.6 Marsh averaged BSi concentration in the different sediment layers (0-1 cm, 1-10 cm, 10-20 cm, 20-30 cm) in 2003.

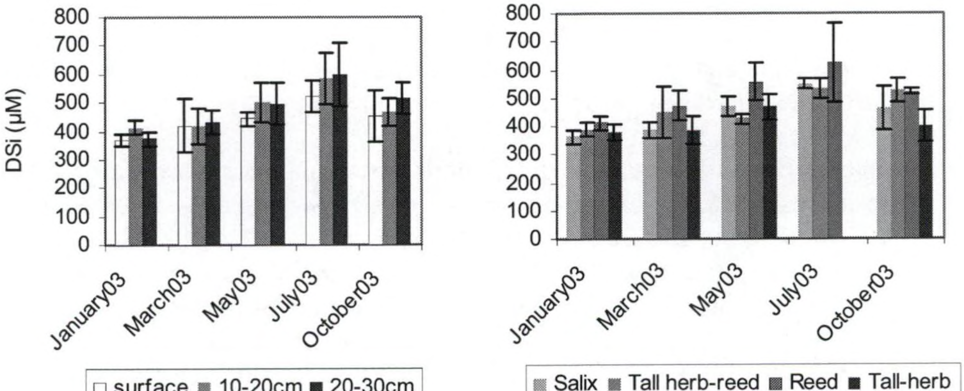

Figure 2.7 Left: Marsh averaged DSi-concentration in porewater at different depths (0-10 cm, 10-20 cm, 20-30 cm). Right: Depth averaged DSi concentration in porewater in the different vegetation types.

2.5 Discussion

Of the plant species studied, *Phragmites australis* accumulated most BSi. Wetland grasses in general are known as silicon accumulators, taking up DSi faster than would be expected from a non-selective entry of DSi with water (Raven 2003). Silicon accumulators contain large amounts of Si relative to dry weight (> 10 mg g^{-1}, Ma et al. 2001). Generally, monocotyledons (e.g. *P. australis)* contain more BSi in their tissues compared to dicotyledons. Indeed, *Impatiens glandulifera, Salix sp.* and *Epilobium hirsutum,* all dicotyledons, contained much less BSi than *P. australis*. *I. glandulifera*, *Salix* sp. and *E. hirsutum* could be identified as non-accumulators, which actively exclude DSi from the plant (BSi content < 5 mg g^{-1}, Ma et al. 2001). *Urticales* are an intermediate category between accumulators and non-accumulators (Ma et al. 2001). The relatively high BSi content observed in *Urtica dioica* (between 5 and 10 mg g^{-1}) was also in accordance to this observation.

Different strategies concerning DSi uptake, may explain why in *U. dioica* leafs contained more BSi than shoots, while in *P. australis* it was opposite and shoots contained more BSi than leafs. BSi in plant tissue is mainly deposited at sites with highest transpiration (e.g. leafs), where transported water is saturated for DSi, resulting in deposition. *P. australis*, in contrast to *U. dioica*, actively enhances DSi concentration in water taken up by the roots. Saturation and deposition of Si can therefore already occur in the shoots. Deposition of BSi in the shoots enhances *P. australis*' capacity to withstand tidal and wind sheer stress in the marsh, and could partially explain its dominance in the system.

Phragmites australis accumulated BSi in its tissue in a linear way during the entire growing season. Linear accumulation of BSi was also observed in *Epilobium hirsutum* and *Urtica dioica,* but in contrast to *P. australis*, it only started from a certain shoot length. *Impatiens glandulifera*, *E. hirsutum* and *U. dioica* all contained relatively high BSi in young plants (shoot length < 50 cm). Accumulation patterns reflect the ability of marsh vegetation to act as a silica sink in tidal wetlands, immobilising Si until decomposition occurs.

Delayed accumulation in *I. glandulifera* and *E. hirsutum* could result from these species actively excluding Si from their tissue. Silica is deposited at sites of major transpirational water losses, and the amount of BSi deposited per unit dry weight depends on the quantity of water transpired per unit dry matter gain and the quantity of DSi taken up per unit water transpired (Raven 2003). Relative biomass gain per unit time was highest in the young plants. Fast accumulation of biomass combined with low amounts of DSi taken up by the non-accumulators could result in an initial decrease in BSi content. In *Urtica dioica*, delayed accumulation may also result from retranslocation of biomass from rhizomes to aboveground biomass in the early growing season.

Roots in general contain low amounts of BSi, because absorbed Si is transferred from roots to shoots and deposition occurs at sites of biggest water loss (Epstein 1994). All non-rhizome root biomass sampled in the Tielrode marsh accordingly contained low amounts of BSi.

Dead *Phragmites australis* shoots contained high BSi contents compared to living shoots. Nitrogen and organic carbon are more labile plant elements than BSi (Eleuterius & Lanning 1987). As these more labile components leached from the plant tissue, the BSi content of the dead shoots increased. Leaching of labile components could also explain the high BSi content observed in decomposing *Epilobium hirsutum*, *Urtica dioica* and *Impatiens glandulifera* shoots. However, litter of fallen *P. australis* shoots, covering the surficial marsh sediments, contained only about one half to one third of BSi observed in dead standing shoots, indicating fast dissolution of BSi once a shoot has collapsed.

In contrast to non-rhizomeous roots, considerable BSi content was observed in *P. australis* rhizomes. This is in contrast to results obtained in Ontario (Canada), where no or very little BSi was detected in *P. australis* rhizomes, except for some leaf like outer bracts (Sangster 1982). Si accumulation in rhizomes could however be age and environmentally related. Very few studies have focused on this issue yet. In the same study (Sangster 1982), Si deposits were found in the rhizomes of *P. australis* clones which differed from the Ontario clones as to age, size, soil type and origin. These deposits were detected in epidermal cells and around the outer side of air canals in the outer cortex.

The variability in BSi content, both between rhizomes of different age and size and between rhizomes of different clones, could explain the variation observed in BSi content of rhizomes at our study site. Seasonal variability due to retranslocation of BSi is most unlikely, as Si is immobilized after deposition in the aboveground biomass.

BSi in marsh sediments is mostly attributable to diatom BSi imported during flood, BSi produced by benthic autochthonous marsh diatoms and plant phytoliths buried after a plant decays. BSi concentrations measured in the upper 10 cm of the freshwater marsh sediments were comparable to BSi measured at a mesohaline tidal marsh in North Carolina (USA) (Norris & Hackney 1999). However, total amounts of BSi stored in the freshwater marsh sediments were much higher compared to the mesohaline tidal marsh (597 g m^{-2} vs. 82 g m^{-2} in the upper 10 cm), because of higher bulk density of the sediment at our study site. A clear depth gradient was apparent, with BSi content highest in the upper layers. This depth gradient shows the capacity of freshwater marsh sediments to act as an important DSi source to the estuarine ecosystem in periods of DSi depletion. This recycling capacity was shown during the whole tidal ecosystem exchange studies (chapter 3 and 4). The older sediment, which is buried deeper in the marsh, has lost a substantial part of about one-third of its amorphous silica through dissolution of DSi to the porewater. The porewater is drained from the tidal marsh at flood tides and recycled DSi is resupplied to the estuarine system.

No clear seasonal variation of BSi content in the marsh sediments was observed. This is probably because of the large capacity of marsh systems to trap BSi. The upper 30 cm of sediments in our study area (3500 m^2) would, according to the measured BSi concentrations, contain around 5,3 tons (+/- 2,0 tons) of BSi. The export of DSi from the same marsh system to the main channel is reported to be around 100-200 kg each year (chapter 3 and 4). Considering the large amount of BSi measured in the sediments, it would be impossible to distinguish any interannual variation in BSi content resulting from this DSi export from the marsh. The sediments underneath the *P. australis* vegetation generally contained more BSi than sediments in other vegetation types. This could show that along with BSi import to the marsh from the main river channel at high tide, burial of *P. australis* phytoliths could also attribute to BSi accumulation in the marsh sediments (although in chapter 6, it is shown that *P. australis* BSi recycling is very efficient).

DSi concentrations in porewater in natural tidal marshes range between 130 and 650 µM. The Tielrode marsh ecosystem is situated at the high end of this range. The DSi concentration in the freshwater marsh porewater was highest in summer and lowest in winter. A similar trend was reported in North Carolina in a mesohaline tidal marsh (Norris & Hackney 1999). Dissolution of BSi into the porewater is enhanced by higher temperature and bacterial activity. High porewater DSi concentrations in summer further add to marsh DSi recycling capacity, as recyling is highest in periods of low DSi concentrations in the main river channel. Based on a porewater volume of 67 % (Van De Moortel & Deckers 1998), the total amount of DSi stored in the studied freshwater marsh is around 10 kg. Compared to the yearly DSi export of around 100-200 kg, it is clear that porewater drainage is well capable of being the driving force for DSi export to the main river channel.

Using aboveground *Phragmites australis* and tall herb biomass production data in different vegetation types, it was possible to estimate total BSi stored in aboveground vegetation in freshwater marshes. The total area of freshwater marshes along the Scheldt is about 450 ha, although this area could increase in the future through environmental restoration projects. About 200 ha are covered with *Salix* sp., while the tall herb vegetation and *P.australis* dominated vegetation each cover about 50 ha. The other 150 ha is mainly covered with individual trees and poplar woods, which were not present in the study area, and these vegetation types were left out of extrapolation. At peak biomass in September, aboveground herbaceous vegetation contained about 75-130 tons of BSi, 70-125 tons of which were stored in *P. australis*. In our extrapolations, aboveground tree nd shrub biomass (*Salix* sp.) was not incorporated, due to lack of data about biomass production of *Salix* sp. along the Scheldt. However, *Salix* sp. contained very low amounts of BSi compared to *Phragmites*.

Low observed BSi contents in roots were reflected in only 5-10 tons of BSi stored in non-rhizomeous roots in the upper 30 cm. BSi in *P. australis* rhizomes would account for about 10-20 tons of BSi, if we estimate rhizome biomass production at 2500 g.m^{-2} (Schierup 1978; Asaeda & Karunaratne 2000). In total, root and aboveground biomass along the freshwater Scheldt contained 90-160 tons of BSi.

The upper 30 cm of sediment along the freshwater Scheldt estuary was estimated to contain 4000-9000 tons of BSi over 450 ha. The amount of BSi stored in the sediment is by far the largest stock of BSi in the freshwater tidal zone of the estuary. Still, the export of DSi from freshwater tidal marshes to the adjacent estuarine waters was estimated to be around 100-200 tons yearly in the Scheldt freshwater (chapter 3 and 4), with this export contributing significantly to DSi availability in nearby coastal waters in summer and spring months. Given the high turnover of the reed and tall-herb vegetations in the studied freshwater marsh (and freshwater marshes in general), recycling of DSi from litter could still contribute significantly to estuarine Si cycling, despite relatively low amounts of BSi stored in vegetation compared to sediment.

For another freshwater marsh along the Scheldt estuary, we have modelled the sequestration of BSi in the sediment, through the combination of short-term year round sediment trap data with a long-term sedimentation model (chapter 5). 40 % of the BSi imported with tidal floodwater was found to be ultimately buried in the marsh sediments, with the other 60 % being recycled as DSi. About 7 % of the yearly discharge of BSi through the freshwater estuary was estimated to be deposited on freshwater marshes (40 g m^{-2} y^{-1}). This clearly shows that the marsh sediments not only present a very large BSi stock along estuarine waters; the stock is also subject to significant exchange processes with the nearby coastal waters. Freshwater tidal marshes are huge reservoirs of BSi, available for recycling of DSi when concentrations in the nearby coastal waters become depleted.

The only comparable tidal marsh study was conducted in a mesohaline tidal marsh in North Carolina (Norris & Hackney 1999). The amount of BSi stored in the upper 10 cm in our study was high compared to the mesohaline marsh study (597 g m^{-2} vs. 82 g m^{-2}), and in the *Phragmites australis* vegetation, the BSi content was about tenfold the content in the mesohaline *Juncus roemerianus* and *Spartina alterniflora* vegetation (85 g m^{-2} vs. 7.1 g m^{-2}). The stocks in the aboveground *Phragmites australis* vegetation were comparable to those found in an Amazon rain forest (83.4 g BSi m^{-2}) (Lucas et al. 1993), while BSi in the upper 30 cm of sediment was comparable to phytolith content in the soil of an equatorial rain forest in Congo (1124 g BSi m^{-2}) (Alexandre et al. 1997). BSi in aboveground biomass was much higher compared to a deciduous forest (~18 g BSi m^{-2}) (Bartoli 1983) and a coniferous forest (~9 g BSi m^{-2}) (Bartoli 1983).

Around 80 % of the reed is yearly deposited as litter on the marsh floor. The yearly litterfall deposition of BSi in the reed wetland is much higher compared to forest ecosystems (*Phragmites australis*: 68 g BSi $m^{-2} y^{-1}$; forest systems 0.5 – 4.1 g BSi $m^{-2} y^{-1}$), and we observed that surface litter contained only half of the BSi found in standing dead shoots, indicating fast recycling. As *Phragmites australis* is one of the most widely distributed plant species on Earth (Soetaert et al. 2004), reed may not only be an overlooked highly recyclable sink of BSi in estuarine systems, but also in the global biogeochemical cycle of Si, in which the important role of terrestrial fixation of BSi in plants has only recently been recognized (Conley 2002).

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Chapter 3

Freshwater marshes as dissolved silica recyclers in an estuarine environment (Scheldt estuary, Belgium)

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(Hydrobiologia 540: 69-77)

3.1 Abstract

Compared to knowledge about N and P processing in the aquatic continuum of lakes, wetlands and estuaries, knowledge concerning transport and cycling of Si is only fragmentary. Furthermore, Si research in estuaries has mainly been focused on subtidal benthic sediments and uptake and recycling by diatom communities. The biogeochemical cycling of Si in tidal wetlands, which can contain large amounts of Si, has thus far been neglected. We have conducted several whole ecosystem Si mass-balances on a freshwater marsh located in the Scheldt estuary (6 tidal cycles, 2 with BSi included). Our measurements show that the freshwater marsh acts as an important source of dissolved Si to the main river (1-18 % more export than import, on average 0.114 g m^{-2}). This export is compensated by import of biogenic silica into the marsh (19-55 % more import than export). The marsh was shown to act as a silica recycler, resupplying biologically available dissolved Si to the estuarine ecosystem. Extrapolations show that during summer and spring months, when dissolved silica is depleted due to diatom growth, almost half of the total dissolved silica load in the main river channel could result from marsh recycling.

3.2 Introduction

In recent years, the transformation, retention and transport of nutrients through the vast continuum of rivers, lakes, wetlands and estuaries to coastal waters was the subject of many large research projects including the LOICZ-Programme (Land-Ocean-Interactions-in-the-Coastal-Zone-Programme), a core project of the International Geosphere-Biosphere Programme (IGBP) (Kondratyev & Pozdnyakov 1996; Billen et al. 2001; Cave et al. 2003; Humborg et al. 2003). Compared to our knowledge concerning N and P processing, transport and cycling of dissolved silica in the aquatic continuum is significantly less known (Conley et al. 2000). In contrast to N and P, with large human inputs, anthropogenic input of Si to estuarine systems is negligible. The amount of dissolved silica that eventually reaches coastal waters through estuaries is, however, essential in influencing the occurrence of eutrophication problems in the coastal zone. High anthropogenic inputs of N and P can eventually induce dissolved silica limitation of diatoms and subsequent succession of a phytoplankton community dominated by diatoms to a non-diatom phytoplankton community (Schelske et al. 1983; Lancelot 1995; Smayda 1997; Billen et al. 2001).

Silicon research in estuaries has mainly been focused on subtidal benthic sediments and uptake and recycling by diatom communities (e.g. Yamada & D'Elia 1984; Conley & Malone 1992, Garnier et al. 1995; Muylaert et al. 2001). Intertidal systems have often been neglected in terms of their functioning within the estuarine Si cycle. Vegetated intertidal systems, which often represent a large amount of biomass, can contain a huge amount of amorphous silica (Conley 2002). In the Cape Fear estuary, it was shown that the amorphous silica content in the upper sediment layers (10 cm) and the aerial portions of plants was about 36% of the yearly riverine input (Norris & Hackney 1999).

In this paper, we present the first results of an integrated and detailed study, aimed at determining the role of freshwater intertidal marshes in estuarine Si cycling. We will demonstrate how freshwater intertidal habitats can act as an important area for recycling of Si in the estuarine environment. We conducted several tidal cycle mass balances in a tidal marsh, to quantify the export and import of DSi (dissolved silica) and BSi (biogenic silica and amorphous particulate silica) to and from the main river channel. Intertidal habitats were shown to be important sinks for BSi and significant sources of DSi, thus converting large amounts of amorphous silica to biologically available DSi.

3.3 Materials and methods

Field measurements

All exchange studies were conducted at the Tielrode freshwater marsh. In 1997-1998, four intensive study periods were conducted for the whole marsh area in the main creek (Ø ca. 16 m) entering the marsh in order to compute mass-balances. In 2002, two intensive studies were conducted on the artificially isolated study area of approximately 3500 m^2 within the marsh, fed by one single creek (Ø ca. 4 m). Artificial isolation by dikes ensured water could only enter the isolated study area through this creek at high tide, and not over the marsh edges.

For both creeks, detailed flow models were developed, covering the angle of water flow to the banks and temporal, vertical and horizontal flow variations during bulk tidal phase. Water velocity was continuously measured with OTT-mills and a Valeport Model 801 electromagnetic flow meter. Vertical (bottom and surface OTT-mill) and lateral profiles (electromagnetic flow meter, 10 lateral points) of water velocity were continuously carried out. This allowed us to make an accurate water balance, an essential condition to construct detailed mass-balances (error calculations in chapter 4).

Discharged volumes were calculated by multiplying flow velocity and cross surface area (subdivided into more than 40 lateral subsections) every minute during the bulk tidal phase and every hour during the seepage water phase. Bulk tidal phase is the period of approximately 3 hours (on average 75 minutes inflow, 105 minutes outflow) during which large amounts of water flow in and out the marsh through the creek (around high water in the main river). Seepage water is exported out of the marsh between two bulk tidal phases, when the tide in the main river is approaching low tide or rising to the threshold water level where water starts flowing into the marsh (= bulk tide). The seepage water is water leaving the sediments and includes no or very little surface drainage.

In 1997-1998, DSi samples were taken every half hour. In 2002, BSi was added to the variables analysed. DSi and BSi samples were taken every 15 minutes during the bulk tidal phase, and every hour in the seepage water. All samples were surface samples, taken in the middle of the creek.

Analysis

To analyse for BSi in 2002, three 30 ml samples were filtered from a well-mixed total sample of 200 ml onto a 0.45µ-polycarbonate filter. BSi was extracted from the filters in a 0.1 M Na_2CO_3 solution at 80°C. Subsamples were taken at 80, 120 and 160 minutes. Blank extractions were conducted to correct for possible DSi released from the filters or from DSi in the chemicals. Blank concentrations were very small (< 0.2 mg L^{-1}). BSi was calculated by extrapolating the linear line through the three extraction points in a time-extracted silica plot (DeMaster 1981). DSi was analyzed spectrophotometrically on an IRIS ICP.

3.4 Results

Water balances

Water balances for all tidal cycles are shown in table 3.1. Incoming and outgoing water volumes were nearly conservative during 5 out of 6 of the intensive studies. In April 1998, the exported water volume greatly exceeded the incoming volume. A possible reason is that water that entered the marsh during the previous tidal cycle had not completely flowed out of the marsh yet. This is more likely to occur at higher tides and the April 1998 studies were carried out at a higher tide than the other whole marsh samplings (Table 3.1). Water volumes exchanged between the main river and marsh varied according to the maximum water height. Water height during tidal cycles varied between 533 and 597 cm TAW.

	Date	Maximum water height cm TAW	Bulk Incoming m^3	Bulk Outgoing m^3	Seepage m^3	Balance m^3	Balance % import/export %
whole marsh	01/07/1997	541	9834	-9601	-750	-517	-5.3
	07/10/1997	562	12649	-11415	-1090	144	1.1
	27/01/1998	533	10221	-9843	-99	279	2.7
	29/04/1998	570	26000	-23501	-6066	-3567	-13.7
isolated area	26/05/2002	597	1700	-1642	-61	-3	-0.2
	30/05/2002	589	1376	-1305	-65	6	0.4

Table 3.1 Water balances during all tidal cycles conducted, with separate indication of seepage-, bulk inflowing and bulk outflowing water. Maximal water height is indicated in cm TAW, the Belgian national tidal reference. The balance is indicated as percentual import (+) or export (-).

Concentration profiles

DSi concentrations were lowest during the bulk tidal phase, i.e. both in the main inflowing and in the main outflowing water (from 4.1 mg L^{-1} in October 1997 to 6.4 mg L^{-1} in January 1998). DSi concentrations strongly increased in the seepage water phase during 5 out of 6 mass balances (Fig. 3.1) and reached an eventual value of around 9-10 mg L^{-1}, a two- to threefold increase. Only in January 1998 was DSi concentration increase in the seepage water minor, with DSi rising from 6.2 mg L^{-1} to 8 mg L^{-1} (Fig. 3.1).

Contrary to DSi concentration patterns, BSi concentrations were zero during the seepage water phase, and at their maximum (up to 1.2 mg L^{-1}) during the early inflowing bulk water (Fig. 3.1e-f). BSi concentrations fairly constantly lowered during the bulk tidal water, until reaching the zero level of the seepage water.

Si balances

Mass balances for DSi and BSi are shown in table 3.2. During 5 out of 6 tidal cycles DSi was net exported from the marsh. Only in January 1998, no net exchange of DSi between the marsh and the main river was observed. All net DSi export occurred almost completely during the seepage phase, during which DSi concentrations were maximal. The percentage difference between import and export was highest in October 1997 and April 1998 (up to 17,5%). DSi exchange per squared meter was between 0.01 g in January 1997 and 0.43 g in April 1998. BSi exchange per squared meter was in the same order of magnitude as DSi exchange. Contrary to DSi, BSi was net imported into the marsh during the 2002 tidal cycles. This is in accordance with the BSi concentrations dropping to zero throughout the bulk tidal phase. In between 18 and 56% of the total BSi imported during flood was deposited on the marsh surface.

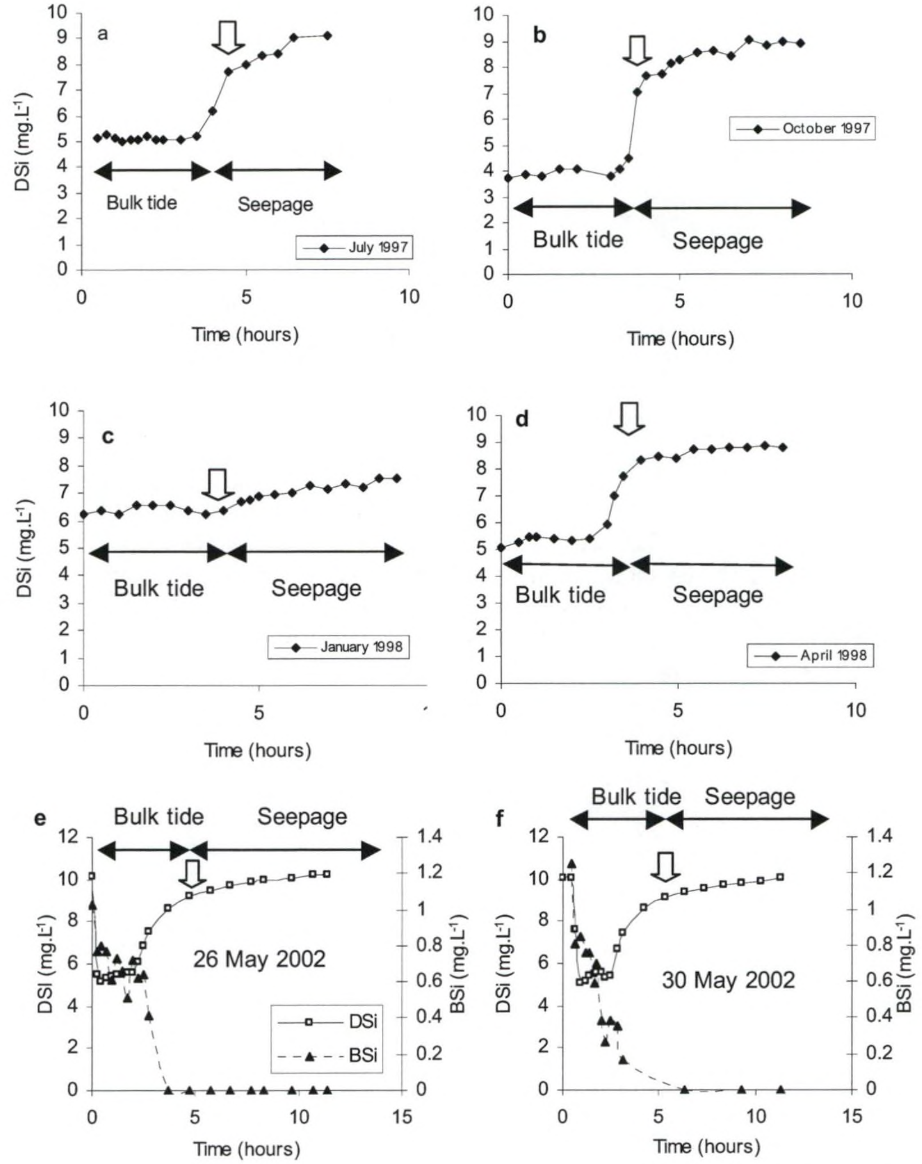

Figure 3.1 Concentration profiles of DSi (a-f) and BSi (only in 2002, e-f) during all studied tidal cycles. Bulk tide and seepage water are indicated with arrows. The block arrow indicates the beginning of seepage water.

DSi-balance

	Date	Bulk incoming		Bulk outgoing		Seepage water		Balance		Balance import/export	
		g	g.m^{-3}	g	g.m^{-3}	g	g.m^{-3}	g	g.m^{-2}	%	conservative %
whole	01/07/1997	50400	5.1	-49467	-5.2	-6533	-8.7	-5600	-0.06	-11,1	-5,9
marsh	07/10/1997	51800	4.1	-50867	-4,6	-9053	-8.3	-8120	-0.08	-15,7	-16,8
	27/01/1998	65333	6.4	-63467	-6,4	-700	-7.1	-1166	-0.01	1,8	-0,9
	29/04/1998	136267	5.2	-126933	-5,4	-51940	-8.6	-42606	-0.43	-31,3	-17,5
isolated	26/05/2002	9422	5.5	-9444	-5,8	-568	-9.3	-590	-0.17	-6,3	-6,1
area	30/05/2002	7641	5.6	-7372	-5,6	-560	-8.6	-291	-0.08	-3,8	-4,2

BSi-balance

	Date	Bulk incoming		Bulk outgoing		Seepage water		Balance		Balance import/export	
		g	g.m^{-3}	g	g.m^{-3}	g	g.m^{-3}	g	g.m^{-2}	%	conservative %
isolated	26/05/2002	1261	0.7	-1023	-0,6	0	0	238	0.07	18.9	19.1
area	30/05/2002	1066	0.8	-468	-0,4	0	0	598	0.17	56.1	55.7

Table 3.2 DSi and BSi mass-balances during all studied tidal cycles, with separate indication of seepage-, bulk inflowing and outflowing water (both absolute flux and g m^{-3}). DSi mass-balances are shown above, BSi mass-balances are shown underneath. The balance is indicated as percentual import (+) or export (-), for both the observed mass-balance and a conservative mass-balance. Net whole balance exchange per squared meter is indicated. The conservative mass-balance is the mass-balance corrected for import or export of water.

3.5 Discussion

It is clear that the freshwater marsh studied here acts as an important source of DSi to the main river. Furthermore, our measurements indicate that this export is compensated by the import of amorphous silica. Thus, the marsh seems to act as Si recycler, resupplying biologically available DSi to the estuarine ecosystem, despite the high potential uptake of DSi by marsh plants and sediments.

Diatoms living on the marsh surface can take up DSi and transform it into BSi, which is finally buried in the marsh sediments. Sediments and plants have been shown to be important sinks for DSi in an estuarine marsh (Norris & Hackney 1999). After the marsh plants take up DSi, it is deposited in the plant tissue as solid amorphous silica in structures of various shape and ornamentation, known as opal phytoliths (Kaufman et al. 1981). Wetland graminae (e.g. *Phragmites australis*), heavily abundant in the marsh and along the Scheldt estuary (up to 14 ton ha^{-1}, worldwide up to 26 ton dry biomass ha^{-1}, Meyerson et al. 2000), can contain Si in concentrations up to 5-15 % of total dry weight (Conley 2002). DSi taken up by vegetation must be dissolved to become available again to the estuarine ecosystem. Plant phytoliths are resistant to decomposition and have been used as indicators for reconstructing past environments (Piperno 1988). Twiss (1983) reported that some phytoliths of plants do not decompose in the soil after the plants decay. More labile components of the plant tissue such as organic carbon and nitrogen leach from the plant during decomposition leading to higher relative Si contents in the dead plants (Gallagher et al. 1976; Eleuterius & Lanning 1987). Recent studies have shown that Si released from weathering of plant phytoliths buried in the soil was twice that of Si released from lithogenic silicate mineral weathering (Alexandre et al. 1997), considered inert at biological timescales. It was shown from our dataset that despite the high potential of freshwater marshes with high plant biomass to act as a DSi sink, DSi was exported from the marsh site to the main river channel in all but one of the six mass-balance studies carried out.

The DSi export was due to the doubling or tripling of DSi concentrations in the seepage water. The seepage water has been in intimate contact with the surface layers of the marsh sediment. Particularly in summer and spring, when DSi concentrations in the main river were depleted due to diatom growth, the sediments could act as a source of DSi for the tidal river water entering the marsh, due to the steeper gradient in DSi concentration between the marsh porewater, which was enriched in DSi concentration and the DSi depleted flood water.

Regeneration of DSi from recently deposited amorphous silica in bottom sediments is known to play an important role in marine and estuarine systems (Long Island Sound, Chesapeake Bay, Cape Hatteras) (Aller & Benninger 1981; D'Elia et al. 1983; Willey & Spivack 1997) and, although less studied, was also observed in freshwater sediments (House et al. 1999). The porewater comes into contact with BSi in the sediments in between two tidal flooding events. Dissolution of DSi from the marsh soil sediments could furthermore occur directly into the floodwater.

BSi was imported into the marsh site over all tidal cycles, mainly due to the absence of suspended matter in the seepage water phase. Diatoms are imported into the marsh in summer and spring and deposited in the marsh during the flood tide. In addition, import of plant phytoliths from the main river, originating from decaying plant material in the river basin, could be a source of amorphous silica. The BSi imported into the marsh, contributes to the potential of the marsh surface sediments to enrich seepage water with DSi.

We extrapolated the exported and imported amounts of Si as observed at our study site to the entire area of freshwater marshes along the Scheldt. This is reasonable because the study site was chosen as a good representation of freshwater marshes along the river. We used the data from the mass balances to perform our extrapolation for both BSi and DSi. The average export of DSi from the isolated marsh was around 400 g over one tidal cycle. This gives an exchange of 0.114 g m^{-2}. The exchange per square meter was of the same order of magnitude over the tidal cycles performed at the main creek, although much higher in April 1998 (0.43 g m^{-2}). The total area of freshwater marshes along the Scheldt is about 450 ha . Over one tidal cycle, this area would export 500 kg. If we would assume the export of silica over ½ tidal cycles on a yearly basis (300), which is a fair assumption considering the observations on the main creek (export in spring, summer and autumn), this would give a total yearly export of 150 tons of DSi. A similar calculation for BSi shows that this export of DSi is accounted for by a similar import of BSi.

Although these exports are low (2-3 %) compared to the total yearly DSi discharges in the main river (6000 tons in 1997), the export could still provide a very important source of DSi, especially in spring and summer, when DSi concentrations in the main river are lowest due to DSi uptake by diatoms and DSi export from the marsh was highest (e.g. May 2002: export of DSi estimated at 10-20 tons, while DSi-discharge in the river in summer and spring months can drop below 50 tons per month). In more natural river-marsh systems, where tidal areas cover larger areas than those in the heavily modified Scheldt, the recycling function of marsh ecosystems could have an even bigger influence.

Although these extrapolations are rough (no evaporation included), they do show that freshwater marshes (and flooded areas in general) along estuaries could play an important role in resupplying DSi to the water column, especially during the diatom growing season. To be able to understand the role of freshwater marshes, and marshes in general, in the estuarine Si cycle, it will be necessary to perform additional tidal cycle mass-balances of DSi and BSi in different seasons in estuarine regions around the globe (in chapter 4 this was done for the Scheldt and the saltwater Baie des Veys). Furthermore, it will be necessary to quantify different Si sinks and sources in the marshes (vegetation, sediment, pore water) along these estuaries (e.g. chapter 2) and to quantify the fluxes between these compartments (chapter 5 and 6 for the Scheldt).

This should allow us to gain an understanding of the important role tidally flooded areas play in the estuarine biogeochemical Si cycle, a role that has not received much scientific attention up to now (Hackney et al. 2000). This understanding is of major scientific importance, as currently it is accepted by most estuarine scientists that microalgae, for which DSi is an essential nutrient, are the most important energetic source for estuarine food chains (Peterson & Howarth 1987; Sullivan & Moncreiff 1990).

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Chapter 4

Tidal marshes and biogenic silica recycling at the land-sea interface

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(Limnology & Oceanography, accepted)

4.1 Abstract

We studied the seasonal exchange of biogenic silica and dissolved silica between a freshwater and a saltwater tidal marsh and the nearby coastal waters. From both tidal marshes export of dissolved Si (DSi) was observed, while concurrently biogenic Si (BSi) was imported along with suspended solids. The export of DSi was highest (23.4 % and 123.8 % in the freshwater and saltwater marsh respectively) in summer when dissolved Si concentrations were low in the nearby coastal waters. Combined data from both marshes suggested a logarithmic decrease in DSi export with increasing DSi concentrations in the inundating waters. BSi import was observed year round in the freshwater marsh, but only in summer in the saltwater marsh. The results show that dissolved silica recycling from tidal marshes, both freshwater and saltwater, contributes significantly to estuarine Si availability in summer and provide new insight in the link between tidal marshes and secondary production in nearby coastal waters.

4.2 Introduction

In chapter 2 and 3 the importance of freshwater tidal marsh habitats, both as recyclers of DSi and sinks for BSi was shown. Although marsh habitats are a major sink for BSi, DSi is exported from tidal freshwater marshes to nearby estuarine waters indicating that tidal marshes may be important sites for Si recycling within estuaries. A continuous supply of DSi from marsh recycling could be essential for autochthonous diatom communities and as a result, be of vital importance in estuarine foodwebs, for which production by diatoms is an important energy source (Sullivan and Moncreiff 1990).

Despite the fact that marshes have a high potential as buffer systems within the estuarine Si cycle, as far as we know, no other complete flux studies have been conducted in saltwater or brackish marshes and there is also no information on the seasonal variation in Si exchange between marshes and estuaries. The flux could differ significantly over the seasons: in summer and spring, diatom production in the estuary can increase BSi concentrations through uptake of DSi and consequently decrease the DSi concentration.

In this study, BSi and DSi fluxes were determined for both a freshwater and a saltwater tidal marsh. Six full tidal cycles were studied in both areas in order to quantify Si recycling capacity of marshes throughout different seasons. For the first time, whole tidal marsh ecosystem functioning within estuarine Si cycling has been quantified at different ambient DSi concentrations. The observed fluxes indicate that tidal marshes may play an important role in enhancing internal BSi recycling in estuarine waters especially in spring and summer, when DSi concentrations are decreased by diatom production.

4.3 Materials and methods

We compared Si exchange at the freshwater marsh near Tielrode (Fig. 4.1b; detailed description also in chapter 1) in the Scheldt estuary with the recently formed salt marsh of the Carmel Polder (France, Fig. 4.1a; detailed description below). Six complete tidal cycle studies were conducted at the freshwater marsh: two in May 2002 (chapter 3), and one in September 2003, October 2003, January 2004, and February 2004. The salt marsh was studied during February and July 2004 and three whole tide exchange studies were conducted during both periods. Both sites were chosen because of their isolated nature, with only one connection to the surrounding estuarine waters, allowing for accurate construction of water balances. The study sites were characterized by representative European tidal saltwater and freshwater marsh vegetation.

Carmel Polder

The saltwater Carmel Polder is located in the Baie des Veys in Northwestern France (Fig. 4.1a). It is a polyhaline (salinity 18-30) macro-tidal bay with a tidal amplitude averaging 7 meters. The polder is now directly connected to the sea, after a storm broke the tidal gate in 1990. Water flows in and out of the polder only through this gate (∅ 1 m). Fifty-eight thousand m^2 are now tidally flooded. About 17,000 m^2 of the total 300,000 m^2 of the polder is covered with salt marsh vegetation. The dominant species are *Salicornia europaea*, *Spergularia marina* and *Puccinellia maritima.*

An area of about 41,000 m^2 in the southern half of the polder presents a shallow impoundment with no rooted vegetation. The level of this shallow impoundment rises with seawater inflows. The daily variations have a maximal amplitude of 20 cm and monthly, the level can vary up to 60 cm. The water in this shallow impoundment is never totally drained. Water flows into the polder at almost every tide, except during the lowest neap tides. The difference between the total flooded surface and the surface of 41,000 m^2 of the impoundment, is the total flooded vegetation covered surface. A detailed description of the polder is provided in Dausse et al. (in press).

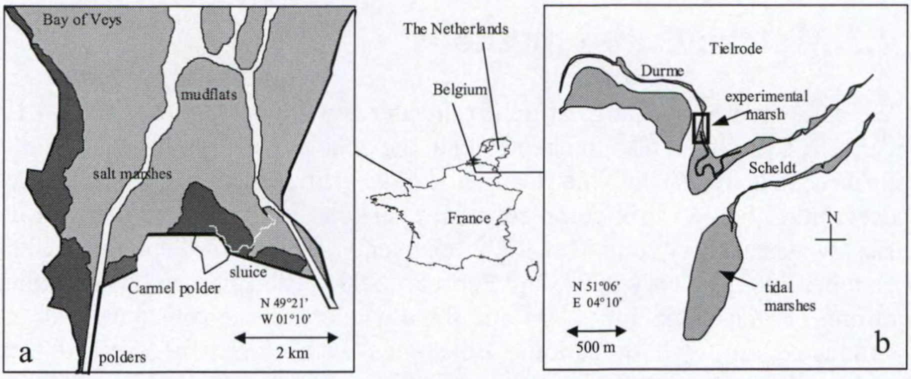

Figure 4.1 a) Location of Carmel Polder in northwestern France (N 49°21', W 1°10'). b) The location of the Tielrode marsh along the Scheldt estuary near the confluence of the Durme and the Scheldt (N 51°06', E 4°10'). The study area is the northern part of a larger marsh system. The location of both areas in Western Europe is indicated on the central map.

Water balances

Tielrode

Water velocities were continuously measured in the centre of the creek just below the surface and near the bottom (OTT-mills or Valeport EMF (Electromagnetic Flow Meter) Model 801) every minute. Simultaneously, lateral velocity profiles were carried out continuously at the creek surface (10 lateral measurement points) with a second EMF. During the 2003 and 2004 cycles, water velocities were available for every lateral measurement point approximately every 1-2 minute. In 2002, lateral velocity measurements were less frequent (approx. every 6 minutes). Here, a simple flow model was developed predicting the ratio between water velocity at any width segment relative to the water velocity in the centre of the creek, using water height, the ratio to the highest water height observed during the tidal cycle or both as predictors (robust linear regression, Rousseeuw and Yohai 1984), and the ingoing and outgoing tides were separately fitted.

Discharged volumes were calculated by multiplying flow velocity and cross surface in over 40 lateral subsections every minute during bulk tidal phase and every hour during seepage water phase.

Bulk tidal phase is here defined as the period of approximately 3 hours during which large amounts of water flow in and out the marsh through the creek (around high water in the main river, incoming bulk = approx. 75 minutes, outgoing bulk = approx. 105 minutes). The seepage water phase was defined as the period after the bulk tide when no decrease in water level was observed for 30 minutes. Seepage water is exported out of the marsh between two bulk tidal phases, when tide in the main river is approaching low tide or rising to the threshold water level where water starts flowing into the marsh (= bulk tide). The seepage water is mainly water leaving the sediments. Flow velocities were very low and stable during the 9 h seepage water phase for all campaigns (as in Fig. 4.2). Accuracy of water balances was evaluated using water volume estimates from a digital terrain model.

Carmel Polder

Discharge was measured directly every minute with an "ISCO Doppler Area velocity flow sensor", mounted at the bottom of the rectangular shaped entrance sluice. In contrast to the Tielrode marsh, water flowed out at a continuous flow rate during the whole outgoing tide. There was no real seepage water phase, and water outflow was mostly surface drainage during the whole ebb stage (Fig. 4.2).

Silica sampling and analysis

At Tielrode, water samples were collected every 15 minutes during bulk tidal phase, and every hour in seepage water, while hourly sampling was conducted during the entire tidal cycle at Carmel Polder. DSi, BSi and suspended solids were analysed from every sample taken. For BSi analysis, three 30 ml subsamples were filtered from a well-mixed total sample of 200 ml onto 0.45 μ-polycarbonate filters. BSi was extracted from the filters in a 0.1 mol L^{-1} Na_2CO_3 solution at 80°C. Subsamples were taken at 80, 120, and 160 minutes. Blank extractions revealed insignificant (< 0.2 mg L^{-1}) DSi release from filters or chemicals. BSi was calculated by extrapolating the linear line through the three extraction points in a time-extracted silica plot (DeMaster 1981). DSi, both from extractions and in the water phase was analyzed spectrophotometrically on an IRIS ICP (Inductively Coupled Plasma Spectrophotometer). All Si concentrations are in mg Si L^{-1}. Suspended solids were determined gravimetrically after filtration on Whatman GF/F filters.

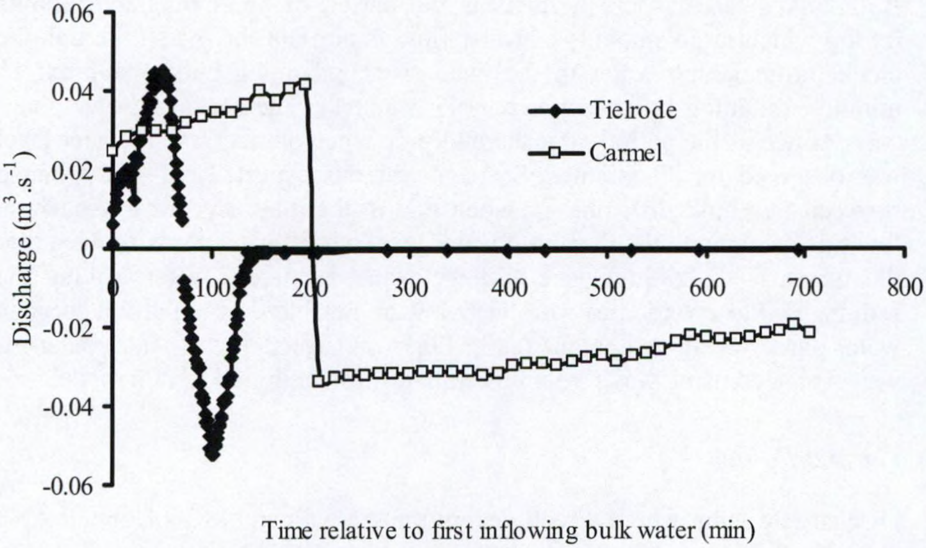

Figure 4.2 Comparison of the water discharge through the main creek at Tielrode (12 September 2003) and water discharge through the sluice at Carmel Polder (17 February 2004). Both tidal cycles had representative flow patterns for the other tidal cycles studied.

Silica transport was calculated by multiplying discharge with measured concentrations continuously throughout the tidal cycles. Weighted average Si concentrations per tidal cycle phase (bulk incoming, bulk outgoing and seepage) were calculated as the ratio of the total amount of transported BSi or DSi and the amount of water discharged during a particular tidal phase.

Nutrient balances were rendered conservative by correcting for the import or export of water (by subtracting percentual import/export of water from percentual nutrient exchange). In a conservative mass-balance, it is assumed that there was no import or export of water. This correction was necessary to allow comparison between tidal cycles, which differ largely in the ratio of imported and exported water volumes.

4.4 Results

Water balances

Calculated water budgets were nearly closed during 4 out of 6 Tielrode freshwater tidal cycles (Table 4.1). Highest high water levels were observed in January and February 2004. Export of water (-5.3%) and import (8.8%) were observed at these tidal cycles respectively. Calculations of the total volume of water covering the study area from a digital terrain model using maximum water levels validate the water balances (Table 4.1). The whole marsh was flooded during all six tidal cycles conducted.

At Carmel Polder, water balances were mostly characterized by significant import or export of water (Table 4.1). There was a large discrepancy between incoming and outgoing water at lower tides (up to –188%), with more water leaving the area than entering. The flooded surfaces in winter tides were between 51,000 and 53,000 m^2. During the August cycles, respectively 39,000, 42,000 and 43,000 m^2 were flooded on 28 July, 31 July and 01 August 2004. Si exchange per squared meter at the Carmel Polder was based on these observed flooded surfaces (and not the complete polder area). More saltmarsh vegetation was covered during the winter cycles than during summer, and no saltwater marsh vegetation was covered on 28 July 2004.

BSi and DSi concentrations

At Tielrode, DSi (Fig. 4.3a) and BSi (Fig. 4.3b) concentrations showed opposite seasonality. Highest BSi concentrations were observed in late summer, early fall and DSi concentrations were concurrently at their lowest. Inflowing DSi-concentrations were between 2.1 - 7.0 mg Si L^{-1}. Within tides, there was very little difference in DSi concentrations between incoming and outgoing bulk. In the seepage water, DSi concentration increased to ca. 9 mg Si L^{-1} for all cycles. Inflowing BSi concentrations varied between 0.7 and 3.6 mg Si L^{-1}. BSi was always highest in inflowing bulk water and dropped by ca. 30% during all cycles in outgoing bulk water, and dropped to very low concentrations in seepage water.

	Date	Water height m	Bulk in m^3	Bulk out m^3	Seepage m^3	Water balance % import/export	GIS m^3
Tielrode	26-May-02	5.97	1700	-1642	-61	-0.2	1800
freshwater	30-May-02	5.89	1376	-1305	-65	0.4	1500
	12-Sep-03	5.75	667	-641	-42	-2.4	986
	10-Oct-03	5.95	1466	-1380	-95	-0.6	1725
	29-Jan-04	6.09	1557	-1584	-55	-5.3	2249
	26-Feb-04	6.08	1763	-1560	-48	8.8	2212
Carmel	17-Feb-04	5.35	425	-853	-	-100.7	-
saltwater	22-Feb-04	6.60	1218	-1221	-	-0.2	-
	25-Feb-04	6.00	1272	-1132	-	11.0	-
	28-Jul-04	5.15	233	-670	-	-187.6	-
	31-Jul-04	6.00	656	-836	-	-27.4	-
	1-Aug-04	6.55	910	-660	-	27.5	-

Table 4.1 The exchanged water volumes during all tidal cycles at Tielrode and Carmel Polder. Water height in m above mean low sea level for Tielrode (TAW, Belgian national tidal reference) and m above lowest astronomical tide for Carmel Polder. Exchanged water volumes are given for the different tidal phases. Water balance is in percentage compared to inflowing bulk (+ = import, - = export). The geographic information systems (GIS) estimate of flooding volume is indicated for Tielrode.

At Carmel Polder, inflowing DSi concentrations were low compared to Tielrode and varied seasonally between 1.0 and 3.5 mg Si L^{-1}. In the absence of a seepage water phase, DSi concentrations increased during all tidal cycles in outgoing bulk water (Fig. 4.3c). In summer, percentual increase in DSi concentration was high compared to winter. Incoming BSi concentrations at Carmel Polder were around 0.5 mg Si L^{-1} in both winter and summer, with the exception of 2.1 mg Si L^{-1} measured on 22 February 2004 (Fig. 4.3d). BSi decreased during outgoing water in winter (ca. 0.4 mg Si L^{-1}, 0.9 mg Si L^{-1} on 22 February 2004). In summer there was little difference between inflowing and outflowing BSi.

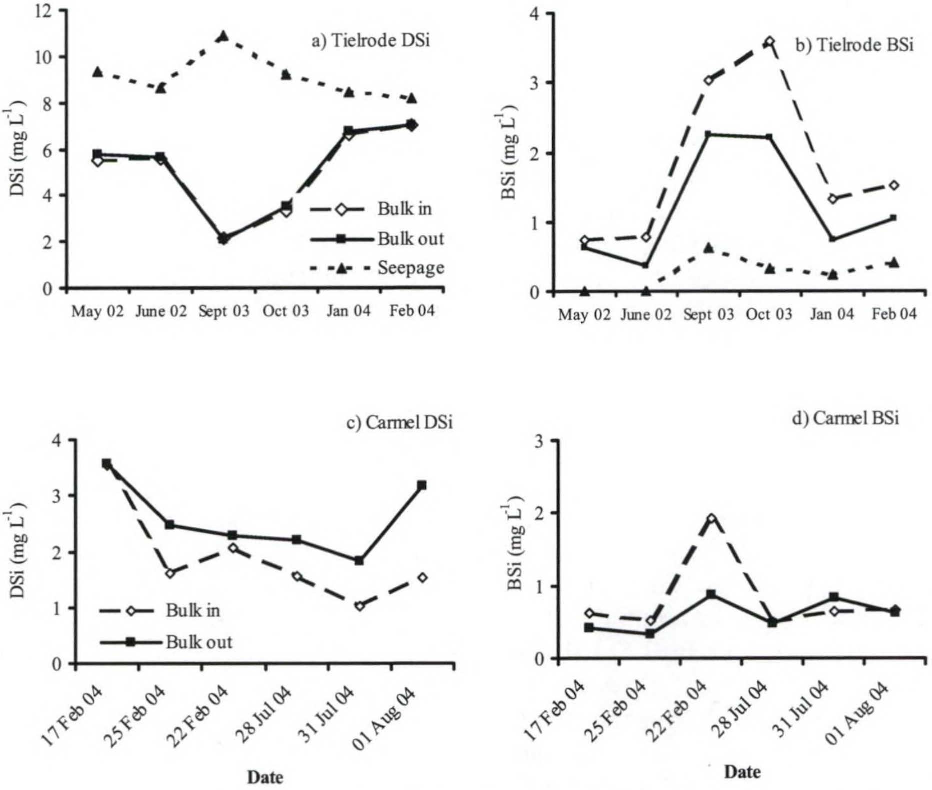

Figure 4.3 DSi and BSi concentrations in the inundating water at (a,b) the Tielrode freshwater marsh and (c,d) the saltwater Carmel Polder for all six exchange studies at both locations. Results for bulk inflowing, bulk outflowing and seepage water at Tielrode and during bulk in and bulk out at Carmel Polder.

Balance uncertainties

Tielrode

A proper estimate of uncertainty associated with the balance calculations is important for the interpretation of the Si exchange rates (Table 4.2). At the freshwater site, uncertainty to the balances can come both from the errors associated with balance calculation itself, and from the error inherent to the non-continuous measurement of Si and water velocities at all depths and lateral points. The standard errors associated with ICP measurement of DSi concentration (0.01 mg L^{-1}) and EMF flow measurements (0.02 m s^{-1}) were very small, while DSi concentrations were very stable during both bulk tides and seepage. The error on the DSi balances resulting from the calculation itself was always smaller than 3% (on the percentual balance, i.e. if we calculated 0% export, the uncertainty interval resulting from calculation is between 3% export and 3% import). For BSi concentration, we took a standard error of 1 mg L^{-1} to reflect the higher uncertainty associated with BSi measurements. This error also corresponds to the maximal standard deviation in BSi concentrations during a single tidal phase. The resulting calculation error on the BSi balances was always lower than 7 %.

We added a conservative tracer (Br^-) both in May 2002 and September 2003, during tides where no Si was sampled, to verify our ability to accurately construct the water balance (See Gribsholt et al., in press, for details). Both tracer additions indicated a near closed water budget. This indication is supported by the visual observation that no significant pools of water were left on the marsh surface after bulk tide. All water budgets were therefore assumed approximately balanced, and conservative correction with the water balance of the silica balances was considered to correct for imbalance in the calculated water budget.

In addition, the GIS digital terrain model estimates of water volume were used to estimate the possible over- or underestimation of water balances. During both May 2002 tides the GIS estimate was respectively 6 and 8 % (around 100 m^3) bigger than ingoing and outgoing water (Table 4.1) This difference could be explained by the volume of vegetation and litter, which was not accounted for in the GIS budget. In 2003 and 2004, the discrepancies between GIS and calculated water balances were larger, especially at the highest tides (between 259 and 692 m^3, respectively 15 and 31 % underestimation).

The maximal underestimation of the exchanged water volume in the calculated water balance was thus 31 %. We applied this maximal underestimation of the water balance of 31 % to all silica balances, and added the uncertainty resulting from the calculation errors (+/- 3% DSi, +/- 7% BSi, see earlier), which resulted in the uncertainty range in table 4.2. These ranges indicate that the calculated fluxes were in general very good indications of the real fluxes, and error on the balances was relatively small.

Carmel Polder

The saltwater water budget was measured directly and continuously with an acoustic Doppler, with a relative error of 2%. Again, 0.01 mg L^{-1} was used as standard error for ICP DSi analysis. In saltwater, with generally lower BSi-concentrations, we applied 0.5 mg L^{-1} as standard error for BSi measurement, which was the maximal observed standard deviation in concentrations during a single tidal cycle phase. Resulting errors are shown in table 4.2 as the uncertainty range.

Silica balances

All mass balances were rendered conservative by correction for import or export of water, to allow comparison and as a correction for errors in the freshwater balance (see earlier). In the freshwater, rendering conservative mostly effected the winter cycles, due to the observed imbalance between ingoing and outgoing tides.

At Carmel Polder, effects were larger during the lowest tides (one each season), due to the larger imbalances observed between incoming and outgoing tides (Table 4.1). Uncertainty to the balances was very high for BSi in saltwater, because of the relatively high error estimate for BSi compared with the low observed BSi concentrations, and very small differences in BSi concentrations between ingoing and outgoing water volume.

DSi was always exported from the marsh sites, but export was very low during winter (Table 4.2). In Tielrode, the percentage export was between 0.2% (February 2004) and 23.4% (September 2003). Exchange per squared meter per tidal cycle was highest in late summer 2003 (216 mg m^{-2}) and lowest in winter (6 mg m^{-2}). At Carmel Polder, percentage export was also highest in summer (between 78.7 and 123.8 %) and lower in winter (2.0 – 47.6%). Exchange ranged between 1 mg m^{-2} and 25 mg m^{-2}.

BSi was always imported into the freshwater marsh site at Tielrode. Percentage import was between 19.1% and 55.7% (both May 2002). Exchange per squared meter was highest in October 2003 (639 mg m^{-2}) and lowest in May 2002 (69 mg m^{-2}). At Carmel Polder import of BSi was only apparent in winter and was between 32.3% and 64.6%; import per squared meter was between 0.3 and 25 mg m^{-2}. In summer, BSi was net exported from the marsh site during 1 out of 3 cycles (-40%, 3 mg m^{-2}). During the other summer cycles, BSi acted nearly conservative.

There was a consistent negative relationship between percentage export of DSi from the marsh sites and DSi concentration in the inundating water (Fig. 4.4a). In the freshwater, a significant relationship was also observed between tidal height and percent export ($F_{1,4}$=8.42, p=0.044, R^2 = 0.68, Fig. 4.4b), but the relationship of export with inundating DSi was much stronger (R^2=0.97, Fig. 4.4a). In the saltwater, no consistent relationship between export and tidal height was observed (Fig. 4.4b).

Percentual export of DSi was highest when inundation concentration was lowest (Fig. 4.4a). At the freshwater Tielrode marsh, the negative relationship was significantly linear. A similar significant linear relationship was not observed at saltwater Carmel Polder (p=0.07). At Carmel Polder, inundating DSi concentrations were much lowering than at Tielrode. Percentual export increased more rapidly with lower inundating DSi concentrations than at Tielrode. Results obtained from both Carmel Polder and Tielrode span a wide range of inundating DSi concentrations. Combined results from both areas show a logarithmic relationship between inundating DSi concentration and percentual export of DSi (Fig. 4.4a). The highest import of BSi per m^2 was observed when deposition of suspended solids was maximal, suggesting import of BSi with suspended solids (Fig. 4.5).

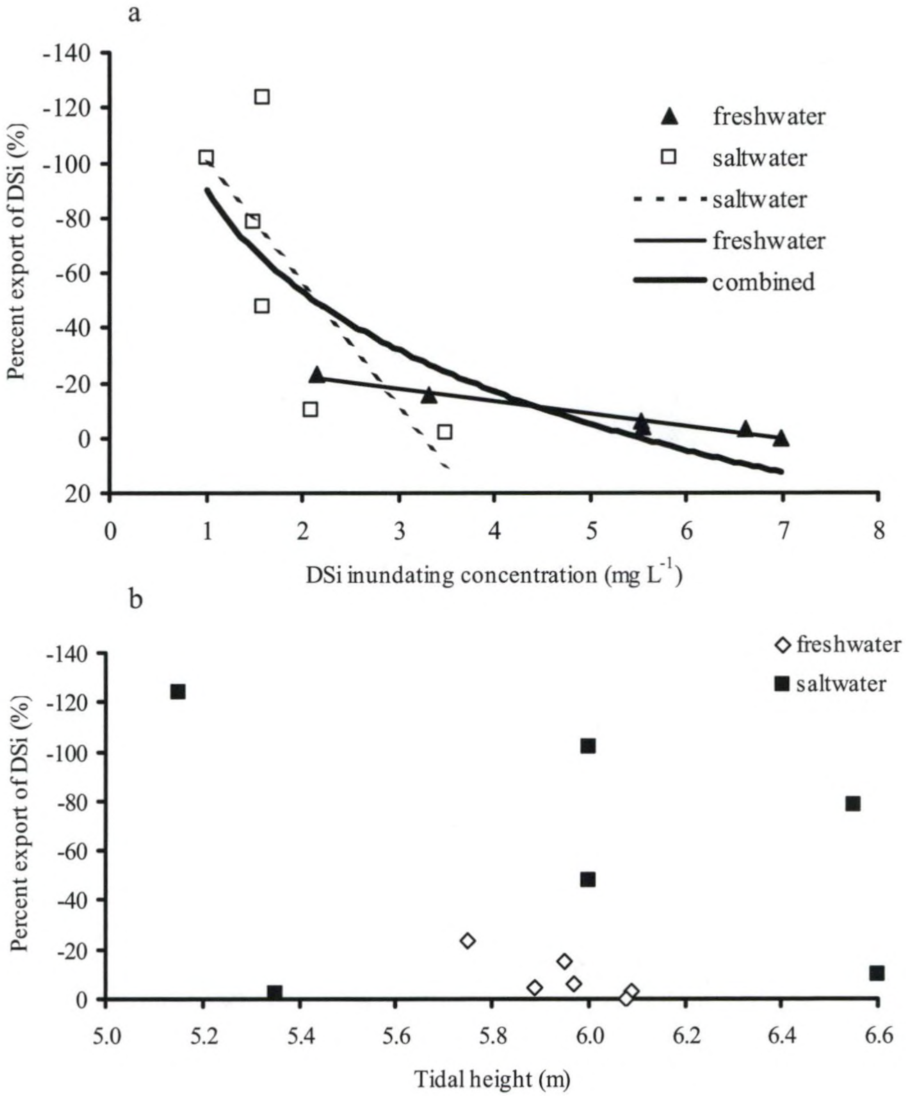

Figure 4.4 (a) The percentual export of DSi from the Tielrode (freshwater) and Carmel Polder (saltwater) wetlands in relation to the inundating DSi concentration (Linear regression: Tielrode: $F_{1,4} = 144$, $R^2=0.97$, $p<0.001$; Carmel Polder $F_{1,4} = 5.61$, $R^2=0.58$, $p=0.08$). Combined datasets result in a logarithmic relation ($F_{1,10} = 18.2$, $R^2=0.64$, $p<0.002$). (b) The percentual export of DSi vs. tidal height (in m above mean low sea level).

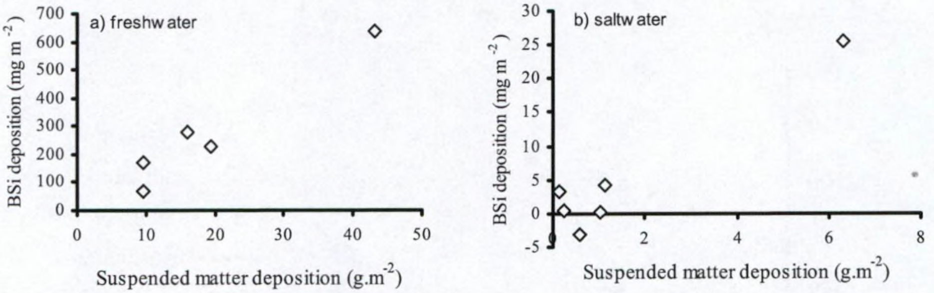

Figure 4.5 Import of BSi per meter squared vs. surface averaged import of suspended matter at (a) freshwater marsh Tielrode and (b) saltwater marsh Carmel Polder.

		DSi exchange			BSi exchange		
Location	Date	%	Uncertainty	mg m^{-2}	%	Uncertainty	mg m^{-2}
Tielrode	26-May-2002	-6.1	-1.6 | -9.1	-164.9	19.1	12.1 | 26.1	69.1
freshwater	30-May-2002	-4.2	-0.3 | -7.2	-93.3	55.7	48.7 | 62.7	170.7
	12-Sep-2003	-23.4	-16.8 | -26.4	-96.5	29.9	22.8 | 37.0	173.2
	10-Oct-2003	-15.4	-10.1 | -18.4	-216.0	42.1	35.0 | 49.2	639.2
	29-Jan-2004	-3.0	0.6 | -6.0	-90.2	47.3	40.2 | 54.4	278.0
	26-Feb-2004	-0.2	3.2 | -3.2	-5.7	29.9	22.8 | 37.0	229.8
Carmel	17-Feb-2004	-2.0	-1.0 | -3.0	-0.6	64.6	28.6 | 110.6	3.2
saltwater	22-Feb-2004	-10.1	-9.1 | -11.1	-5.0	55.4	47.4 | 63.4	25.5
	25-Feb-2004	-47.6	-46.6 | -48.6	-19.0	32.3	4.3 | 50.3	4.1
	28-Jul-2004	-123.8	-121.8 |-125.8	-11.4	12.8	-44.2 | 69.8	0.3
	31-Jul-2004	-101.7	-100.7 | -102.7	-16.2	-39.8	-65.8 | -13.8	-3.0
	1-Aug-2004	-78.7	-79.7 | -77.7	-25.4	2.8	-17.2 | 22.8	0.4

Table 4.2 The percentual import (+) and export (-) and the exchange per squared meter per tidal cycle of BSi and DSi during all tidal cycles at Tielrode and Carmel Polder. All mass balances were corrected with the water balance to allow comparison and for correcting balance errors in the freshwater. An uncertainty range is given for all percentual mass balances.

4.5 Discussion

A consistent export of DSi was observed from both tidal marshes investigated in this study. In both systems, highest relative export of DSi was observed at low DSi concentrations in the inundating water. At the saltwater site, the percentage export of DSi was independent of the tidal height. At Tielrode, a significant relation between tidal height and percent export was observed, but this relationship was only driven by the very low tidal height during the September cycle. Without this tidal cycle, no significant relationship was observed. As a result of the minor influence of tidal height on percentual export of DSi, a larger exchange per m^2 occurred at highest water levels. This explains why, despite the very low inundation concentration during the September 2003 Tielrode cycle (2.2 mg Si L^{-1}, the lowest observed), exchange per m^2 was relatively low. Low water height resulted in about 35 % of the marsh being only inundated with very shallow water (< 9 cm). Relatively high exchanges per m^2 on 22 February and 01 August at Carmel Polder could be explained similarly by differences in the tidal volumes.

In contrast to the export of DSi observed, the freshwater marsh at Tielrode was subject to BSi deposition year round, while at the saltwater Carmel Polder BSi was imported in winter. It was the amount of suspended matter imported which mainly appeared to control the imported BSi load into the marsh. The low exchanged water volumes at the saltwater site and bigger surface compared to the freshwater site, result in much lower BSi deposition per squared meter here.

Import of BSi into the marsh and export of DSi out of the marsh seem to be intricately dependent on each other. Marshes have been shown to accumulate large quantities of BSi, stored in sediments, plants, and porewater (chapter 2). Deposition of BSi, imported during flood tides in both the saltwater (only in winter) and freshwater marsh, could be an important factor controlling this accumulation. The BSi-rich sediments, deposited in the marsh, can contribute directly to the observed export of DSi. At the Tielrode freshwater marsh, the concentration of BSi in the imported suspended matter during this study was about twice the concentration found in the surficial (0-1 cm) sediment layer covering the marsh. Furthermore, it has been observed that BSi concentration in the marsh sediments decreases with increasing depth and age in marsh sediment cores in the Tielrode marsh (chapter 2). BSi in the marsh sediments dissolves to DSi in the marsh porewater.

The freshwater marsh sediments are hence characterized by porewater DSi concentrations, which clearly exceed the concentrations of DSi found in nearby estuarine waters (Hackney et al. 2000). At the studied freshwater site, porewater concentrations in summer were as high as 16 mg L^{-1}, clearly exceeding the observed flood water concentrations between 2.1 and 7 mg L^{-1} in this study.

Marshes act as a leaky dam, slowly releasing the porewater in between two tidal floodings as seepage water, when porewater is refreshed (Hackney et al. 2000). Most export of DSi (+90% during 5 out of six tidal cycles) observed from the freshwater marsh in Tielrode was directly attributable to the highly DSi enriched seepage water, which has been in intimate contact with marsh porewater and is largely uncoupled from bulk surface water flows.

The role of higher plants growing in the marsh can also not be neglected in the DSi export. Higher plants take up DSi from porewater and deposit the DSi in cell wall structures known as opal phytoliths (Piperno 1988). BSi remains in the plant until dissolution after plant decay. At the freshwater site, dissolution of BSi from decomposing *Phragmites australis* litter could contribute significantly to the total amount of DSi exported from the marsh, up to 50% (chapter 6). Porewater concentrations were significantly higher in *Phragmites* vegetations compared to other vegetations (chapter 2), indicating that the contribution of litter to DSi recycling could also pass through the seepage water.

A major difference between the saltwater site and the freshwater site was the absence of a seepage water phase at the saltwater site. At the saltwater site, export flow of water is buffered by drainage from the never fully drained impoundment, keeping export flow at a continuous higher level compared to the freshwater site. Although no seepage water phase as such existed at the saltwater Carmel Polder, similar export patterns of DSi were observed as in the freshwater marsh. In between high tides, water was drained from the sediments into the shallow impoundment and the creeks. This drainage leads to higher DSi concentrations in the outflowing water, and as observed in Tielrode, the percentual increase was highest when the inundation concentration was lowest. The absence of a seepage water phase could explain why DSi exchange per squared meter was much lower at Carmel Polder compared to Tielrode.

In contrast to Tielrode, the Carmel polder was only a sink for BSi in winter. This could relate to the relative Si enrichment of marshes compared to nearby estuarine waters. Low observed DSi availability could limit diatom production in the surrounding coastal waters, while DSi is still readily available in the DSi-enriched marsh. Furthermore, benthic microalgae are extremely rich in silicon compared to their planktonic counterparts (Sigmon and Cahoon 1997; Hackney et al. 2000). Both factors could explain why in summer, BSi is net exported from the marsh site at Carmel Polder.

At both locations, the percentual enrichment of the flooding water with DSi was highest when the inundating DSi concentration was lowest. At the saltwater, this negative relationship was much steeper than at Tielrode. Data from saltwater and freshwater together suggest an exponential relationship between inundating DSi and DSi enrichment of floodwater. Silica dissolution rates have been shown to increase exponentially from deep-sea sediments and diatom frustules with increasing undersaturation (e.g., Greenwood et al. 2001; Rickert et al. 2002; Passow et al. 2003). The higher percentual export at the saltwater site could further be the result of highly enhanced rate of BSi dissolution in saltwater environments (Yamada & D'Elia 1984).

From this study it is however impossible to attribute the differences between both sites solely to salinity difference. Major other differences exist between both sites. Apart from the difference in hydrodynamics, with no seepage water at the saltwater site, the two sites differ in tidal connectivity. The saltwater site has only recently been connected to the surrounding tidal waters, and sediments could be low in BSi concentration, because of the limited time interval during which BSi has accumulated from BSi import. This would in turn result in lower porewater DSi concentrations, as previously observed in recently restored tidal wetlands (Hackney et al. 2000) and could partially explain the low export per m^2 observed at the saltwater polder.

Low exchanged water volumes per squared meter at the saltwater site could result in high percentual export at the saltwater polder compared to the freshwater, because of the relatively much higher available reaction surface for DSi dissolution to flood water. Furthermore, vegetation in both sites is completely different; the saltwater site has not yet evolved into a fully vegetation-covered marsh site, and large parts remain unvegetated.

While Si in vegetation, sediment and porewater has been intensively studied in the Tielrode freshwater marsh site (chapter 2), little or nothing is known about the total stocks of Si within the saltwater polder or saltwater marshes in general. It was therefore not possible to expand conclusions about sediment and vegetation contribution to within-freshwater marsh Si cycling to the saltwater site.

The obtained results do however indicate that tidal marshes, both saltwater and freshwater may play an important role in the self-regulatory capacity of the estuarine systems with regard to DSi availability. DSi concentrations can drop below 0.4 mg Si L^{-1} in summer months in the freshwater part of the Scheldt estuary. According to the relation observed between percentual DSi export and inundating DSi concentration in the freshwater, export of DSi from the marsh could exceed import by around 30% (or even more if the combined relationship from both sites is considered), and exchange per square meter could rise over 400 mg m^{-2} per tidal cycle. This is about 4 times higher than estimated in previous work, which was based on observations in May only (chapter 3). Total monthly discharge of DSi in the main river channel in months with DSi concentrations below 0.4 mg Si L^{-1} can drop as low as 10,000 kg. With a total area of freshwater marshes along the Scheldt estuary of about 450 ha (however, this area is expected to increase significantly in future years according to nature development plans), only 6 tidal cycles in a summer month each exporting around 400 mg m^{-2}, are sufficient to recycle 10,000 kg of DSi.

This extrapolation clearly indicates how important freshwater marsh recycling of DSi in estuaries may be in maintaining ecosystem functioning during periods with high phytoplankton development in upper parts of the estuary. Results obtained at Baie des Veys indicate that saltwater marshes seem to function similarly in the lower parts of the estuary and in the coastal zone. The results are too limited to draw conclusions about the influence of salinity on the Si fluxes, but they do show that similar patterns of BSi and DSi fluxes existed at two estuarine settings which differed in salinity, hydrodynamics and tidal connectivity.

Restoration of tidal wetlands has been based on the observed relationship between tidal marshes and production of economically valuable fish and invertebrates (Hackney et al. 2000). Tidal marsh plants production and uptake in the detrital food chain have been suggested as an explanation for this link, plant detritus being the energetic source for secondary consumers (Teal 1962; Odum and De La Cruz 1967).

Hackney et al. (2000) hypothesized tidal marsh ability to sequester and enhance internal cycling of Si could provide an alternate explanation for the observed link between tidal marsh production and secondary production in the coastal zone. Our results support the importance of this hypothesis, which relates Si stockage and recycling in tidal areas to secondary production.

However, the scale of the importance of biogeochemical processing of Si by marsh habitats remains as of yet unknown. Our results suggest that Si retention and processing by tidal marsh systems may be an important though overlooked component in continental and global biogeochemical cycling of Si. Integrated research at other marsh sites, combining both quantification of BSi stocked in marsh systems and quantification of DSi/BSi processing by these sites, will be necessary to allow us to advance from local, small scale ecosystem conclusions, towards quantifying importance of Si processing in tidal inundated areas on a continental and even global scale.

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Chapter 5

Biogenic silica sequestration in freshwater tidal marshes: relation with marsh developmental stage

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(Submitted to Biogeochemistry)

5.1 Abstract

The sequestration and recycling of biogenic silica (BSi) in freshwater tidal marshes was modelled through the combination of short-term year round sediment trap data with a long-term sedimentation model, MARSED. The modelling covered the complete evolution from a young rapidly rising marsh to a marsh with an elevation close to mean high water. BSi in imported suspended matter was higher in summer (10.9 mg BSi g^{-1} sediment) than winter (7.6 mg BSi g^{-1} sediment). However, the deposition of BSi on the marsh surface was higher in winter compared to summer, due to the higher sedimentation rates. Deposition of BSi was correlated to the suspended matter deposition. In the old marsh, yearly about 40 g BSi m^{-2} was deposited, while in the young marsh deposition could rise to 300 g m^{-2}. Young marshes retained up to 85 % of the imported biogenic silica. Recycling efficiency (60%) increased drastically for older marshes.

5.2 Introduction

From chapter 3 and 4, it is clear that freshwater marshes are important Si cycling surfaces in the tidal environment. Biogenic silica (BSi) is imported into the marshes, while dissolved Si (DSi) is exported to the surrounding estuarine waters. In this chapter, we focus on the role of the sediments in the recycling process.

BSi is imported into marshes along with suspended matter: sedimentation is clearly an important factor controlling the accumulation and retention of BSi in tidal marshes. Tidal marshes act as net sinks for sediment, which leads in the long term to a vertical rise of the marsh surface. Young marshes, which have a low elevation relative to mean high water level, are rapidly built up, due to a high inundation frequency and consequently a high sedimentation rate. As the marsh surface rises, the inundation frequency, height and duration decreases. As a result, the sedimentation rate decreases and the marsh surface elevation finally tends to an equilibrium elevation close to mean high water level (Temmerman et al. 2004). Then, the marsh can continue to aggrade under rising sea level, if suspended sediment input is high enough (e.g. Shi 1993; Orson et al. 1998).

A number of models have been developed to simulate this long-term (50-1000 years) vertical rise of tidal marshes, based on a zero-dimensional time-stepping modelling approach, simulating vertical marsh accretion at one point, considered representative for the whole marsh platform (e.g., Krone 1987; French 1993; Allen 1997; Temmerman et al. 2003a; Temmerman et al. 2004).

As far as we know, no studies have quantified the process of BSi deposition and dissolution through the vertical accretion of tidal marsh sediments. The ultimate burial of BSi in the deeper marsh sediments, which is lost to the estuarine system on biological timescales, is dependent on the ratio between deposition of BSi and dissolution of DSi to the pore water and subsequent export with flood water. Both in the ocean (Van Cappellen 2003) and several terrestrial ecosystems (Conley 2002; Derry et al. 2005) intense internal biogeochemical recycling of DSi has been reported.

The DSi recycling capacity of tidal marshes has recently been hypothesized to partially explain the observed relationship between marsh surface area and coastal secondary production of economically valuable fish and invertebrates (Hackney et al. 2000), and results have supported this hypothesis (chapter 3 and 4); this clearly stresses the importance of quantifying the retention time and ultimate burial of BSi in tidal marsh sediments.

In this study, field data are shown of short-term (bi-weekly) variations of BSi import due to sediment deposition during a one-year period in a freshwater tidal marsh. These short-term data were combined with a long-term sedimentation model, MARSED (Temmerman et al. 2004), to simulate the long-term deposition of BSi. Simultaneously, deep sediment cores were analyzed for BSi content and the observed exponential decrease of BSi with increasing depth was used to model DSi dissolution from the sediment. Combining these results enabled to quantify the ability of freshwater marsh sediments to retain and recycle Si through the complete development of a tidal marsh, from its initial birth to the stage of equilibrium with mean high water.

5.3 Materials and methods

Study area

The study area, the Notelaar marsh, is located in the most seaward part of the freshwater zone of the Scheldt estuary (Fig. 5.1). The marsh is situated near the turbidity maximum (mean suspended solid concentrations of 100-200 mg L^{-1}) (Temmerman et al. 2003b). The local mean tidal range is about 5.9 m during spring tides and 4.5 m during neap tides. Average yearly discharge in the freshwater part of the estuary is between 25 and 75 $m^3 s^{-1}$ (Struyf et al. 2004). The Notelaar marsh has a total area of 27 ha and extends 2 km along the stream channel. The vegetation is characteristic for old temperate freshwater tidal marshes, with domination of *Phragmites australis* in the lower elevations and a *Salix* sp. community at higher elevations. Both plant communities produce very dense vegetation covers, with *Phragmites australis* reaching exceptional heights of up to 4 m. The *Phragmites australis* vegetated part is in equilibrium with the mean high water level since 1965, while the *Salix* sp. vegetated marsh part is in equilibrium stage since it evolved from pasture grassland (until 1958) to a tidal marsh (Temmerman et al. 2003a). This means that the vegetated marsh platform is only flooded during spring tides.

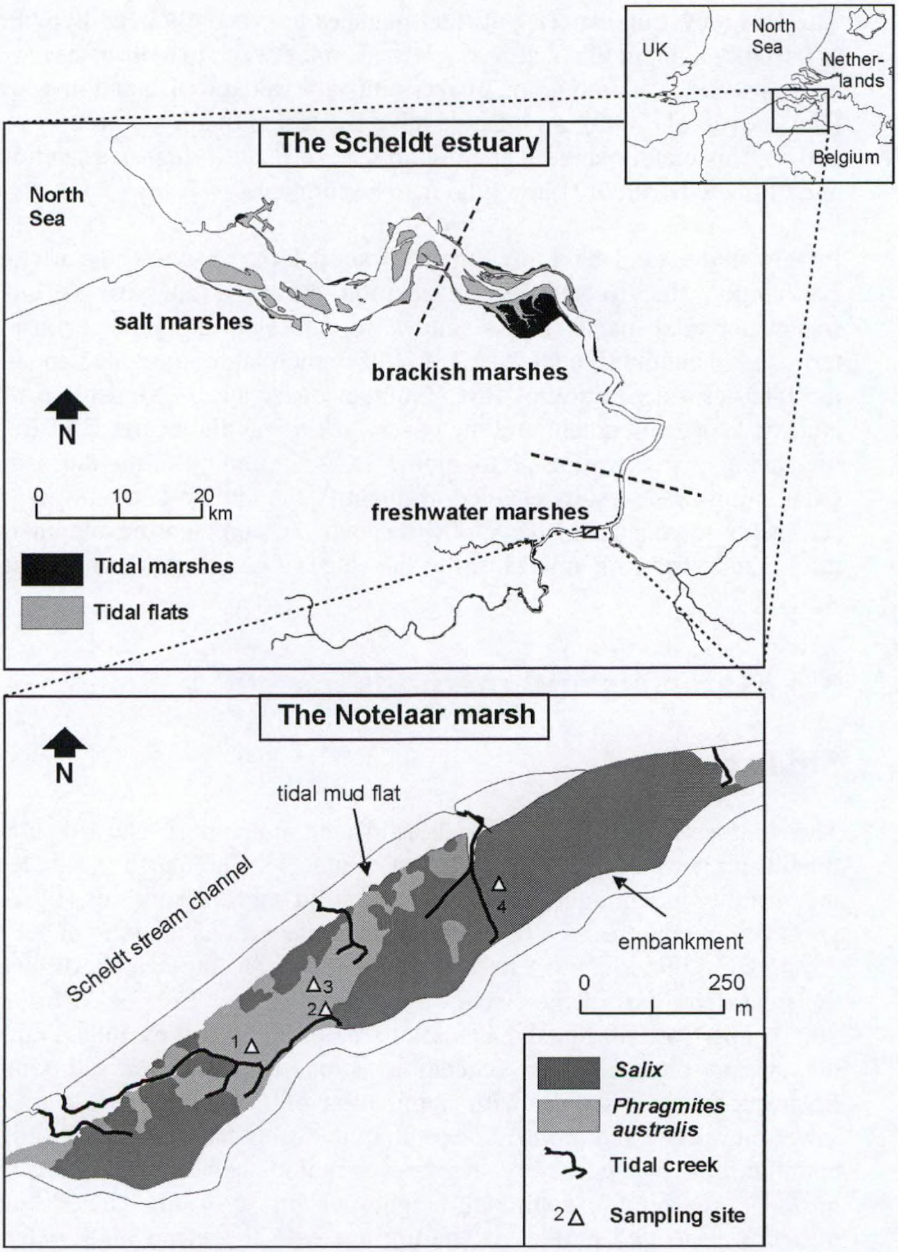

Figure 5.1 The Scheldt estuary with location of the Notelaar marsh. Below: The location of vegetation types and sampling sites within the Notelaar marsh site.

Monitoring of BSi deposition on the marsh surface

During a one-year period (April 2000-May 2001), we sampled the sediment that was deposited on the marsh surface using circular sediment traps (Ø 0.233 m) for bi-weekly time intervals (i.e., each time interval was one neap-spring-neap tidal cycle). The traps were attached to the marsh surface using steel claws and were constructed with a floatable cover to protect the deposited sediment from splash by raindrops during low tides. The amount of deposited sediment was determined in order to study spatial and temporal variations in sedimentation rates (see results of this sedimentation study in Temmerman et al. 2003b). For this study, the BSi content in the deposited sediments was determined (see method below) for 4 sampling sites across the marsh (Fig. 5.1) and for 13 spring-neap cycles, spread evenly over the whole year. The deposition of BSi was calculated by multiplying sedimentation rate and BSi content in the deposited sediment.

BSi in deep sediment cores

At two sites in the marsh, one in the *Salix* sp. vegetation and one in the *Phragmites australis* vegetation, undisturbed sediment cores were collected with a 'Beeker-sampler', a piston corer with thin-walled tubes of 5.7 cm in diameter and 150 cm in length and an inflatable valve at the bottom that prevents sediment loss while raising the corer to the surface. For *Salix* sp. and *Phragmites australis* vegetation respectively, marsh sediments were found up to a depth of 50 cm (dated 1958) and 122 cm (dated 1947) (see detailed description and dating of sediment cores in Temmerman et al. 2003a). Below, remains of pasture grassland (*Salix* sp.) and unvegetated tidal flat sediments (*Phragmites australis*) were present. For this study, BSi content was analysed in subsamples taken approximately every 10 cm in both cores (every 5 cm in upper 20 cm) up to the depth where no marsh sediments were found anymore.

BSi-analysis

Collected sediment, both from sediment traps and cores, was sieved at 500μm, to remove macroscopic plant or shell material and oven-dried at 105°C. BSi was extracted from the sediment (25 mg) in a 0.1 M Na_2CO_3 solution at 80°C. Subsamples were taken after 150, 210 and 270 minutes. DSi in the extractions was analysed spectrophotometrically on an IRIS ICP (Inductively Coupled Plasma Spectrophotometer).

BSi content (in mg g^{-1} dry sediment) was calculated by extrapolating the linear line through the three extraction points in a time-extracted DSi plot (DeMaster 1981), as in other estuarine studies of BSi (Conley 1997; Norris & Hackney 1999).

Modelling long-term BSi sequestration

To estimate the long-term (~50 years) accumulation of BSi in the marsh, the short-term (2000-2001) field data on BSi content in imported sediment were used as input in a long-term marsh sedimentation model, MARSED. This sedimentation model is extensively described, calibrated and validated against field data for the Scheldt estuary in Temmerman et al. (2003a) and Temmerman et al. (2004).

In essence, the MARSED model simulates sediment deposition and elevation change with time at one point in space, based on a physical formulation of the settling of suspended sediments from the water column that floods the marsh surface. Thus, the main input for the model is the suspended sediment concentration in the inundating water and the frequency-height distribution of tidal inundations. The resulting rise of the marsh elevation affects the tidal inundation regime and suspended sediment concentration and consequently the sedimentation rate through a feedback loop.

For this study, the MARSED model was extended to simulate (1) BSi deposition, (2) BSi dissolution after deposition, and (3) net BSi sequestration (i.e., deposition minus dissolution) during vertical marsh accretion. First, BSi deposition was modelled simply as a fraction of sediment deposition, given by the BSi content in the deposited sediment samples (2000-2001). The suspended sediment concentrations, in the water that floods the Notelaar marsh, were significantly higher during winter (October-March) than during summer (April-September) (Temmerman et al. 2003a). Therefore, we used in the model the BSi content averaged over the winter and summer period of 2000-2001 separately. The winter and summer average was calculated based on all 4 sampling sites and was used then to calculate the seasonal import of BSi into both the *Phragmites australis* and *Salix* sp. vegetation since early marsh development.

Secondly, the yearly rate of BSi dissolution was calculated based on the exponential decrease in BSi concentration in the upper sediment layers of the cores (upper 50 cm, because there was little or no decrease in BSi content below this depth), using a constant sedimentation rate of 1.3 cm year^{-1} and a constant sediment dry bulk density of 350 kg m^{-3} (Temmerman et al. 2003a). The assumption of a constant sedimentation rate in the upper 50 cm of the sediment column is reasonable, since this sediment has been deposited during the stage of marsh equilibrium with mean high water level, which has been rising quite steadily the last 40 years (Temmerman et al. 2003a). This relationship between depth and yearly BSi dissolution rate was then implemented in the sedimentation model to simulate the amount of BSi that has been dissolved for each depth layer since its deposition on the marsh surface.

Thus, for each sediment layer deposited in a certain year, its depth below younger sediment deposits was tracked for each subsequent year, as was its BSi dissolution rate and remaining BSi content. The deposition/dissolution ratio was calculated for sediments deposited at different stages of marsh development. Based on these results, the theoretical depth gradient of BSi in the marsh sediments was modelled and compared to the observed depth gradient.

5.4 Results

Monitoring of BSi deposition on the marsh surface

The sedimentation rate on the marsh surface varied seasonally (Fig. 5.2). Highest sedimentation rates were observed in the period October-March, with peak sedimentation rates in early March 2001 (maximum observed 2154 g sediment deposited m^{-2} per spring-neap cycle) and average sedimentation rate of 451+/-525 g m^{-2} per spring-neap cycle. In the period April-September, the sedimentation rate was much lower, on average 60+/-50 g m^{-2} per spring-neap cycle (detailed description of sedimentation in Temmerman et al. 2003b).

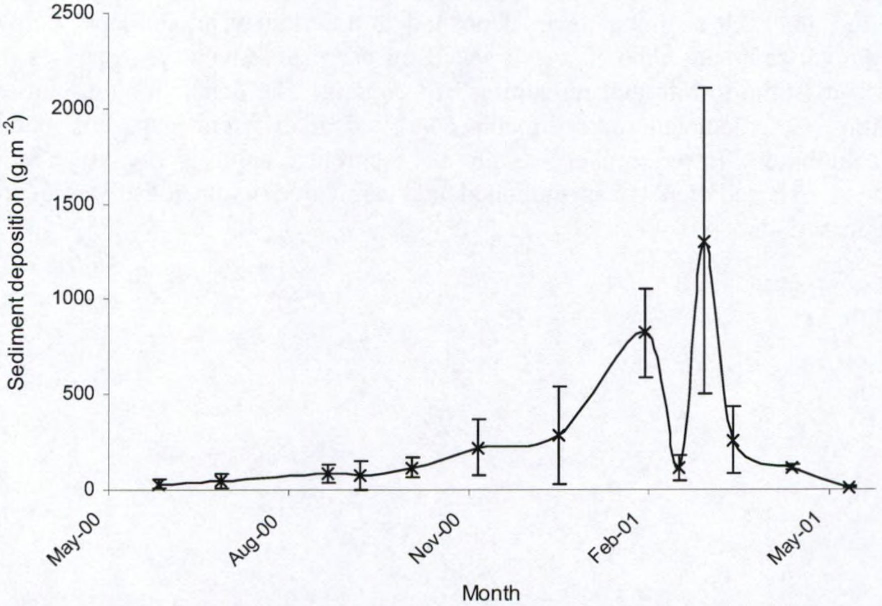

Figure 5.2 The total sediment deposition per neap-spring–neap cycle, averaged for all 4 sampling sites (Notelaar, May 2000-May 2001).

A clear seasonal variation was also observed in the BSi content of the deposited sediments (Fig. 5.3) at all 4 sampling spots. The average BSi content in the deposited sediments over the whole year of sampling was 9.1 ± 3.4 mg Si g^{-1} imported sediment.

Average BSi content for the 4 sampling sites (used in the modelling) was lowest in the period October-March (7.6 ± 3.3 mg Si g^{-1}) and highest in the period April-September (10.9 ± 3.0 mg Si g^{-1}).

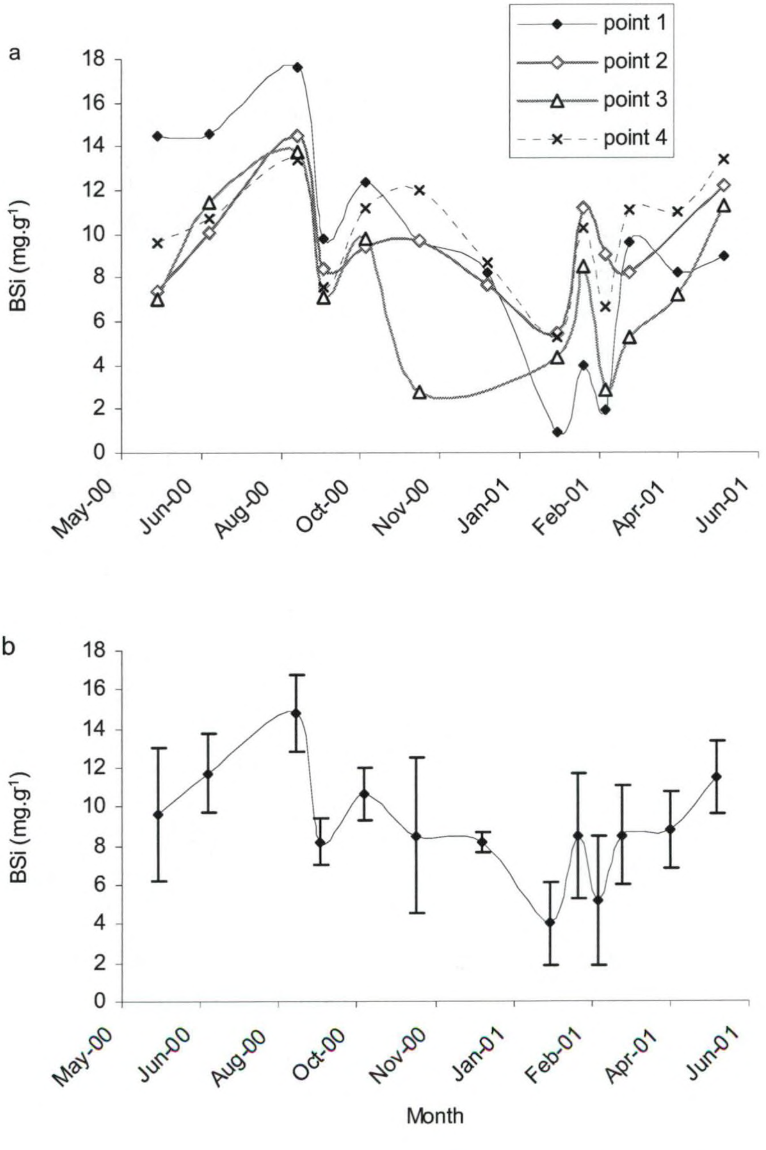

Figure 5.3 The concentration of BSi in deposited sediments at all 4 sampling sites (a) and averaged over all 4 sampling sites (b) (Notelaar, May 2000-May 2001).

The BSi deposition rate on the marsh varied seasonally in accordance with the deposition of sediments onto the marsh (Fig. 5.4). Although the BSi content in the deposited sediments was lowest in winter months, highest import of BSi was observed during these months due to the higher import of sediments. There was a significant correlation between imported sediments and imported BSi (Spearman $r = 0.92$, df = 48, $p < 0.001$). In the summer period (April-September), the BSi deposition rate was on average 643 ± 533 mg BSi m^{-2} per spring-neap cycle, while in the winter period (October-March), the average BSi deposition was 2012 ± 1849 mg BSi m^{-2}. On average, yearly BSi deposition was 39114 ± 12588 mg BSi m^{-2} y^{-1}.

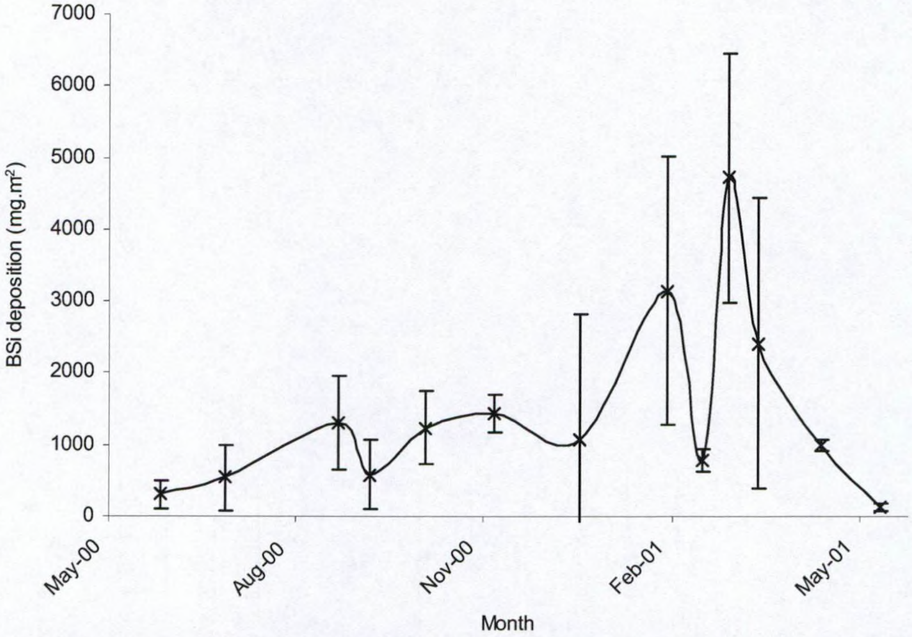

Figure 5.4 BSi deposition per spring-neap cycle averaged for all 4 sampling locations (Notelaar, May 2000-May 2001).

BSi in deep sediment cores

In the *Phragmites australis* marsh sediment core, BSi content dropped from 10.9 mg BSi g^{-1} to a value of 3 mg BSi g^{-1} in the upper 53 cm (Figure 5.5a). There was however a large scatter on the decreasing BSi concentrations in this marsh layer. The *Salix* sp. marsh core showed a similar decreasing trend. In the *P. australis* marsh core, the constant BSi-concentration was found up to a depth of 74 cm.

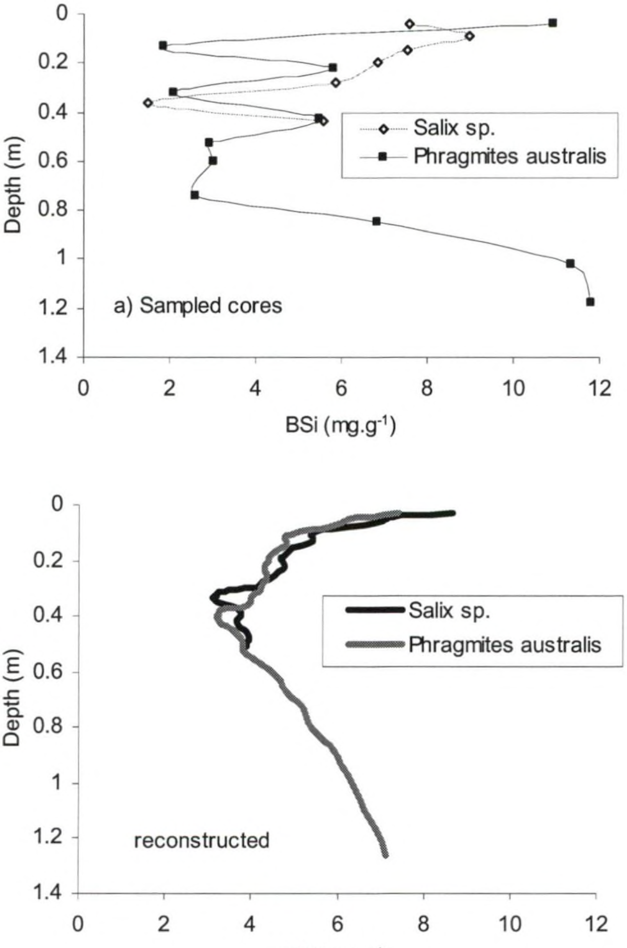

Figure 5.5 BSi content in the sampled (a, above) and reconstructed (b, below) sediment depth profiles in *Salix* sp. and *Phragmites australis* vegetated sites.

A significant exponential decrease of BSi-concentration with depth was found if data for the upper parts of both cores were fitted together (Figure 5.6, $R^2 = 0.52$, $F_{1,13} = 14.07$, $p < 0.003$). In the *P. australis* marsh core below 74 cm depth, there is a strong increase of BSi concentration up to 11.4 mg BSi g^{-1} sediment at a depth of 102 cm and 11.8 mg BSi g^{-1} sediment at 118 cm depth.

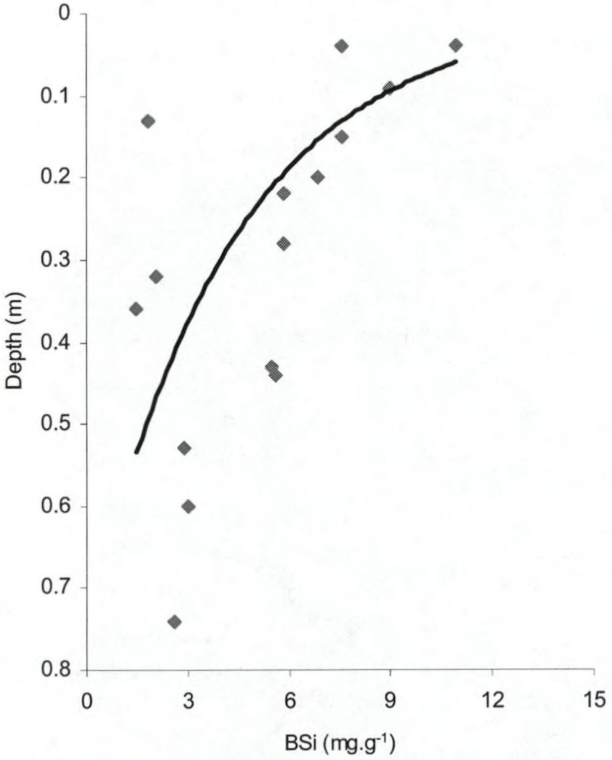

Figure 5.6 Exponential decrease in BSi concentration with depth (results combined from cores taken in *Phragmites australis* and *Salix* sp. sites).

Modelling long-term BSi sequestration

The amount of BSi deposited in both marshes was estimated by implementing the observed BSi concentrations (2000-2001) in the sedimentation model (Figure 5.7a,b). Modelled BSi deposition was always higher during winter than during summer. In the first stages of development of the *P. australis* marsh, when the marsh elevation was rapidly rising (Figure 5.7c), BSi-deposition on the marsh was concurrently at its highest (Figure 5.7a). Yearly BSi-deposition then steadily dropped with increasing marsh elevation. When the marsh attained an equilibrium (both sites) with mean high water, the yearly BSi-deposition onto the marsh dropped to a fairly constant level comparable to the observed deposition on the sediment traps in 2000-2001 (~40,000 mg m^{-2}).

The relationship (calculated from the exponential BSi depth gradient in the sediment) between depth and yearly BSi-dissolution rate is shown in figure 5.8. This relationship between depth and yearly BSi-dissolution rate was implemented in the sedimentation model to estimate the amount of BSi that has been dissolved for each depth layer since its deposition on the marsh (Figure 5.9a,b). During early marsh development of the *P. australis* marsh more than 80% of the BSi imported into the marsh was buried in the sediments. The oldest sediment layers deposited during the marsh equilibrium stage (which are now more than 50 cm below the marsh surface, both for the *P. australis* and *Salix* marsh) show an average burial of around 40% of imported BSi (Figure 5.9a,b).

Based on the modelled dissolution and deposition of BSi, the BSi depth gradient in the marsh sediment was reconstructed (Figure 5.5b). The patterns were similar to the patterns observed in the sampled marsh cores (Figure 5.5a,b). However, the BSi in the upper and deepest sediment layers was strongly underestimated compared to the sampled marsh cores (Figure 5.5a,b). In the lower 40 cm, the sampled marsh core showed a much steeper increase of BSi with depth. There was a large scatter on the exponential decrease of BSi in the upper sediment layers in the sampled marsh cores, which was not apparent in the modelled depth profiles.

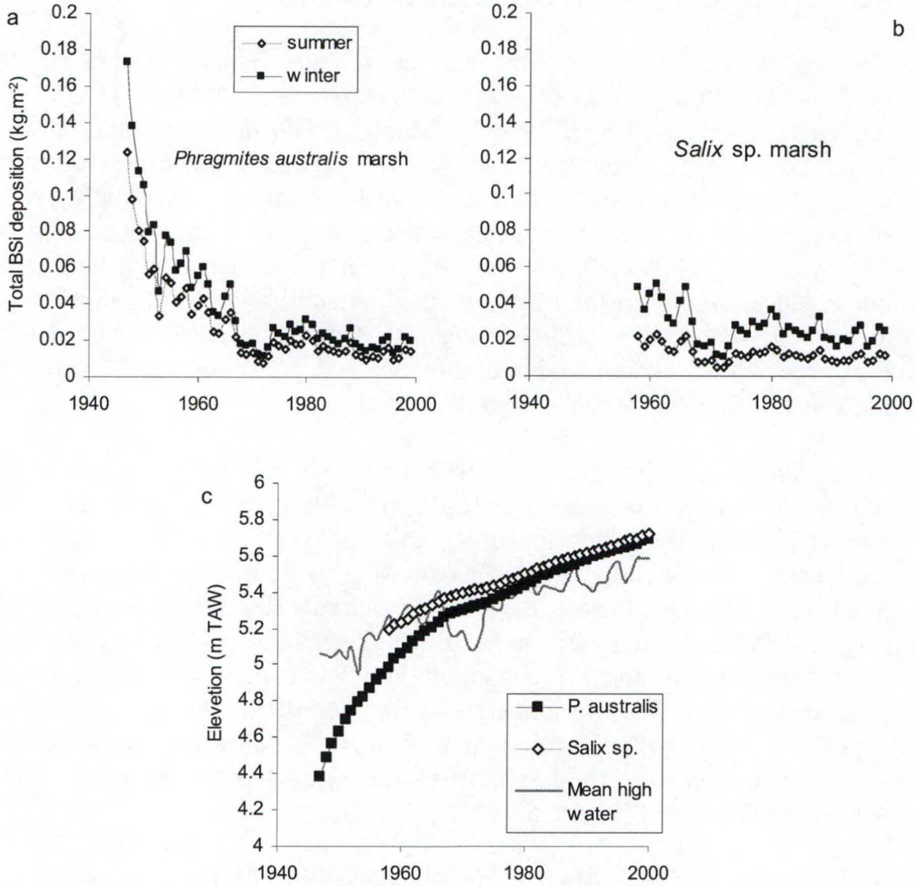

Figure 5.7 Modelled BSi deposition on the *Phragmites australis* (a) and the *Salix* marsh (b) in winter and summer through the history of the sites. Marsh elevation evolution in comparison to mean high water level (c). Arrows indicate beginning of equilibrium stage of marsh elevation with mean high water. Water level in m TAW (= Belgian Ordnance Level, corresponding to height over mean sea level at low tide).

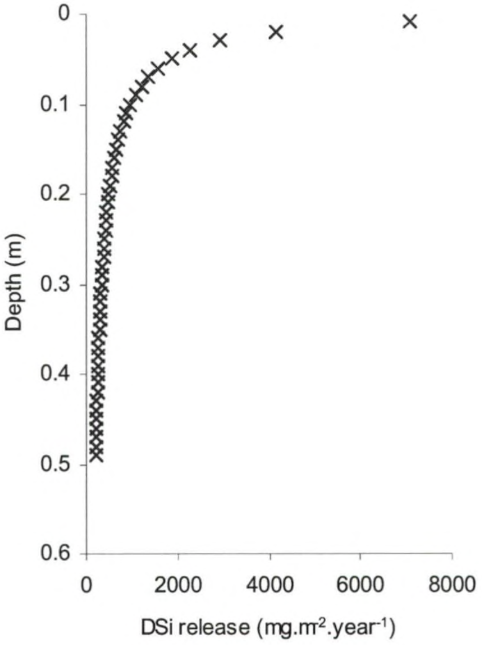

Figure 5.8 The modelled DSi release from the sediment at different depth layers, according to the observed exponential decrease of BSi concentration in the cores (see Fig. 5.6).

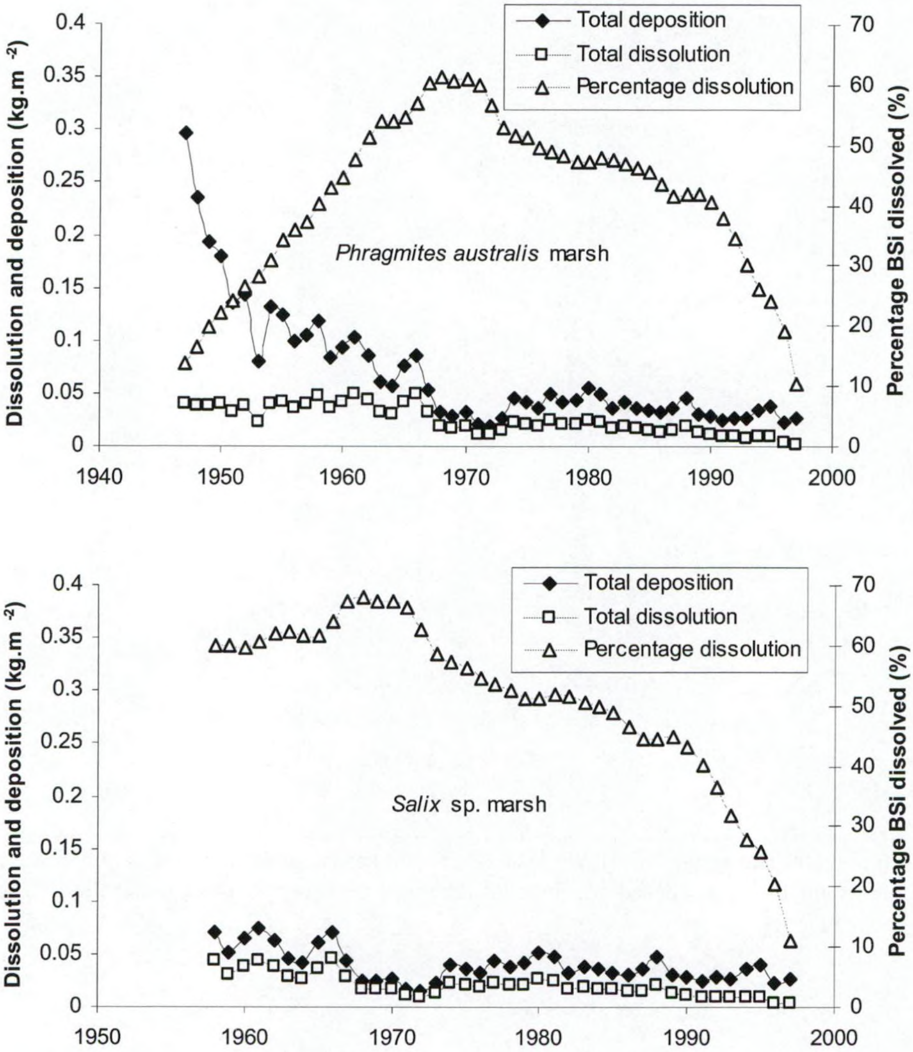

Figure 5.9 Modelled recycling efficiency for BSi in deposited sediments for both marsh sites. The total yearly deposition of BSi on both marsh sites (top *Phragmites australis* site, down *Salix* sp. site) throughout their history is indicated, and compared to the total amount of DSi that was recycled up to the year 2000 from these deposited sediments.

5.5 Discussion

Our results show that the retention and processing of Si by tidal marshes is subject to major changes through the evolution from a young, rapidly rising tidal marsh to an old marsh in equilibrium with mean high water level. Although the modelled depth gradient of BSi content in the freshwater marsh sediments underestimated the observed BSi content in both the upper and lower parts of the sampled cores (possible explanations are discussed below), the results do show the mechanisms which underlie the functional changes in the marsh' role in estuarine Si cycling as the marsh develops.

At the beginning of marsh development, the elevation of the young *P. australis* marsh was far below mean high water level (Figure 5.7c). High sedimentation rates, due to high inundation frequency, height and period, caused a rapid rise of the marsh elevation. As a result, decreasing frequency, height and period of tidal inundation reduced the sedimentation rate and the vertical rise of the marsh (e.g. Allen & Rae 1988; Temmerman et al. 2004). The sedimentation rate directly controls the deposition of BSi, as indicated by the observed correlation between BSi deposition and sediment deposition in 2000-2001. Import of BSi into tidal marshes on a shorter time scale of a single tidal cycle has also been correlated to suspended matter import (chapter 4). Thus, the high sedimentation rate during the early stage of marsh development resulted in a high deposition rate of BSi.

The sedimentation rate also indirectly controls the dissolution of DSi from the deposited sediment. During the first years of marsh development, the high sedimentation rate caused a rapid burial of BSi to deeper sediment layers. The model suggests that about 85 % of the early deposited BSi was buried in this way in the marsh sediments, and became unavailable for recycling to DSi (Figure 5.9a). This estimate assumes that sediments deposited during early marsh development behave similarly to recently deposited sediments, where no decrease in BSi concentration was observed below 50 cm.

As the sedimentation rate decreased with marsh elevation, deposited sediments were subject to BSi dissolution to pore water and subsequent mixture and export with floodwater for a longer time-period, which resulted in a gradual decrease in BSi burial efficiency. BSi concentrations in the sediment decreased concurrently. Since the 1960^{ies} both the *P. australis* and *Salix* sp. marsh have been in equilibrium with the overall linearly rising mean high water level, so that the sedimentation rate was relatively constant during this period (Fig. 5.7c; Temmerman et al. 2003a).

Sediments deposited during the first years of equilibrium are now approximately 50 cm under the marsh surface and BSi at this depth is considered as buried (based on the gradient of BSi content in the sediment). The results indicate that around 40 % of the BSi imported during early equilibrium years has been buried in the marsh sediments. Recycling efficiency of the marsh for BSi imported with suspended matter strongly increased during marsh development, from 15 % for the early young marsh to 60% during the actual stage of equilibrium.

Below 50 cm depth, the fairly constant BSi value in the sampled cores (~ 2.5 mg g^{-1}) was low compared to the modelled BSi-content at these depths (~ 4 mg g^{-1}). This suggests that we might underestimate recycling by excluding it below 50 cm. Diffusion of porewater DSi from deeper layers to the upper 50 cm of sediment porewater could occur, and could be compensated for by additional BSi dissolution at deeper sediment layers. Nevertheless, and although only two seasonal average values of BSi in imported sediment were used, obtained from one year of sampling, the general form of the depth profile of BSi in the marsh sediments could be reconstructed relatively well through this basic mechanism. However, the absolute values of reconstructed and observed BSi content differ, especially in the upper and lower sediment layers within the *P. australis* core.

Functional explanations can be provided for these differences between observed and modelled BSi contents. BSi content in marsh sediment cores has a high spatial variability, even within the same habitat (chapter 2). Both spatial and temporal variability in BSi in imported suspended matter could result in the scatter observed in the sampled marsh cores. The modelled BSi profile strongly underestimated the BSi concentration in the upper sediment layers. The average concentration of BSi in the imported sediment (7.6 mg Si g^{-1} in winter and 10.9 mg Si g^{-1} in summer), which was used in the sedimentation model, is low compared to the observed concentration in the upper parts of the sampled marsh cores (11-12 mg g^{-1}). This difference could be explained by autochthonous marsh diatom development and resulting deposition of BSi. Due to the high concentration of DSi in tidal marsh porewater, the potential for diatom growth is high (Hackney et al. 2000). In addition, *Graminae* vegetations (e.g. *Phragmites australis*) are known to accumulate vast quantities of BSi in the aboveground biomass (Conley 2002). Phytoliths have been found to accumulate in soil samples from several ecosystems (e.g. Bartoli 1983, Runge 1999, Derry et al. 2005), and BSi storage in soils as phytoliths is an essential component in ecosystem Si balances (Conley 2002).

Our decomposition experiments (chapter 6) do however indicate that phytolith burial in the freshwater marsh study site is negligible.

While these factors could also explain the underestimation of BSi concentration in the deepest sediment layers, the low modelled BSi concentrations here could also be explained by an overestimation of dissolution rate during the early marsh development. DSi-flux rates in tidal mudflat sediments (Mortimer et al. 1998; Asmus et al. 2000) have been reported to be both into the sediments and out of the sediment in European temperate estuaries, and high DSi influx rates have been observed. Marsh development on the Notelaar marsh started by the establishment of colonizing marsh plants on a bare mudflat (Temmerman et al. 2003a). Thus, in the early stages of marsh development, influx of DSi into the marsh sediments could have occurred instead of export.

The observation that the Tielrode freshwater marsh was a net sink for Si in the estuarine environment, by comparing import of BSi and export of DSi during whole tidal cycles (chapter 3,4), is in correspondence with the 40 % burial that was observed in this study. The accumulation of BSi enhances the capacity of the freshwater marsh to recycle DSi to the main channel in summer and spring. This study indicates that most of this accumulation occurs during winter due to the high sedimentation rates.

Based on a yearly average concentration of BSi in the freshwater Scheldt of 1.8 mg Si L^{-1} (chapter 4) and a yearly average water discharge of 47 m^3 s^{-1} (Struyf et al. 2004), yearly about 2600 tons of BSi are discharged through the freshwater reaches of the Scheldt. Our deposition data, both modelled and observed, show that yearly about 40 g BSi m^{-2} are deposited on the marsh surface. Freshwater marshes along the Scheldt are approximately 450 ha, so that 180 tons of BSi would accordingly be deposited every year on freshwater marshes along the Scheldt, which is about 7% of the yearly discharge. Conley (1997) estimated that about 16 % of the gross riverine Si load to world oceans is delivered as BSi. The modelled burial data show that retention in tidal marshes could be a significant yet unexplored sink in the biogeochemical cycle of Si, especially on longer time scales. BSi retention in tidal brackish and saltwater marshes is however virtually unstudied. Retention of BSi in saltwater marshes could be less efficient, as recycling capacity of tidal marshes for DSi is expected to increase with salinity. Dissolution of BSi from sediment cores drastically increased from a salinity of 10 ‰ (Yamada & D'Elia 1984).

The recent progress achieved in the study of silica cycling in tidal marshes has stressed the importance of these habitats in the global biogeochemical Si cycle. Human alterations to tidal habitats could have a strong impact on the role these areas play in global Si cycling. Enhanced BSi production as a result of eutrophication (Conley et al. 1993) could enhance the retention of BSi in tidal marshes. Restoration and creation of tidal marshes could initially drastically enhance the retention efficiency for BSi in estuaries, given the high BSi burial efficiency of young, developing marshes. In addition, marshes are very sensitive to environmental changes, such as sea-level rise (Van Wijnen & Bakker 2001; Adam 2002; Temmerman et al. 2004). Increased flooding can degrade marshes to bare tidal mudflats, which could drastically reduce their DSi recycling efficiency. It is clear that more research is needed to relate the local scale ecosystem conclusions to an assessment of the role of tidal marshes in global Si cycling, and to assess human impact on this role.

Our study provided a first estimate of the capacity of freshwater tidal marsh sediments to retain and recycle Si in the estuarine ecosystem on a longer time scale. Although BSi content in the imported sediments was highest in summer, most BSi was deposited on the freshwater marsh during winter, due to the high sedimentation rates. There was a clear correlation between BSi and sediment deposition. The recycling efficiency of BSi deposited in marsh sediments drastically increased through its development from a young rapidly rising marsh to a marsh in equilibrium with mean high water level, from 15 to 60 % respectively. We can conclude that retention of BSi in tidal marshes could be an essential yet overlooked component in the global cycling of Si.

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Chapter 6

Phragmites australis and Si cycling in freshwater tidal marshes

6.1 Abstract

In situ and *ex situ* decomposition experiments were conducted with *Phragmites australis* stems. In a freshwater tidal marsh, litterbags were incubated at different elevations and in both winter and summer. No significant difference in biogenic Si dissolution at different tidal heights was observed. Both in winter and summer, biogenic Si concentrations decreased according to a double exponential decay model in the litterbags (from ca. 60 mg g^{-1} to ca. 15 mg g^{-1} after 133 days). Si was removed much faster from the incubated plant material compared to N and C, resulting in steadily decreasing Si/N (from 7 to 2) and Si/C ratio's (from 0.15 to 0.03) in the litterbags in both winter and summer. *Ex situ*, decomposition experiments were conducted in Scheldt water, treated with a broad-spectrum antibiotic, and compared to results from untreated incubations. The bacterial influence on the dissolution of dissolved Si from *Phragmites australis* stems was only minor: the rate constant for dissolved Si dissolution decreased from 0.004 h^{-1} to 0.003 h^{-1}, but eventual amount of BSi dissolved and saturation concentration in the incubation environment were similar in both untreated and treated experiments. *Phragmites australis* enhances dissolved Si recycling capacity of tidal marshes: in reed-dominated freshwater tidal marshes, more than 40% of DSi export was observed to be attributed to reed decomposition.

6.2 Introduction

Phragmites australis (common reed) is one of the most widely distributed wetland plant species on Earth. In the tidal environment, it is typically a freshwater species, but its salt tolerance allows it to invade brackish and even marine environments (Meyerson et al. 2000a; Soetaert et al. 2004). In Europe, *Phragmites australis* is considered a highly valuable wetland species (Van der Putten 1997). However, in the USA, dense monospecific stands of an invasive non-native genotype (Salstonstall 2002), have outcompeted other native wetland vegetation types, and here common reed is often considered an undesirable pest species (Weinstein & Balletto 1999).

Phragmites australis is a highly competitive species and produces a dense aboveground biomass, typically around 1000 g dry weight m^{-2}, but reported values extent as high as 7700 g dry weight m^{-2} (Soetaert et al. 2004). The dense biomass of *Phragmites australis* is known to have a significant ecological impact on the tidal habitat. The sequestration of N in living and dead biomass is high compared to other species. Nitrogen dynamics in reed dominated tidal wetlands have received a lot of scientific attention (e.g. Meyerson et al. 2000b; Windham & Meyerson 2003). *Phragmites* stands also indirectly affect nutrient cycling, through the oxidation of the rhizosphere (e.g. Armstrong & Armstrong 1988; Sorrell et al. 1997).

The high biomass production results in an abundance of concentrated litter on the marsh floor, which is covered year round with dead *Phragmites australis* material (Meyerson et al. 2000a). The litter generates a roughness layer, which encourages the settlement of particles from flood water, and common reed increases the rate of vertical accretion in wetlands, an interesting finding in the light of considerable losses of marshes as a result of sea-level rise (Rooth et al. 2003).

Despite the substantial scientific attention *P. australis* dominated tidal wetlands have received, Si cycling in these systems has long remained virtually unstudied. The possible role of *Phragmites australis* litter decomposition in marsh Si cycling has as of yet not been quantified. Yet, common reed accumulates large quantities of BSi in its tissue and along the Scheldt tidal freshwater, it was estimated to contain over 90% of all BSi in living freshwater marsh vegetation (chapter 2). The abundance of Si-rich reed litter on freshwater tidal marsh surfaces has a high potential to contribute to the DSi recycling in marshes.

Previous studies on *Phragmites australis* litter decomposition have mainly examined rates of mass loss (e.g. Gessner 2000), patterns of microbial respiration (e.g. Kuehn et al. 2004) and changes in nutrient (N,P,K) concentrations (e.g. Mason & Bryant 1985).

Recently it was hypothesized that Si cycling through the detrital cycle in *Phragmites* vegetations could contribute to the dominance of reed over other plant species through the formation of Si-Al complexes in the rooting zone (Meyerson et al. 2000b). Si-Al complexes have the potential to strongly enhance P fixation in soils, reducing P availability for plant uptake.

We have conducted both *in situ* and *ex situ* experiments to quantify the potential contribution of common reed litter to Si cycling in a freshwater tidal marsh. *In situ*, litterbags were incubated in winter and summer, to identify possible seasonality in DSi dissolution, and at different marsh elevations, to study if higher flooding frequency enhances the rate of DSi dissolution. Concurrently, C and N content of the litter was analysed, to compare DSi dissolution rates to the loss rates of C and N. During the *ex situ* experiments, antibiotics were used to suppress bacterial activity, in order to understand the influence of bacteria on initial leaching of DSi.

6.3 Materials and methods

Study area

Standing dead common reed stems were sampled in the freshwater marsh along the Scheldt estuary near Tielrode (chapter 1.6). The Scheldt water for *ex situ* dissolution experiments was sampled near the Tielrode freshwater marsh. *Ex situ* decomposition experiments were conducted in the freshwater marsh.

Ex situ decomposition experiments

After drying for 30 days at room temperature the reed stems (sampled end of May 2003) were cut into lengths of approximately 10 cm. 10 replicates of 13 g (air-dried) of reed stem material were then incubated in 2 L of 2.5 μm filtered (to avoid interference by diatom dissolution) Scheldt water at 12°C. The full length of the stem was homogeneously present in all replicates. Reed stems were used because they are slowest to decompose as compared to leafs and plumes. A broad-spectrum antibiotic (penicillin-G, streptomycin and neomycin, SIGMA, P3664), an inhibitor of cell-growth for both gram-positive and gram-negative bacteria, was initially added to 5 replica's at a concentration of 10 mL L^{-1} Scheldt water, to suppress bacterial contribution to DSi dissolution. The P3664 treatment was repeated every 10 days.

The initial DSi concentration in the filtered Scheldt water was 0.026 mg Si L^{-1}. DSi concentration in the incubation water was analysed after 24h, 72h and then approximately every 72h. Concentrations were corrected for evaporation and used to calculate the amount of DSi released from the incubated reed stems. After 67 days, when an equilibrium concentration had been reached in the incubations, the water was completely refreshed with newly sampled and filtered (2.5μm) Scheldt water with an initial DSi concentration of 0.23 mg Si L^{-1}.

In situ decomposition experiments

Reed stems were sampled 30 days before incubation. After drying for 30 days at room temperature, the reed stems were cut into equal lengths of approximately 2 cm. Litterbags (1 mm mesh size) were filled with 2 g of air dry stem material.

On 12/11/2003, 135 litterbags were incubated in the freshwater marsh: 45 were incubated at 5.35 m TAW (TAW = Belgian Ordnance Level, corresponding to the height of mean sea level at low tide), 45 at 5.55 m TAW and 45 at 5.75 m TAW. Flooding frequencies for these elevations were respectively 76 %, 65 % and 49 % of the tides (based on 2002 tidal data). At each elevation, 5 litterbags were sampled after 9, 20, 34, 56, 69, 86, 101 and 133 days. A similar experiment was conducted in summer 2004. On 31/05/2004, at an elevation of 5.35 m TAW, 60 litterbags were incubated. 10 litterbags were sampled after 10, 25, 40, 53, 70 and 98 days.

Sediment was removed from the sampled litterbags; the content was then dried at 80°C for 48 hours. After drying, remaining dry mass was determined and the plant material was ground with a motor mill and analysed for BSi, N and C content.

Analysis

To extract biogenic silica, 25 mg of grounded plant material was incubated for 4 hours in 0.1 M Na_2CO_3. Dissolved silica was analysed spectrophotometrically on an IRIS ICP. N and C were analysed through dynamic flash combustion on a "NC 2100 SOIL" (Carlo Erba Instruments).

6.4 Results

Ex situ decomposition experiments

The initial BSi concentration in the incubated reed litter was 60 mg BSi g^{-1} air dry weight of reed material. The exponential increase in BSi dissolved per gram incubated plant dry weight, fitted very well to a first order exponential increase model (Greenwood et al. 2001) of the form "$C_t = C_{sat}(1-e^{-kt})$", in which C_t is BSi dissolved at time t, C_{sat} is BSi dissolved at saturation concentration in the incubation water and k is the dissolution rate constant (Fig. 6.1). In the non-P3364-treated replicates, the amount of dissolved BSi increased exponentially to a saturation constant of 8,8 mg BSi g^{-1} incubated plant dry weight. In the P3664-treated replicates, the saturation constant was 8.6 mg BSi g^{-1}. The dissolution rate constant was higher in the non-treated experiments than in P3664-treated sediments (0.0040 h^{-1} and 0.0030 h^{-1}). After refreshing of the incubation water, the same first order exponential increase models as fitted on the pre-refreshing data, still fitted for both the P3664 and non-P3664 treatment (Fig. 6.1).

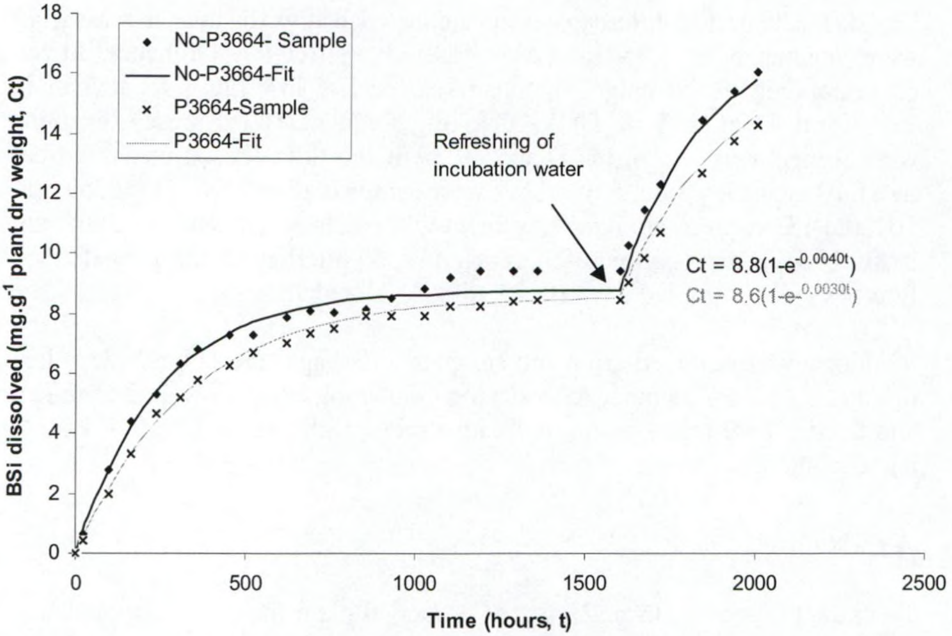

Figure 6.1 Average BSi dissolved from Phragmites australis stems during the ex situ incubation experiments. P3664-samples were treated with the broad-spectrum antibiotic P3664. Initial DSi incubation concentration was 0.026 mg Si L-1. After refreshing of incubation water, DSi concentration was reduced again to 0.23 mg Si L^{-1}.

In situ decomposition experiments

Silica

BSi content decreased rapidly in the incubated litterbags during both winter and summer experiments. No consistent increase or decrease of BSi dissolution with flooding frequency was observed (Fig. 6.2a,b). Observed BSi dissolution during the winter experiment was highest at the intermediate flooding frequency (555 cm TAW) and lowest at the highest flooding frequency (535 cm TAW). After 133 days, only between 9-20 % of the incubated BSi had not yet been dissolved.

The decrease in BSi concentration in the litterbags averaged for all flooding frequencies is nicely fitted by a composite exponential decay model (Fig. 6.2c) of the form "$B_t = (B_0\text{-}B_1)e^{(-Lt)} + B_1e^{(-Rt)}$", in which B_t is the BSi concentration at time t, B_0 is the initial BSi concentration at incubation, B_1 is the refractory portion of BSi and R and L are rate constants for respectively the initial fast BSi dissolution and the subsequent slow BSi dissolution (Carpenter 1982). A composite exponential decay model recognizes inherent heterogeneity of plant detritus and assumes that litter can be partitioned into two components, an easily decomposed and a more refractory fraction. Organic matter decay according to a two-component model has been observed in both equatorial Pacific sediments (Hammond et al. 1996) and during bacterial decomposition of plankton (Westrich & Berner 1984).

To test potential seasonality in BSi dissolution, the litterbag experiment was repeated at one marsh elevation in summer. Initial concentration of BSi in the litterbags was much lower in summer compared to winter (56 $mg.g^{-1}$ vs. 39 $mg.g^{-1}$). If this is taken into account, by setting the incubation time for the summer litterbags from day 0 to day 4, the summer litterbag data are nicely fitted by the composite exponential decrease observed in winter (Fig. 6.2c). The composite exponential decrease model observed in both winter and summer suggests that over 98 % of BSi in reed litterfall is recycled to DSi in 365 days.

Biomass, nitrogen and carbon

Remaining average biomass decreased gradually in both winter and summer in the incubated litterbags (Fig. 6.3). The decrease was faster in summer than winter. In winter, initial C concentrations in the incubated litter were lower than in summer, while N concentrations were initially higher in winter (Fig. 6.4a,b). N concentrations doubled in summer and remained constant in winter. C concentrations were between 346 and 415 mg g^{-1} during the complete incubation period in both winter and summer. Si dissolved much faster compared to N and C, and Si/N and Si/C ratio's rapidly decreased during the decomposition process (Fig 6.4c,d). There was an increase in C/N ratio in both winter (from 45 to 63) and summer (from 72 to 94) in the initial 10 days of incubation. Afterwards, the C/N ratio remained constant at around 60 in winter, while it decreased from 94 to 40 in summer.

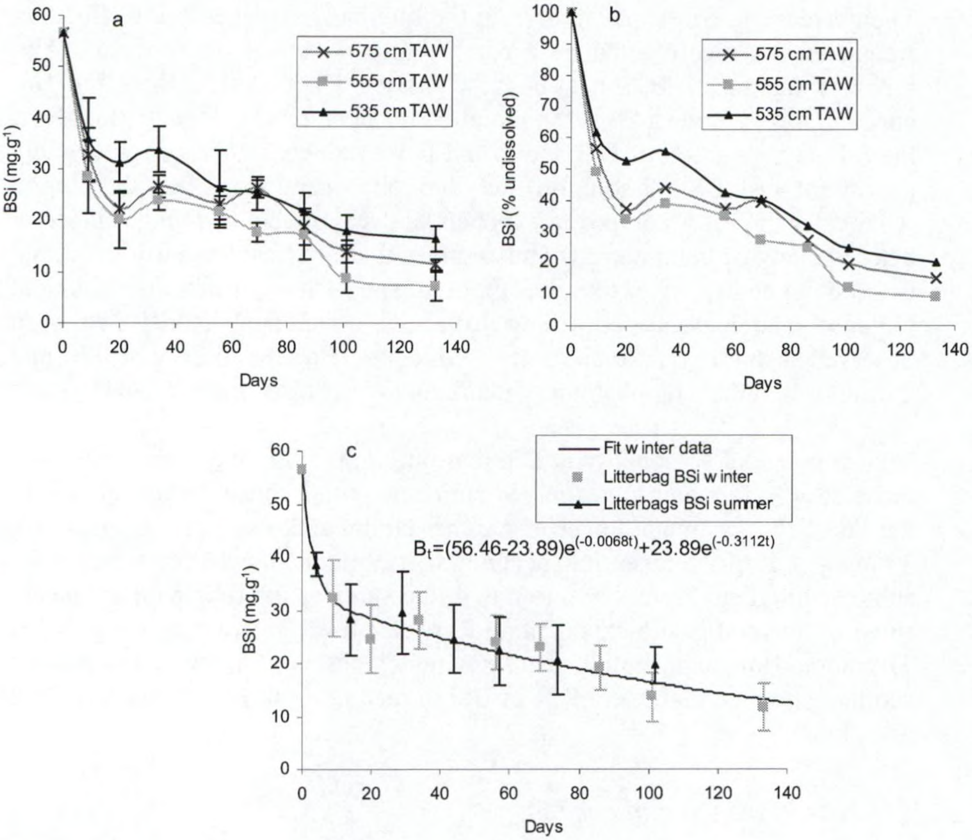

Figure 6.2 *Phragmites australis* during *in situ* decomposition experiments a) The average decrease in BSi concentration in litterbags incubated at different elevations (TAW = height above mean low sea level) in winter 2003-2004. b) Percentage of BSi dissolved during the winter incubation at different elevations. c) Comparison of average decrease in BSi concentration in litterbags in summer and winter. The double exponential model was fitted to the winter data.

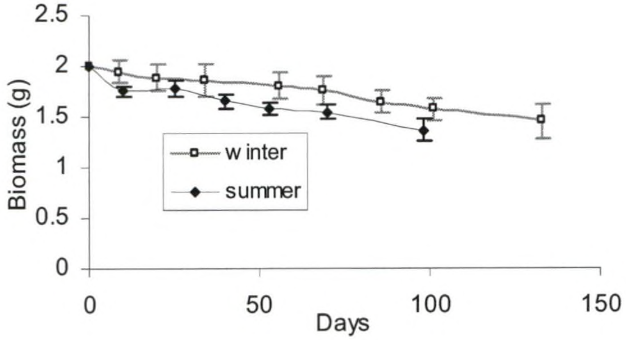

Figure 6.3 Average biomass decrease in *Phragmites australis* stems incubated in summer and winter 2003-2004.

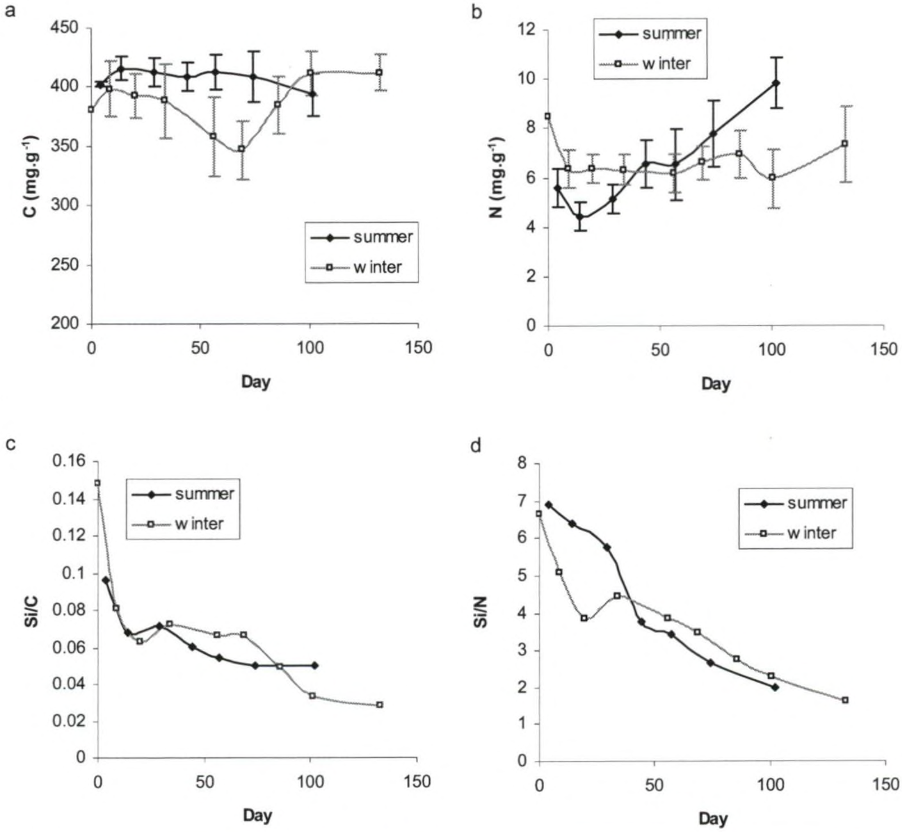

Figure 6.4 Carbon (a) and nitrogen (b) content in *Phragmites australis* stems in litterbags incubated in summer and winter. The Si/C ratio (c) and Si/N ratio (d) in the incubated litterbags.

6.5 Discussion

Our experiments showed that bacterial activity is only of minor influence in the dissolution of DSi from reed litter. The initial dissolution rate was lower in the experiments treated with antibiotics, but the eventual influence on turnover time of the reed was negligible. A similar conclusion could also be drawn from the absence of any difference in BSi dissolution during summer and winter *in situ* experiments. This in large contrast with studies on diatom BSi dissolution. Diatom frustules are coated by a three layer (polysaccharide, lipid and protein layer) organic coating (Hecky et al. 1973). DSi dissolution from diatoms is dramatically enhanced when bacterial degradation removes the protective organic matrix (Patrick & Holding 1985; Bidle & Azam 1999). Hydrated amorphous Si in plants is mainly deposited in cell walls, cell lumens and external layers, and is as a result probably more directly available for dissolution compared to diatom BSi. The deposited silicon provides rigidity to plant tissues and enhances protection against abiotic and biotic stresses (Epstein 1999).

The dissolution of BSi was independent of the flooding frequency in our experiments. This may indicate that the main part of the BSi does not dissolve directly into the flooding water, but to the marsh porewater in between tidal flooding events. This is consistent with the observation that almost all export of DSi observed from the studied freshwater marsh to the main channel (chapter 3 and 4) was attributable to export during the seepage water phase, which is a mixture of flood water and porewater, slowly flowing out of the marsh between two tidal floodings.

Si was removed from the decomposing plant litter much faster in comparison to N and C, resulting in steadily decreasing Si/(C,N) ratio's. This is in contrast with observations by Eleuterius & Lanning (1987), who observed continuously increasing Si content in decomposing *Juncus roemerianus* leafs. In the *Juncus roemerianus* study, decomposition was in standing dead leafs, mainly by saprophytic fungi. This indicated that Si was removed from the *Juncus roemerianus* leafs only after collapse, as opposed to N and C, which were already removed in the standing leafs. Similar processes could cause the high Si content in the standing dead reed stems.

During our summer experiment, the relative increase in N content in the decomposing litter added to the decreasing Si/N ratio. Increasing N content in decomposing *Phragmites* (*communis* and *australis*) litter has been attributed to the uptake of N by microorganisms, associated with the decomposing litter (Mason & Bryant 1975; Dinka et al. 2004). The N-content in the decomposing litter in our study was similar to this studies.

The fast dissolution of DSi from decomposing reed litter might add to the DSi recycling capacity of tidal marshes in estuarine systems. Tidal marshes have been found to import BSi, while on the other hand exporting DSi (chapter 3 and 4). Sediment BSi, imported into the marsh along with suspended solids at high tides, is recycled slowly. After approximately 30 years, 60 % of the BSi in an old (= elevation approximately in equilibrium with the mean higher water level) Scheldt freshwater marsh had been recycled to DSi (chapter 5). In comparison, the BSi recycling from the *Phragmites australis* vegetation is much faster. The reed vegetation in tidal areas is highly dynamic. In the study site, it was observed that at peak biomass (September), 2 in 10 standing *Phragmites australis* stems in reed dominated vegetation were dead (1872 shoots counted in 24 plots, chapter 2). This is an indication that approximately 80 % of the shoots from the previous growing season had collapsed, while litterbag results suggest that once a reed shoot collapses, over 98 % of Si dissolves within one year. A BSi stock study in the Tielrode freshwater marsh indicated that vegetation in the 3500 m^2 area contained approximately 115 kg of BSi, 111 of which were attributable to *Phragmites australis* (chapter 2). This *Phragmites australis* BSi can almost completely be recycled in one year, due to the highly dynamic character and high DSi dissolution rate in the *Phragmites australis* vegetation.

Although BSi content in the *Phragmites australis* vegetation in the studied freshwater marsh was low compared to sediment BSi content (approximately 5300 kg in the upper 30 cm for the full 3500 m^2) (chapter 2), yearly flux of DSi from the sediment was modelled (chapter 5) to be similar, 40 g m^{-2} or 140 kg for the total 3500 m$^{2.}$ This indicates equal contribution of reed litter and sediment to marsh DSi recycling capacity.

Moreover, in the Tielrode marsh, *Phragmites australis* vegetation had significantly higher DSi concentrations in porewater compared to tall-herb and *Salix* sp. vegetations (chapter 2), which could be contributed to the observed rapid dissolution of DSi from the reed litter. This clearly shows that *Phragmites australis* is a high turnover sink for BSi in tidal marshes, which through rapid recycling has the potential to enhance Si cycling in tidal marshes. This could add new insight in the ecological value of *Phragmites australis,* often considered an undesirable pest species in the USA (Weinstein & Balletto 1999). *Phragmites australis* vegetations have the potential to actively enhance DSi export from tidal marshes.

We can conclude that although *Phragmites australis* vegetation comprises only a small stock of BSi in tidal marshes as opposed to sediment, it is also a far more rapidly recyclable sink as compared to sediment. Moreover, DSi recycling from reed litter in tidal marshes is almost 100 %, as opposed to sediment, where around 40 % of imported BSi is buried and becomes unavailable for recycling. *Phragmites australis* actively enhances Si cycling in tidal environments, and this could be essential in its dominance in the system, not only through the beneficial effects of Si fixation in plant tissue (Epstein 1999), but also through formation of Si-Al complexes in the rooting zone (Meyerson et al. 2000b). Si-Al complexes have the potential to strongly enhance P fixation in soils, reducing P availability for plant uptake.

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Chapter 7

Conclusions

7.1 Si cycling in freshwater marshes

The mechanism of recycling DSi in marshes

The main hypothesis was confirmed: tidal freshwater marshes do recycle BSi to DSi. The mechanism supporting the observed recycling became clear from the different chapters. Tidal freshwater marshes store large amounts of biogenically fixed Si in vegetation and in sediment. BSi is easily soluble if compared to lithogenic Si. Dissolution of BSi results in high porewater concentrations of DSi in the marsh sediment. Porewater concentrations can be more than 7 times higher than the concentration of DSi in inundation water in summer.

At the highest tides, when the marsh surface is flooded, the porewater is entrained by inundation water from the main estuarine channel. The mixing of DSi-poor flooding water with DSi-enriched porewater results in a steady outflow of seepage water between tides, which year round contains DSi concentrations similar to winter concentrations of DSi in the estuary. It is this seepage water which controls the export of DSi from the studied freshwater marsh. As the enrichment is highest in summer, the highest percentual export of DSi, and highest surface averaged DSi export, was observed in summer.

Although both sediment and vegetation have a similar role in this scheme, a recyclable stock of BSi, the rate of dissolution and the amount of BSi stored in both sinks was quite different. Below, these differences are summarized and put into the perspective of the whole freshwater marsh DSi recycling process.

Vegetation: a small, but rapidly recycled sink for Si

Although all dominant plant species contained BSi in amounts higher than the detection limit, the marsh grass *Phragmites australis* was the only species with a significant influence on freshwater marsh Si cycling. In the total study area, the aboveground non-*Salix* biomass was 4.2 ton (+/-2.6 ton), 62% of which *Phragmites australis*; however, 96 % of the 116 kg (+/-7 kg) of Si in the plant biomass was biologically fixed in the reed. *Salix* contained such low amounts of BSi, that it could easily be considered insignificant. The belowground biomass, except for reed rhizomes, contained almost no BSi.

Decomposition experiments showed that once a reed shoot has collapsed, the BSi dissolves very rapidly into DSi. Considering the highly dynamic character of the reed vegetation, we concluded that the plant community in the marsh is almost self-sufficient in regard to Si, with almost one hundred percent recycling of biologically fixed BSi to DSi within a single year.

This is a conceptual view on the process. In reality, the vegetation takes up DSi from the marsh porewater, and the continuously decomposing litter layer enhances the DSi porewater concentrations in the tidal marsh, and thus adds to the recycling capacity for DSi of the marsh. According to the calculations, around 50 % of marsh DSi export could be attributable to *Phragmites australis* litter.

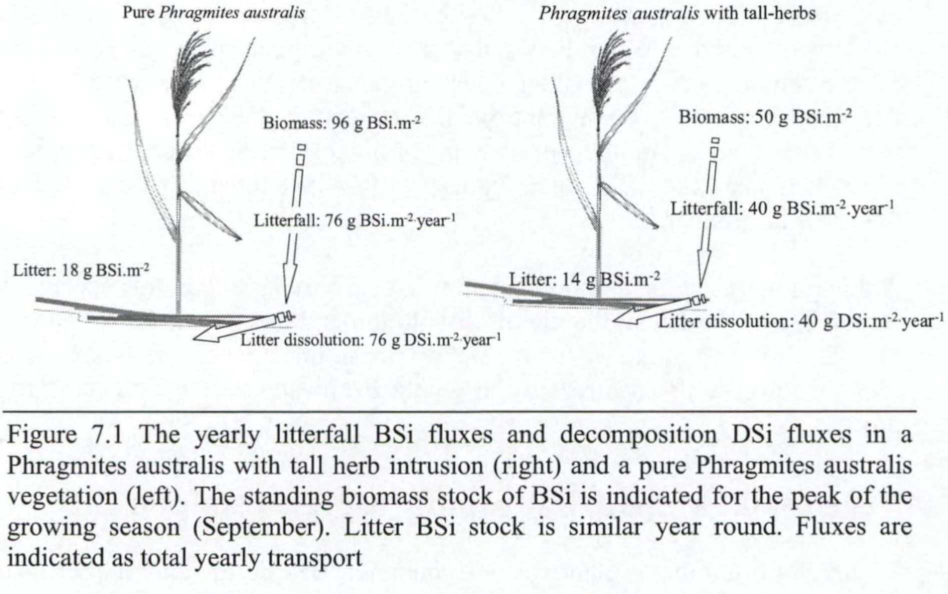


Figure 7.1 The yearly litterfall BSi fluxes and decomposition DSi fluxes in a Phragmites australis with tall herb intrusion (right) and a pure Phragmites australis vegetation (left). The standing biomass stock of BSi is indicated for the peak of the growing season (September). Litter BSi stock is similar year round. Fluxes are indicated as total yearly transport

The porewater DSi concentrations were higher in the pure *Phragmites australis* vegetation compared to the other vegetation types, which most likely is the result of the fast recycling capacity of the reed fixed BSi, once a reed shoot has collapsed. This indicates that *Phragmites australis* can actively enhance Si recycling in freshwater marshes. This might even prove to be a competitive advantage. Through the formation of Si-Al complexes in the rooting zone with a high affinity for phosphorus, *P. australis* could reduce P-availability for its competitors.

Future research might study if reed contains more BSi in sites where external pressures (flooding frequency, sheer stress during flooding) are high. BSi in plants can provide the plant rigidity and resistance to stress. Individuals containing high BSi concentrations in their tissue might have a competitive advantage in sites with high physical stress exposure. The dominance of reed in freshwater marshes of the Scheldt could partially be the result of the high capacity of the species to accumulate Si.

The sediment: A large, slowly recycled sink for Si

Sediment was by far the largest sink for BSi in freshwater marshes along the Scheldt. In the upper 30 cm of sediment, the 3500 m^2 study area of Tielrode stored around 5 tons of BSi, as compared to the 116 kg of BSi stored in plants. BSi is delivered to the sediment each spring tide: it is deposited on the marsh surface along with settling suspended matter. In a marsh with an elevation in equilibrium with mean high water level, around 40-80 g BSi m^{-2} is deposited each year. The BSi in the sediment is recyclable: after suspended matter is deposited on the marsh surface, BSi slowly dissolves, resulting in gradually decreasing BSi concentrations in the sediment with depth.

The sediment might be by far the largest stock for BSi in the marsh, it is also recycling much slower compared to the vegetation. Around 40 g DSi m^{-2} is dissolved each year, which results in a yearly export of 140 kg of DSi from the sediment, which is comparable to the amount of DSi released through decomposition (+/- 100 kg). As opposed to the BSi in vegetation, not all sediment BSi is ultimately recycled to DSi. In an old, developed marsh system, around 40 % of the imported BSi is eventually buried, and lost to the estuarine ecosystem on biological timescales. In a young developing marsh with a high sedimentation rate, recycling of BSi in the sediments is much lower, and over 80 % of initially deposited BSi is eventually lost to the system. The residence time for sediment BSi is much longer compared to plant BSi. Plant BSi is fully recycled within one year. Sediment BSi is only recycled for 60% after approximately 35 years.

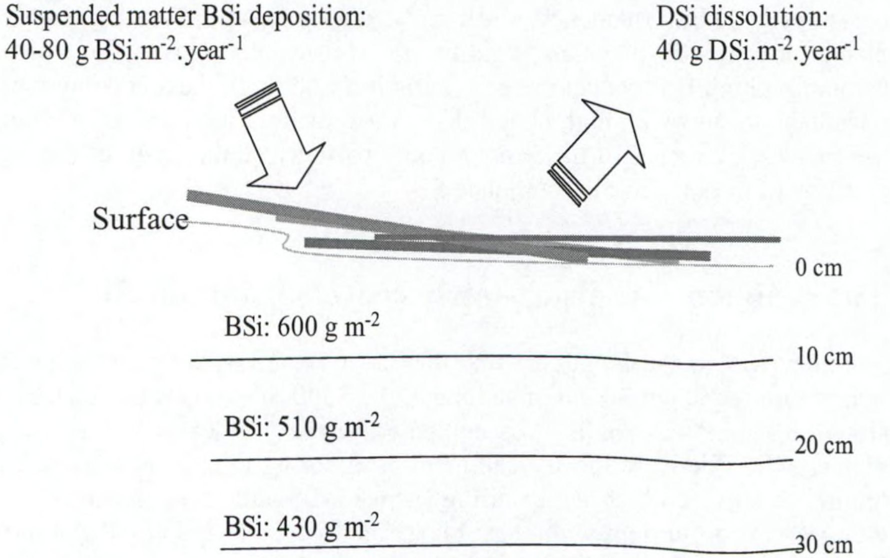


Figure 7.2 The yearly deposition of BSi on the marsh floor through sediment settling (in all vegetation types) compared to the dissolution flux to the porewater and the stocks of BSi in three different layers (0-10 cm, 10-20 cm, 20-30 cm) of the sediment. The flux of dissolved DSi to the porewater is either taken up by plants or exported from the marsh in the seepage water.

The complete flux scheme for Si in the Tielrode marsh

Based on the fluxes observed during 6 tidal cycles year round, we can estimate the yearly fluxes of DSi and BSi to and from the tidal marsh area. Based on the DTM, we can exactly calculate how much of the marsh area of 3500 m^2 is inundated at a particular tidal height (Figure 7.3)

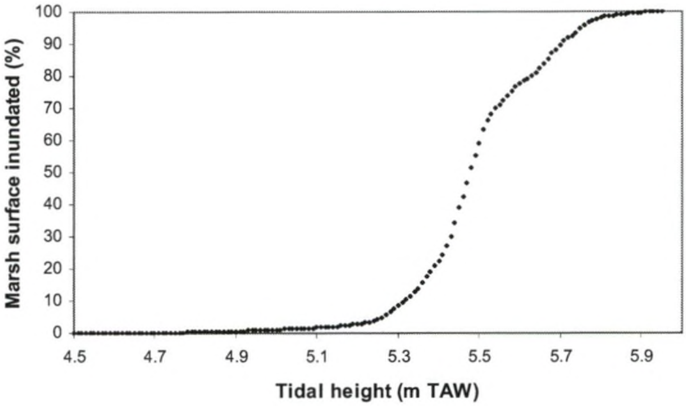


Figure 7.3 The percentage of the Tielrode marsh that is inundated at a particular tidal height. Tidal height is indicated in m TAW, the Belgian national tidal reference.

Based on these inundation date, we can estimate (from average tidal data) that the total marsh area is inundated around 20-30 days each year (there is more days of inundation, but in this calculation, 2 days of 50 % inundation equals 1 day of full inundation). If we then consider the average exchange observed during the tidal cycles (= 73 mg m^{-2} h^{-1} DSi, 165 mg m^{-2} h^{-1} BSi) we are now able to calculate the yearly export of DSi and import of BSi. The combined knowledge obtained from sink and flux studies can then result in a completed schedule of Si cycling within the Tielrode freshwater marsh.

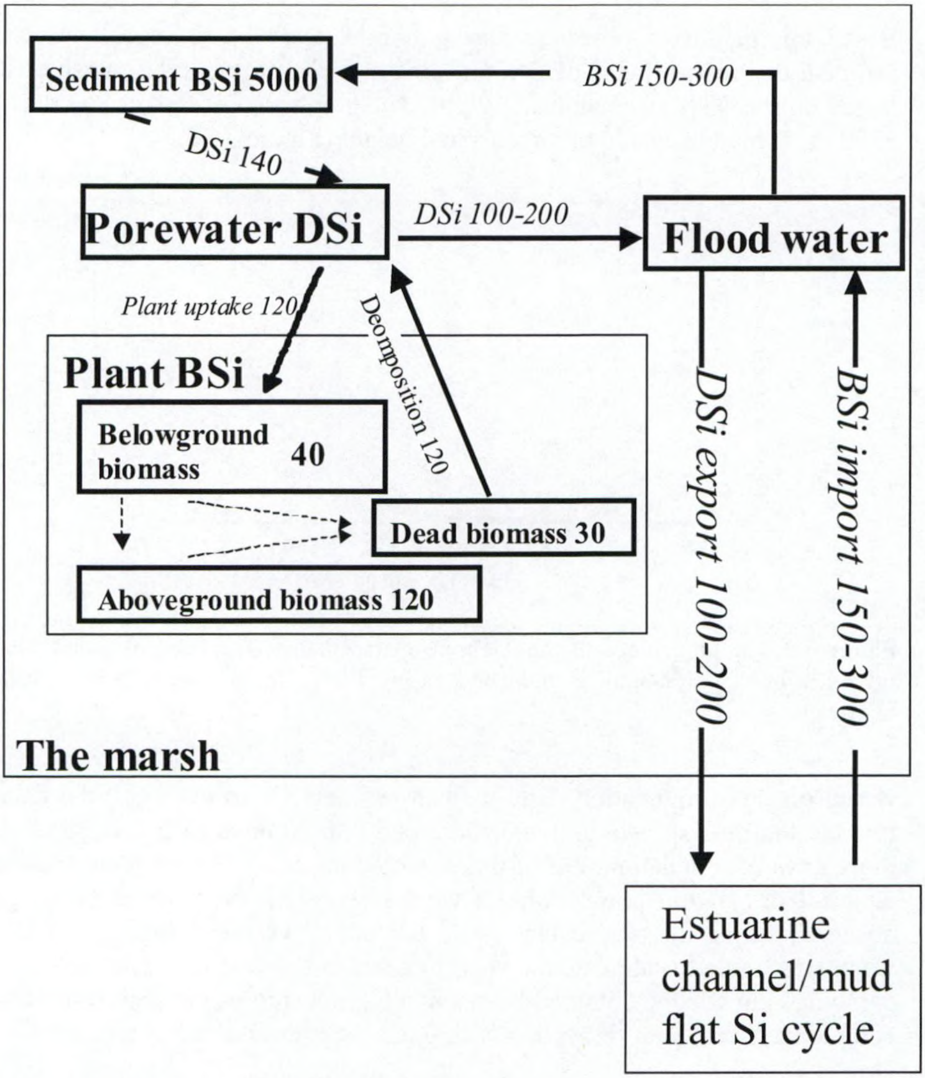


Figure 7.4 The freshwater marsh Si cycling in the 3500 m^2 study area near Tielrode. All numbers are in kg Si. Fluxes (in *italics*) are indicated as yearly total fluxes. Stocks of Si in sediment and vegetation are indicated in bold, and are the total stocks for the complete 3500 m^2 area. Stocks in vegetation are for the peak of the growing season. Stocks in sediment are not subject to seasonal change. The marsh and the estuarine channel are indicated as interacting compartments.

7.2 Tidal marshes, global Si cycling and eutrophication

Case study 1: Does marsh Si recycling matter?

From chapters 3 and 4, it is clear that freshwater marsh DSi recycling capacity is small, compared to yearly discharged loads of DSi in the freshwater estuary (0.5-3%). However, extrapolations indicated that freshwater marshes will become major contributors to DSi discharge in summer (up to 50% or higher). In this case study , the knowledge gathered in previous chapters is applied to provide a more detailed answer to some interesting questions: What is the impact of marshes on the total flux and processing of DSi in the Scheldt estuary? How does processing in different salinity regions compare? Can marshes really affect the flux of DSi from estuaries to the oceans?

In order to provide a more backed-up answer to these questions, we looked in detail to the year round estimated export of DSi for all marshes along the full length of the Scheldt estuary, applying for every tidal cycle, the empirically found exponential relationship between ambient DSi-concentrations and percentual export of DSi (chapter 4). This also allowed us to compare the estimated export from saltmarshes (which cover a much larger surface along the Scheldt) to the export from freshwater marshes, resulting in a “map” of major recycling spots along the estuary. In the end, this allowed us to estimate the total recycling capacity of all marshes of the Scheldt estuary.

This exercise was done twice, once for a dry year (2004) and once for a wet year (2000). As the concentrations of DSi in the Scheldt estuary are discharge-dependent, a significant difference in export of DSi from marshes to the main channel is expected between a dry and wet year. In years of high discharge, the DSi concentrations tend to stay high, as diatom communities are flushed away. In years of low discharge, high DSi uptake by diatom communities leads to very low DSi-concentrations.

Based on average height of tidal marshes in 14 compartments along the estuary (from the upper tidal reaches to the mouth of the estuary), the actual measured tidal heights, and DSi concentrations as measured during a monthly monitoring campaign along the full length of the estuary, we could estimate the DSi export from all tidal marshes along the estuary.

Results are summarized for freshwater marshes (ca. 450 ha of marsh), brackish water marshes (170 ha) and saltwater marshes (2500 ha). The total export of DSi from the marshes was highest in the saltwater in both years (Figure 7.5a,b): available marsh surface is much higher here, and concentrations of DSi are low year round, due to the conservative mixing of estuarine water with seawater. In a wet year, export was lower, mainly because DSi concentrations are higher due to enhanced influence of advective water transport (Fig. 7.5a). In the freshwater (Fig. 7.5a,b) and brackish zone, there is almost no export of DSi from marshes in a wet year: the driving force for export is very low, as high DSi-concentrations occur in the flooding water year round (Fig. 7.5c). However, in dry years, DSi concentrations in the tidal freshwater can drop to near zero (Fig. 7.5d), and DSi export from the marshes concurrently rises.

If we surface average the DSi export, the year round occurrence of low DSi concentrations in the saltwater leads to highest export in the most downstream saltwater marshes (Fig. 7.6a,b). On a yearly basis, saltwater marshes are therefore the single most important recycling spots. However, in the summer of a dry year, the surface averaged export of freshwater marshes becomes equal to that of the saltwater marshes. This indicates that freshwater marshes are equally important compared to saltwater marshes when recycling really matters: in periods of DSi depletion (Fig. 7.6a,b).

In a wet year, the total calculated DSi export from all marshes along the Scheldt estuary was 580 ton, while in the dry year 2004, 1,335 ton of DSi was exported from the tidal marshes. The total export of DSi from the Scheldt to the North Sea at Vlissingen varies from 18,000 to 32,000 ton a year (Struyf et al. 2004), with highest loadings observed in years of high discharge. In a dry year, the amount of DSi exported from marshes amounts to 7% of the total yearly DSi load eventually delivered to the North Sea. In chapter 5, it was also shown that marshes can significantly affect the BSi transport through estuaries to the ocean. Both observations about DSi and BSi fluxes to and from marshes show that marsh processing of Si in the estuarine environment can be an important factor in the global Si cycle. The maximal observed monthly DSi export from tidal marshes in summer was 20 ton for freshwater marshes, and 120 ton for the saltwater marshes. The lowest DSi discharges observed at the mouth and in the freshwater estuary (Struyf et al. 2004) averaged (average for 5 lowest observations) 280 and 20 tons respectively. Comparison of both discharge data clearly validates the conclusions of chapter 3 and 4: in summer months marshes can become major suppliers of DSi for the local diatom community, both in the upper and lower reaches of the estuary.

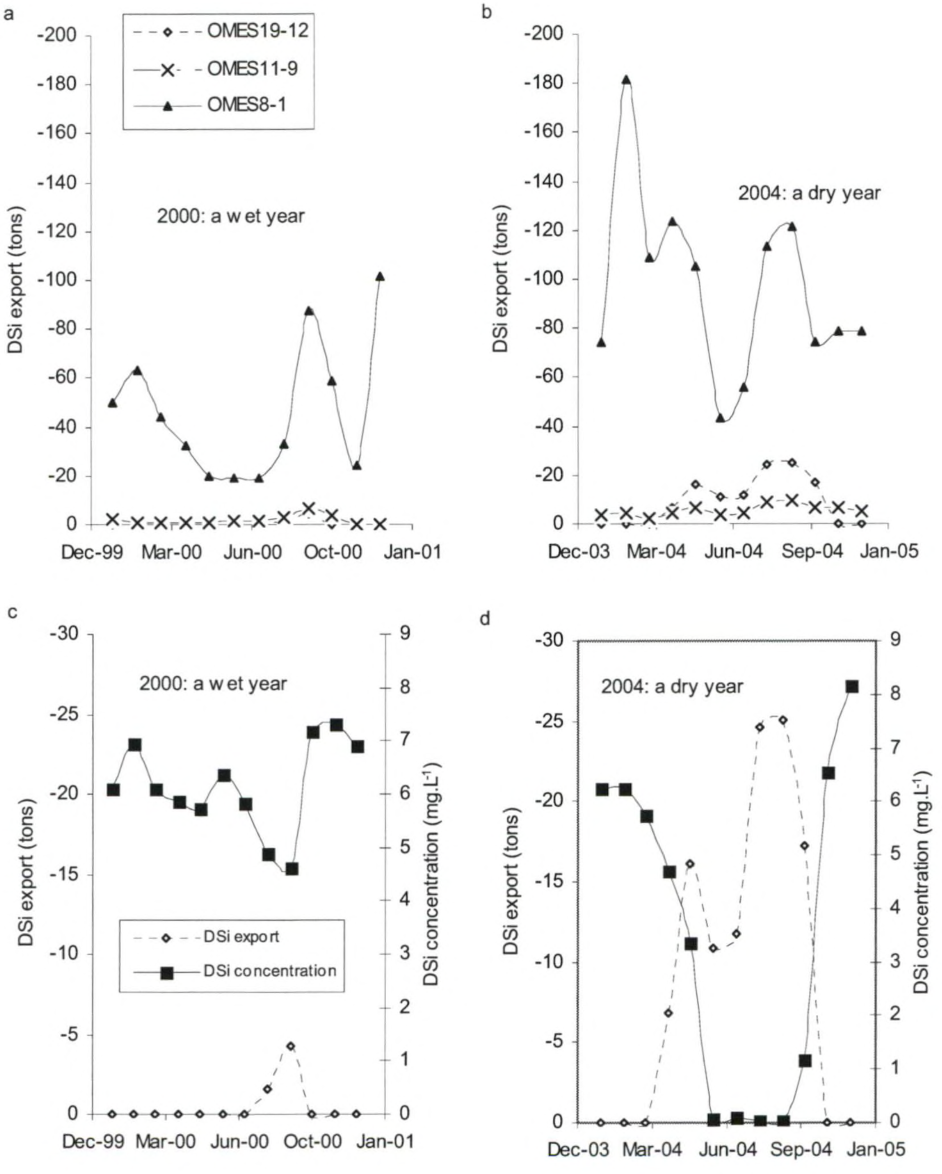
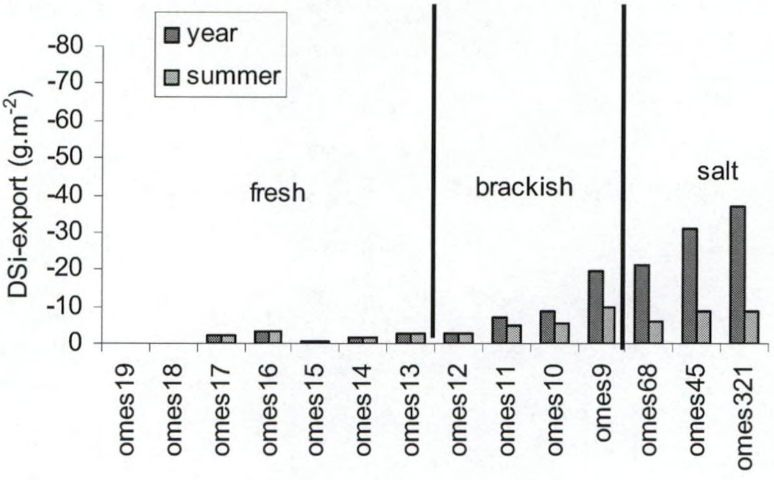
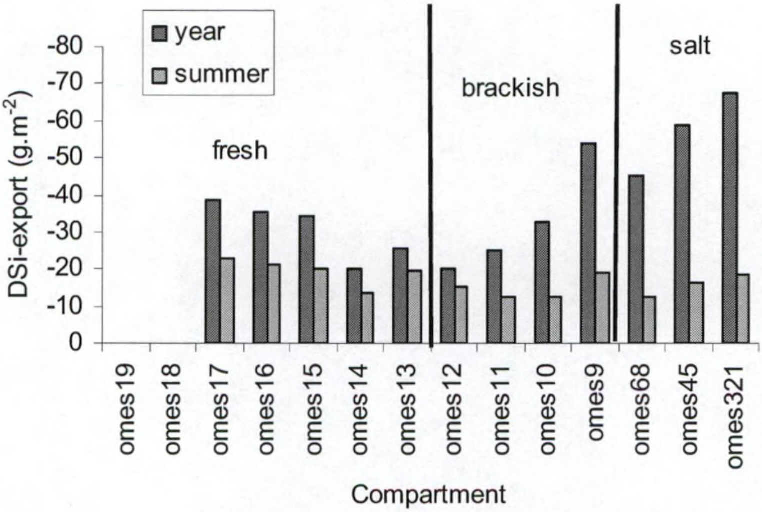


Figure 7.5 (a,b): The total monthly fluxes of DSi from tidal marshes along the Scheldt in the freshwater (omes 19-12), brackish (omes 11-9) and saltwater (omes 8-1) estuary in a wet (a, 2000) and a dry year (b,2004). (c,d): the monthly DSi fluxes in the freshwater in detail, compared to DSi concentration in the freshwater estuary, for a wet and dry year (c = wet, d =dry).





Figuur 7.6 The surface averaged yearly export of DSi for 14 compartments along the Scheldt, from the OMES monitoring campaign (OMES 19 = upper tidal fresh, OMES 1 = mouth), ompared to the toal export observed during summer month (June-September). A wet year(upper graph, 2000) and a dry year (down, 2004) were studied. The boarders of the freshwater, brackish and saltwater are indicated by vertical lines.

Case study 2: Is marsh restoration an option to reduce Si-limitation?

Si limitation is a problem not uncommon to the Scheldt estuary. If we consider that a Si:P ratio smaller than 3 is indicative of Si-limitation, we can conclude that nutrients are delivered in ecologically imbalanced ratio's near the mouth of the estuary during large periods of the growing season, especially in dry years (see Chapter 1, introduction). This case study aims to uncover if it could be possible to, through the restoration of tidal marshes, import the necessary DSi to bring the Si:P (P is limiting if compared to N in the Scheldt estuary) ratio's in the Scheldt estuary to a healthy balance again, and reduce the frequency of occurrence and severity of Si limitation events.

For this study, the total discharged loads of DSi and dissolved phosphorus were compared for the period 1996-2000, both in the freshwater estuary and near the estuarine mouth (Struyf et al. 2004). Months were considered as "problem months", if the molar ratio of Si load to P load was smaller than three. Six problem months occurred in the freshwater and eight near the estuarine mouth. The molar monthly ratio in the freshwater was 0.23 at its lowest, and near the mouth the lowest observed ratio was 0.66 (Table 7.1).

	Vlissingen			Dendermonde		
	PO_4^{3-} kmol	DSi kmol	$DSi:PO_4^{3-}$	PO_4^{3-} kmol	DSi kmol	$DSi:PO_4^{3-}$
May-96	5744	16509	2.87	*	*	*
July-96	6721	4469	0.66	455	393	0.86
August-96	8532	17788	2.08	2224	4651	2.09
May-97	5900	9268	1.57	*	*	*
June-97	7290	15783	2.17	*	*	*
August-97	6022	8128	1.35	*	*	*
September-97	8115	23350	2.88	411	990	2.41
July-98	5006	12200	2.44	*	*	*
August-98	*	*	*	732	166	0.23
August-99	*	*	*	1226	920	0.75
September-99	*	*	*	1007	1049	1.04

Table 7.1 The total molar discharge of PO_4^{3-} and DSi at Vlissingen (mouth of the estuary) and Dendermonde (central tidal freshwater) during all months in the period 1996-2000 in which the $DSi:PO_4^{3-}$ discharge ratio was smaller than 3 at one of both or both locations. Indicated discharges are in kmol. * = ratio was higher than 3.

Based on the data from the first case study, but also on the export data as observed during the whole ecosystem exchange studies (chapter 3 and 4) and the export data from the Notelaar marsh (chapter 5), we estimated an average monthly export of DSi from tidal marshes, both saltwater and freshwater, of 5000 mg (or 0.18 mol) per squared meter in a summer month with DSi depletion. Based on this surface based export, we then calculated the amount of marsh needed to increase the DSi loading in such a way, that Si:P ratio's would become higher than 3.

In the freshwater, it was found that around 1500 ha of extra tidal marshes, could be enough to solve the problem in all of the six problem months (Table 7.2). For the saltwater, 1500 ha was only enough in 3 of the 8 problem months, and up to 8800 ha was required to solve all Si limitation problems (Table 7.2).

	Vlissingen		Dendermonde	
	DSi required kmol	Ha required x10000 m^2	DSi required kmol	Ha required x10000 m^2
May-96	725	406	*	*
July-96	15695	8789	974	545
August-96	7808	4372	2022	1132
May-97	8432	4721	*	*
June-97	6087	3408	*	*
August-97	9938	5565	*	*
September-97	996	558	244	136
July-98	2818	1578	*	*
August-98	*	*	2029	1136
August-99	*	*	2760	1545
September-99	*	*	1973	1105

Table 7.2 The required amount of extra DSi for all "problem months" (see table 7.1) to increase the DSi: PO_4^{3-} ratio to 3. The required surface of marsh to restore is indicated, to export the necessary extra DSi, based on observed flux data of DSi from tidal marshes.

Although pelagic recycling of BSi and phosphorus and the role of marshes as sinks for dissolved P were not considered, these calculations do give a clear indication that restoration of marsh habitat might be a useful way to prevent Si limitation events. However, it is necessary to take into account that recently restored or created tidal marshes might not immediately have the same recycling capacity as older tidal marshes. Due to the high sedimentation rate, recently created marshes mainly trap BSi, while initial DSi recycling is low (chapter 5). As soon as the marsh surface elevation has reached an equilibrium with mean high water, marsh DSi recycling capacity will be most efficient. Sedimentation rates might therefore help to estimate the time period necessary for the marsh to become an efficient Si recycler.

In a natural system, uninfluenced by anthropogenic pressures, Si recycling will probably not be of any necessity to balance the Si:N:P ratio; because of the low input of N and P in such a system, Si will probably never become limiting. Still, considering the high amounts of Si processed in marshes, the intertidal habitat would still be essential in the flux of Si from rivers to the ocean, essential to balance Si cycling in the oceanic environment.

7.3 How to proceed from here…

A lot is known about the significant influence intertidal areas have on N and P cycling in estuarine ecosystems, as sinks or as surface area for chemical transformations. It has also been frequently shown that marshes support a very productive biodiversity of animal species, some, like crustaceans and fishes, important for the fishing industries. The major plant nutrients N and P enter the marsh in dissolved form (ammonia, nitrate, ortho-phosphate). Once in the marsh, N and P are essential for macrophytes and algal communities, which, through photosynthesis, transform solar energy into life energy. These plants and algae then further support the productive marsh ecosystem. Fishes and crustaceans can mature in the system, and afterwards migrate to nearby coastal waters, or just stay in the relative shelter of the intertidal marsh for the rest of their life cycle. Through this mechanism, the intertidal area supplies energy (in the form of biologically fixed C) to the estuarine ecosystem. Tidal marsh area is thus directly linked to estuarine productivity. This relation has often supported claims for tidal marsh conservation and restoration, and continues to do so.

N and P enter the intertidal area in a dissolved form and are exported in organically fixed forms. For Si, it is clear from this thesis, things are the other way round. Biologically fixed Si is imported into the marsh, while biologically available dissolved Si is exported from the marsh. These results support the hypothesis that tidal marshes can further support estuarine productivity through enhanced Si cycling (Hackney et al. 2000). DSi, made available in tidal marshes, supports diatom communities, both within the marsh and in the estuary, thus reinforcing the base of the estuarine food webs, for which diatoms are the most important cornerstone.

Direct evidence for this hypothesis has until now only been shown in this thesis. Direct fluxes of Si between marshes and coastal waters have only been studied in North-Western Europe, in the two tidal systems studied in this thesis: the Scheldt estuary and the Atlantic Baie des Veys. On top, detailed within marshes flux studies of Si are limited to the tidal freshwater of the Scheldt estuary. Knowledge of Si stocks in marshes is restricted to the North Carolina Cape Fear estuary (mesohaline) (Norris & Hackney 1999) and the Scheldt estuary.

Based on this thesis, we now have a very detailed view on Si cycling in Scheldt freshwater marshes. These results only allowed for conclusions on a local scale. The results gathered in a saltwater system supported the hypothesis of similar functioning in saltwater systems, and provide a valuable base for the Scheldt case studies (previous chapter); however it is yet not known if similar mechanisms of internal Si cycling existed in the saltwater study area. The within marsh processes were never studied in a saltwater marsh.

Obviously, an essential step for advancing expertise on tidal marsh Si cycling, is the validation of these results in various other estuarine systems, not limited to a temperate European scale, but expanded to a scale which represents the large variability in intertidal ecosystems found worldwide. Do other intertidal systems - tropical and temperate, saltwater and freshwater, productive and non-productive, large and small- exhibit a similar influence on Si cycling? Within systems, research should focus on differences in functioning between tidal marshes along the salinity gradient. Within the same system, studies on this topic have never focused simultaneously on marshes of differing salinity.

Advancing to a mechanistic understanding of Si cycling in various tidal marshes, should allow us to implement results in mechanistic models of estuarine functioning. Implementation in mechanistic models will provide further understanding of the estuarine ecosystem. It will be an essential tool to accurately predict the possible impact of global change and wetland restoration measures on the fluxes of Si to the ocean, which are essential for both the occurrence of eutrophication events and to balance the oceanic Si budget.

It was also shown that restored tidal areas could initially function very differently from older marshes in their processing of Si. Restoration of tidal areas is a hot topic. A monitoring of the change in the functioning of restored tidal areas in the estuarine Si cycle, from the day of initial flooding, could provide invaluable information in our conception of estuarine Si cycling.

Apart from the upscaling of our knowledge of marsh Si cycling to a continental scale, other research questions include:

- Is dominance of *Phragmites australis* in freshwater marsh ecosystems partially the result of its ability to accumulate large amounts of Si? Growing reed under different DSi concentrations, one could study if its resistance to physical (tidal current), chemical (pollution) and biotic (herbivory) stresses is reduced.
- What forms of BSi are deposited and recycled in marsh ecosystems… phytoliths, diatoms, sponge spicules? Microscopic research could provide the answer. Are some forms buried preferably, while others are more easily recycled?
- What is the role of saprophytic fungi in the recycling through decomposition? Do they influence the dissolution of Si from litter? Experiments with fungicide will provide the opportunity to answer this question.
- Is the functioning on tidal mudflats similar? Does BSi deposition occur here, and if so, how does it compare to tidal marsh systems? Is it recycled in a similar way?
- How do porewater DSi concentrations evolve in between two tidal floodings?

Not only in tidal marshes, but also in the pelagic and benthic compartment, we are still but at the beginning of understanding the cycling of Si in the estuarine system. Together with an increased insight in marsh processes, we should advance our understanding of main channel processes, to compare the potential for Si recycling in marshes to the pelagic and benthic recycling. And beyond, not only the estuary itself should be considered, but we should also advance our scope to the river basin, which is the ultimate source of all Si for the estuary. How do biota here influence the Si fluxes? What about diatoms, macrophytes and sediment in the upper basin? Most questions remain as of yet unresolved.

From all this, it's clear that many more questions exist, as compared to the knowledge already gathered concerning transitional water silica cycling. This is in fact also the case for the general terrestrial (non-oceanic) silica cycle, which is surprising, given the importance of Si weathering in atmospheric CO_2-concentrations and global climate. I hope this thesis will provide a base for researchers to focus more on this element, which has only recently began receiving the ecological attention it deserves.

7.4 References

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Nederlandse samenvatting

Eutrofiëringsproblemen in kustzones worden in sterke mate beïnvloed door de verhouding waarin de nutriënten N, P en Si via estuaria worden aangeleverd. Estuaria vormen de overgangszones tussen terrestrische en mariene ecosystemen. N, P en Si zijn, tijdens het transport doorheen estuaria, onderhevig aan intense estuariene cyclering. Chemische transformatie en opname door biota oefenen een bepalende invloed uit op de chemische toestand en de verhouding in dewelke de nutriënten de kustzone bereiken. In tegenstelling tot N en P zijn er nauwelijks antropogene bronnen van Si. De hoge menselijke input van N en P in estuariene ecosystemen heeft daardoor geleid tot een verschuiving in de ratio waarin N, P en Si de kustwateren bereiken. Dit heeft wereldwijd geleid tot eutrofiëringsproblemen. De diatomeeëngemeenschap, die de basis vormt voor de mariene voedselketen en essentieel Si nodig heeft, wordt vervangen door een fytoplanktongemeenschap gedomineerd door species als *Phaeocystis* sp., *Gonyaulax* sp. en *Chrysochromulina* sp. Naast de negatieve gevolgen voor de mariene voedselketen kan eutrofiëring resulteren in verhoogde turbiditeit, anoxie en giftige algenbloei.

N- en P-cyclering in estuaria hebben de afgelopen decennia veel ruimer aandacht gekregen dan Si-cyclering. De rol van schorgebieden binnen estuariene Si-cyclering was tot op heden nauwelijks bestudeerd. Deze thesis beoogde na te gaan hoe zoetwaterschorgebieden het transport van Si doorheen estuaria beïnvloeden. De thesis bestaat uit drie deelaspecten: 1) een kwantificatie van de hoeveelheid biogeen silicium (nadat opgelost silicium opgenomen is door vegetatie of diatomeeën, wordt het omgezet tot biogeen silicium) in zoetwaterschorvegetatie en -sediment, 2) studie van de interne recyclering van biogeen silicium tot opgelost silicium (DSi) in het zoetwaterschorgebied, 3) studie van de wisselwerking tussen schor en hoofdbedding binnen de estuariene siliciumcyclering. Door de studie van deze 3 deelaspecten werd in dit proefschrift de hypothese nagegaan dat een efficiënte sequestratie van BSi (biogeen silicium) in schorvegetatie en -sediment leidt tot een hoge mate van recyclering van opgelost silicium binnen het schorgebied. Binnen deze hypothese voeren schorren enerzijds biogeen silicium in, terwijl ze anderzijds opgelost silicium exporteren, door de aanrijking van overstromingswater met opgelost siliciumrijk poriewater.

In **hoofdstuk 2** werd de kwantificatie van biogeen silicium in vegetatie en sediment behandeld in een zoetwaterschor (Tielrode) langsheen het Schelde-estuarium. *Phragmites australis* (riet) was de grootste vegetatieve stock van BSi: meer dan 96% van het BSi aanwezig in vegetatie werd teruggevonden in riet. Dode rechtopstaande rietstengels waren het rijkst aan Si. Het riet accumuleert BSi tijdens zijn groei; dit biogeen silicium komt pas terug vrij tijdens het decompositieproces nadat de rietstengel is omgevallen. Het BSi-gehalte van het sediment nam geleidelijk af met de diepte. Dit toont aan dat sediment-BSi, dat in het schorsediment terechtkomt door de depositie van zwevende stof uit overstromingswater, geleidelijk aan wordt gerecycleerd tot opgelost silicium in het poriewater. Dit poriewater is dan ook verrijkt aan DSi ten opzichte van het overstromingswater. Er werden geen verschillen waargenomen in het BSi-gehalte van het sediment tussen de verschillende vegetatietypes. De bovenste 30 cm schorsediment bevatten ongeveer 1500 g BSi m^{-2}, terwijl de rietvegetatie maximaal 140 g BSi m^{-2} bevatte. Sediment vormde dus duidelijk het grootste reservoir aan biogeen silicium binnen het zoetwaterschor.

In **hoofdstuk 3** werden de resultaten getoond van pioniersmetingen in het Tielrode-zoetwaterschor in 1997 en 1998, welke aantoonden dat schorren in belangrijke mate DSi exporteren naar de nabijgelegen estuariene hoofdbedding. Aanvullende metingen in mei 2002 toonden dat deze export aan DSi wordt gecompenseerd door de import van BSi met het overstromingswater. Deze resultaten ondersteunden de hypothese van schorren als potentiële recycleringsgebieden voor opgelost silicium binnen het estuariene milieu. Deze rol van schorgebieden in de estuariene siliciumcyclering is opvallend verschillend met stikstof- en fosforcyclering. N en P worden veelal geïmporteerd in schorren in opgeloste vorm, terwijl organisch vastgelegde vormen worden geëxporteerd. In de siliciumcyclering is het omgekeerd: de organisch vastgelegde vormen worden geïmporteerd, terwijl de biologisch beschikbare opgeloste vorm wordt geëxporteerd.

De waargenomen patronen van BSi-import en DSi-export in en uit schorgebieden werden seizoenaal bestudeerd in **hoofdstuk 4**. In het Tielrode-zoetwaterschor werden zes dertienuursmetingen uitgevoerd, verspreid over het gehele jaar, om na te gaan hoe de functionaliteit van zoetwaterschorgebieden in estuariene Si-cyclering veranderd doorheen de seizoenen. Deze metingen werden aangevuld met 6 dertienuursmetingen in een zoutwateroverstromingsgebied in Frankrijk (Normandië, Baie des Veys).

In beide gebieden werd vastgesteld dat de export van opgelost silicium toenam, naarmate de DSi-concentraties in het overstromingswater afnamen. Schorgebieden kunnen daarom beschouwd worden als bufferzones in de estuariene siliciumcyclus: wanneer in de omliggende wateren de DSi-depletie het hoogst is door opname van DSi door diatomeeën (in lente en zomer), zal de export van opgelost silicium uit de schorgebieden het hoogst zijn. Een vergelijking van de DSi-vracht in de zoetwaterzone van het Schelde-estuarium in de zomermaanden met de potentiële export van DSi uit schorgebieden, toonde aan dat de export van opgelost silicium uit schorren in het diatomeeën-groeiseizoen in belangrijke mate (tot meer dan 50%) kan bijdragen tot de beschikbaarheid van DSi.

Verschillende onderzoeken hebben aangetoond dat er een positief verband bestaat tussen de oppervlakte schorgebieden langsheen een estuarium en de secundaire productie van economisch belangrijke vis- en schaaldiersoorten in de nabijgelegen kustwateren. De opname van detritus van schorvegetatie door secundaire consumenten werd vaak vernoemd als een verklaring voor dit verband. De export van opgelost Si uit schorgebieden kan een additionele verklaring vormen: het DSi stimuleert de diatomeeëngroei in de kustwateren nabij het schor. De diatomeeën vormen op hun beurt de basis voor de estuariene voedselketen.

Eerder werd aangetoond dat in zoetwaterschorren het sediment het belangrijkste reservoir vormt van BSi. Het sediment vormt dan ook een potentieel zeer belangrijke bron voor gerecyleerd DSi. In **hoofdstuk 5** werd de verwerking onderzocht van biogeen silicium in schorsedimenten doorheen hun ontwikkeling. Jonge zoetwaterschorren worden gekenmerkt door hoge sedimentatiesnelheden. Hun hoogteligging is immers vaak nog enkele tientallen centimeters onder de gemiddelde hoogwaterlijn, wat resulteert in hoge overstromingsfrequenties en –volumes. Jonge schorren hogen dan ook snel op. De overstromingsfrequentie en het overstromingsvolume nemen consequent af. Men spreekt van een schor in evenwicht wanneer de hoogteligging van het schor overeenkomt met het gemiddelde hoog water.

Door middel van sedimenttraps werd de depositie van BSi op het zoetwaterschor “de Notelaar” langsheen de Schelde een jaar lang gemonitord. Hoewel het BSi-gehalte van het geïmporteerde sediment het hoogst was in de zomermaanden (10.9 mg BSi g^{-1} sediment in de zomer, 7.6 mg BSi g^{-1} sediment in de winter) werd er toch meer BSi geïmporteerd in de wintermaanden, omdat de sedimentdepositie in de winter sterk verhoogd was in vergelijking met de zomermaanden.

Er werd een duidelijke correlatie vastgesteld tussen sedimentdepositie en BSi-depositie. Door incorporatie van de verzamelde depositiegegevens in een lange-termijn sedimentatiemodel (MARSED) voor zoetwaterschorren, werd de recyclagecapaciteit voor DSi van deze schorren gemodelleerd doorheen de ontwikkeling van een jong schor tot een zoetwaterschor in evenwicht met de gemiddelde hoogwaterlijn. De recyclagecapaciteit van jonge snel ophogende schorren voor DSi is enorm laag: 85 % van het geïmporteerde BSi wordt definitief begraven in het sediment. Naarmate het schor ophoogt, wordt ook de recyclagecapaciteit hoger: een schor in evenwicht recycleert tot 60% van het geïmporteerde BSi tot DSi.

In **hoofstuk 6** werd bestudeerd in hoeverre ook de recyclering van riet gebonden BSi bijdraagt tot de recyclagecapaciteit van schorren voor DSi. Het BSi in rietmateriaal wordt bijzonder snel gerecycleerd tot DSi nadat een dode rietstengel neervalt. De dissolutie van DSi uit rietstrooisel verloopt volgens een dubbel exponentieel patroon: in de eerste twee weken wordt reeds meer dan de helft van het beschikbaar BSi omgezet tot DSi, daarna verloopt de dissolutie aan een lagere snelheid. Na een jaar is reeds alle BSi in het strooisel omgezet tot DSi. Door deze hoge recycleringssnelheid, speelt het rietstrooisel een belangrijke rol bij de export van opgelost silicium uit het schorgebied, hoewel de hoeveelheid beschikbaar BSi veel lager is in vergelijking met het sediment.

Dit proefschrift toont aan dat zoetwaterschorren enerzijds biogeen silicium importeren, en anderzijds opgelost silicium exporteren. Zoetwaterschorgebieden vormen bufferzones in de estuariene silicium-cyclering: de export van opgelost silicium is het hoogst, wanneer de DSi-concentraties in het nabije estuarium het laagst zijn. Binnen het schor dragen vegetatie- en sedimentgebonden BSi in gelijke mate bij tot de recyclering van opgelost silicium. Bovendien werden gelijkaardige uitwisselingspatronen vastgesteld in een zoutwaterschor. Om de invloed van schorren op Si-cyclering op continentale en globale schaal te kunnen inschatten is verder onderzoek in ecosystemen wereldwijd noodzakelijk. Schorren zouden een tot op heden niet herkende, maar belangrijke component kunnen vormen binnen de globale biogeochemische cyclus van Si.