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Dynamics of biogenic Si in freshwater tidal marshes: Si regeneration and retention in marsh sediments (Scheldt estuary)

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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 was implemented through 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 up to 300 g m^{-2}. Young marshes retained up to 85% of the imported biogenic silica. Recycling efficiency (60%) increased drastically for older marshes. The study shows that marshes act as important sinks for BSi along estuaries. The recycling of the imported BSi to DSi in summer and spring is most likely an essential factor in the buffering role of tidal marshes for estuarine DSi concentrations.

Keywords Biogenic silica dynamics · Numerical modelling · Freshwater tidal marshes · Scheldt estuary

Introduction

The amount of dissolved Si (DSi), transported through estuaries to the coastal zone, is an essential factor in the eventual occurrence of eutrophication problems in the coastal zone. High anthropogenic inputs of N and P may induce dissolved Si limitation in diatoms and cause a succession of the coastal phytoplankton community to non-diatom species (Schelske et al. 1983; Lancelot 1995; Smayda 1997) (e.g. Phaeocystis sp., Gonyaulax sp., Chrysochromulina sp.). The result is a less efficient transfer of carbon to (economically important) higher trophic levels; this can have severe effects on coastal foodwebs.

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Enhanced non-diatom phytoplankton production can have several further negative consequences including increased water turbidity, anoxic conditions and appearance of toxic algal blooms (Gazeau et al. 2004).

Because of its importance in the eutrophication problem, Si processing and retention in estuaries has received a fair amount of scientific attention, mainly focusing on subtidal benthic sediments and uptake and recycling by pelagic diatom communities (e.g. Yamada and D'Elia 1984; Conley and Malone 1992; Garnier et al. 1995; Muylaert et al. 2001). Recently, it has been shown that tidal marshes also contribute significantly to Si processing and retention in transitional waters (Norris and Hackney 1999; Struyf et al. 2006).

Freshwater tidal marshes along the Scheldt have been studied in detail for their role in estuarine silica cycling (Struyf et al. 2005a, b, 2006). They contain large amounts of biogenic Si (BSi, SiO_2nH_2O) in sediment and vegetation. Vegetation takes up DSi from marsh pore water, and incorporates it as BSi in siliceous bodies, known as phytoliths. Along the freshwater Scheldt, more than 90% of the vegetation bound BSi is found in *Phragmites australis*, while *Salix* sp. contains almost no BSi (Struyf et al. 2005b). In addition, BSi is directly imported into tidal marshes along with suspended matter. The resulting BSi in marsh sediments is a very heterogenic pool, potentially consisting of both buried phytoliths from different plant species and diatom BSi. In this paper, the term BSi refers to the total BSi pool, without differing between different fractions. The amount of BSi stored in the freshwater marsh sediments is high compared to the BSi pool stored in vegetation (up to 100 g BSi m^{-2} in vegetation, ca. 1500 g m^{-2} in upper 30 cm of marsh sediments, Struyf et al. 2005b). BSi in the marsh surface litter and sediments dissolves into the pore water, enriching it with DSi compared to the adjacent estuarine channel. When the marsh is flooded, the contact between tidal floodwater and DSi enriched pore water results in a net export of DSi from tidal marshes. Export is highest when the inundating DSi concentrations are lowest (Struyf et al. 2006). Marshes essentially act as DSi recyclers and buffers in estuarine environments, recycling most biologically available DSi from biogenically fixed Si when depletion in the pelagic waters is highest. These results supported the hypothesis that the biogeochemical Si recycling capacity of tidal marshes can partially explain the observed relationship between marsh surface area and coastal secondary production of economically valuable fish and invertebrates (Hackney et al. 2000).

BSi in marsh sediments is partly originating from import at high tides along with suspended solids: sedimentation is therefore an important factor controlling the accumulation and retention of BSi in tidal marshes. Despite the importance of Si retention and recycling in estuaries for the coastal eutrophication problem, 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 on the one hand and dissolution of DSi to the pore water and subsequent DSi export with ebb water on the other hand.

Marsh development (elevation, vegetation) is tightly linked to the sedimentation process. Tidal marshes act as net sinks for sediment, in the long term resulting in 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). 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).

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 (see Temmerman et al. 2004), to simulate the long-term regeneration of DSi and retention of BSi in freshwater marsh ecosystems. 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. The integration of the results, enabled to model Si generation and retention in freshwater marshes at different developmental stages, from early marsh development (low elevation, rapid sedimentation) to the latter stages with lower sedimentation rate and elevation equilibrium with mean high water.

Materials and methods

Study area

The Scheldt estuary (Fig. 1), located in Northern Belgium (Flanders) and the Southwest of the Netherlands, has a history of extensive anthropogenic pollution (Heip 1988; Van Damme et al. 2005). The estuary is known as highly eutrophic and receives large inputs of inorganic nutrients. A full gradient from salt to fresh tidal water is present along the estuary. A large freshwater tidal marsh area characterizes the Scheldt. The total surface area of freshwater marshes is approximately 450 ha on a total of 3,000 ha of tidal marshes. Detailed descriptions of the Scheldt estuary have been published elsewhere (Heip 1988; Meire et al. 2005; Soetaert et al. 2006).

The study area, the Notelaar marsh, is located in the most seaward part of the freshwater zone (Fig. 1). The marsh is situated near the turbidity maximum in the Scheldt estuary (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 elevation 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 to a tidal marsh (1958) (Temmerman et al. 2003a). This means that the vegetated marsh platform is only flooded during spring tides.

One-year 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, characteristic for tidal systems). 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 four sampling sites across the marsh (Fig. 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

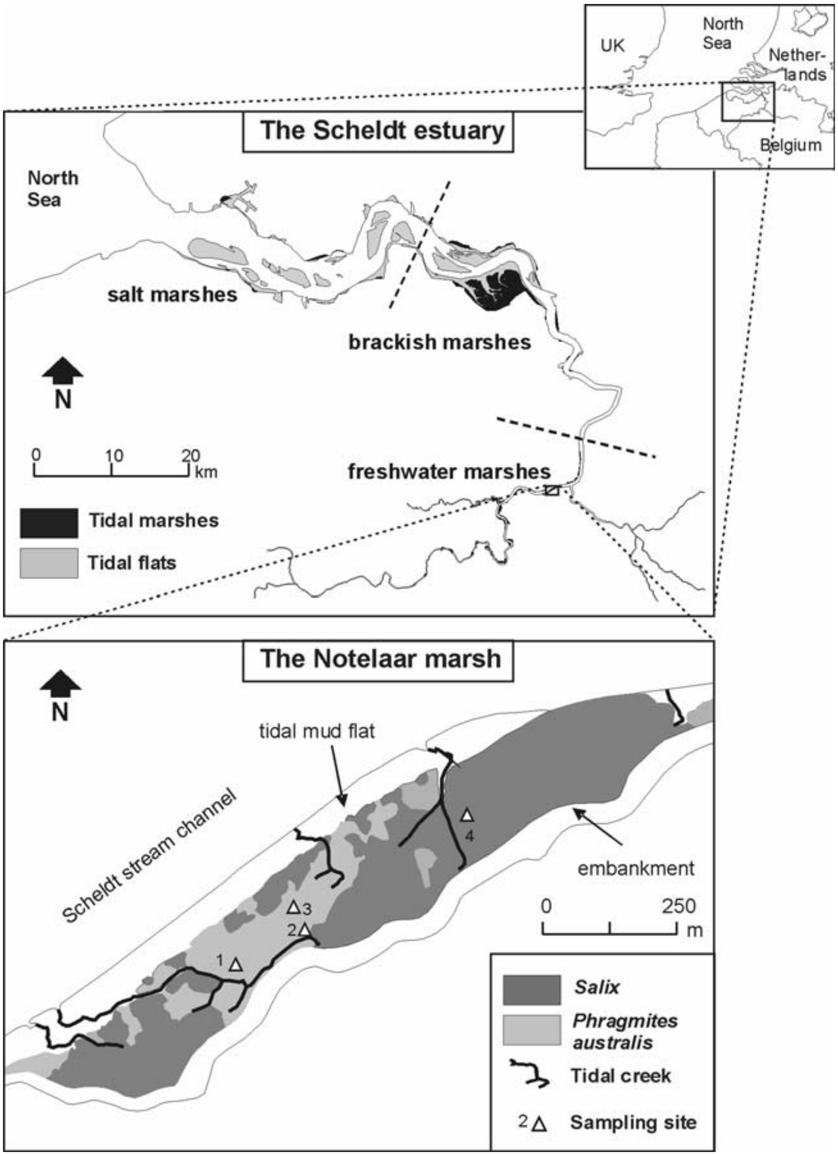

Fig. 1 The Scheldt estuary with location of the Notelaar marsh. Below: The location of vegetation types and sampling sites within the Notelaar marsh site

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, tidal 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 in tidal marsh sediments was analysed in subsamples taken approximately every 10 cm in both cores (every 5 cm in upper 20 cm).

BSi-analysis

Collected sediment, both from sediment traps and cores, was sieved at 500 µm, 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 min. 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). The BSi wet-alkaline extraction is prone to additional release of DSi from amorphous mineral silicates; our reported BSi values can contain a portion of Si extracted from this lithogenic amorphous silica. There is however no decent alternatives for wet alkaline extraction, especially because the method is also capable of fully dissolving phytolith BSi (Saccone et al. 2006). Related estuarine BSi studies have also applied the alkaline extraction method (Conley 1997; Norris and Hackney 1999); despite its flaws, BSi wet-alkaline extraction is for the moment still the most representative method to analyse for BSi.

Modeling 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 is modeled 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, are 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 four 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 modeled and compared to the observed depth gradient.

Results

One-year monitoring of BSi deposition on the marsh surface

The sedimentation rate on the marsh surface varied seasonally (Fig. 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 neap–spring–neap cycle, i.e. the period between two neap tides) and average sedimentation rate of 451 ± 525 g m^{-2} per neap–spring–neap cycle. In the period April–September, the sedimentation rate was much lower, on average 60 ± 50 g m^{-2} per neap–spring–neap cycle (detailed description of sedimentation in Temmerman et al. 2003b).

A clear seasonal variation was also observed in the BSi content of the deposited sediments (Fig. 3) at all four 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 four sampling sites (used in the modeling) 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}).

The BSi deposition rate on the marsh varied seasonally in accordance with the deposition of sediments into the marsh (Fig. 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 neap–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}.

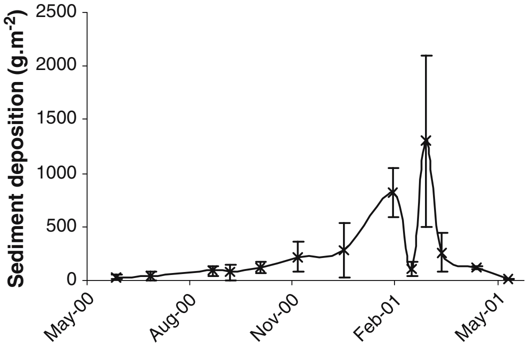

Fig. 2 The total sediment deposition per neap–spring–neap cycle, averaged for all four sampling sites (Notelaar, May 2000–May 2001)

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 (Fig. 5a). There is however a large scatter on the decreasing BSi concentrations in this marsh layer. The *Salix* sp. marsh core shows a similar decreasing trend. In the *P. australis* marsh core, the constant BSi-concentration is found up to a depth of 74 cm. A significant exponential decrease of BSi-concentration with depth was found if data for the upper parts of both cores were fitted together (Fig. 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.

Modeling 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 (Fig. 7a, b). Modeled 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 (Fig. 7c), BSi-deposition on the marsh was concurrently at its highest (Fig. 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 into the marsh dropped to a fairly constant level comparable to the observed deposition on the sediment traps in 2000–2001 (~40000 mg m^{-2}).

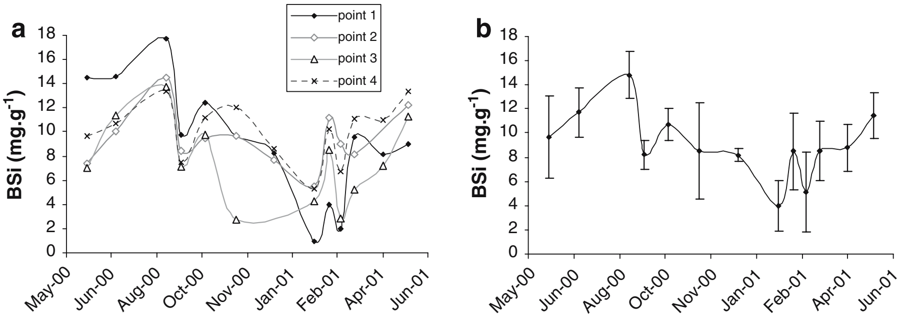

Fig. 3 The concentration of BSi in deposited sediments at all four sampling sites (**a**) and averaged over all four sampling sites (**b**) (Notelaar, May 2000–May 2001)

The relationship (calculated from the exponential BSi depth gradient in the sediment) between depth and yearly BSi-dissolution rate is shown in Fig. 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 (Fig. 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 (Fig. 9a, b).

Based on the modeled dissolution and deposition of BSi, the BSi depth gradient in the marsh sediment was reconstructed (Fig. 5b). The patterns were similar to the patterns observed in the sampled marsh cores (Fig. 5a, b). However, the BSi in the upper and deepest sediment layers was strongly underestimated compared to the sampled marsh cores (Fig. 5a, b). In the lower 40 cm,

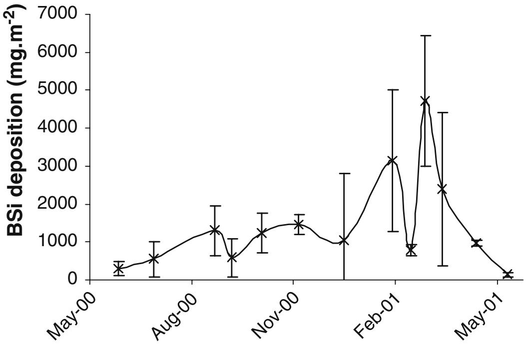

Fig. 4 BSi deposition per spring–neap cycle averaged for all four sampling locations (Notelaar, May 2000–May 2001)

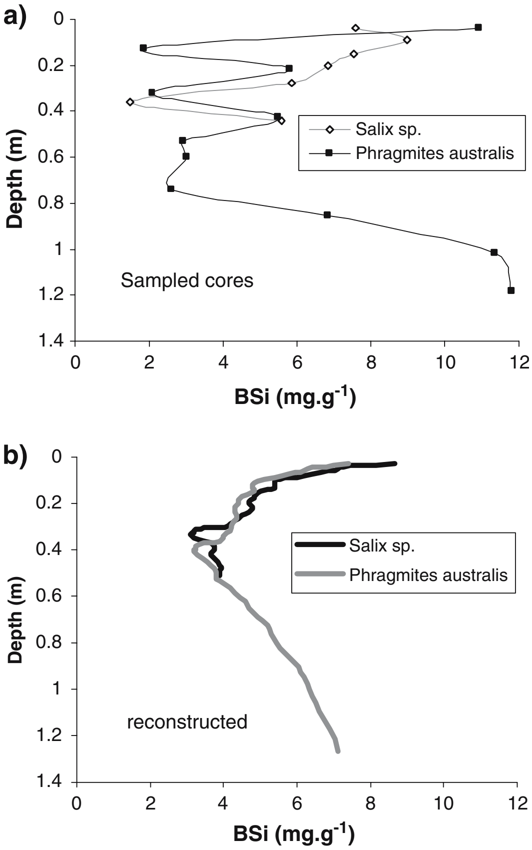

Fig. 5 BSi-content in the sampled (**a**, above) and reconstructed (**b**, below) sediment depth profiles in *Salix* sp. and *Phragmites australis* vegetated sites

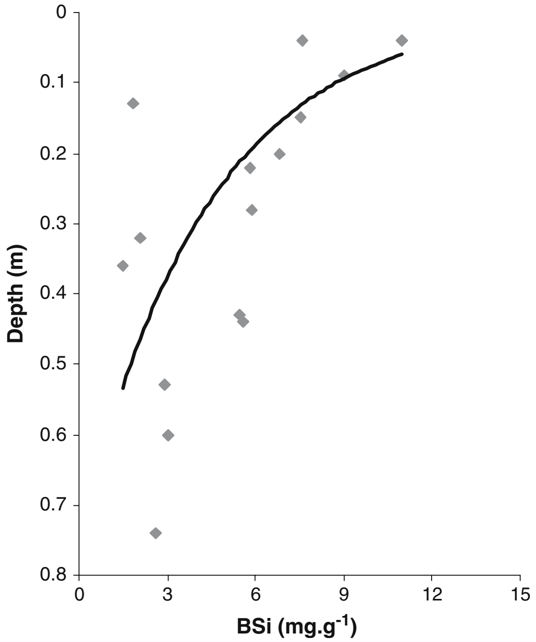

Fig. 6 Exponential decrease in BSi-concentration with depth (results combined from cores taken in *Phragmites australis* and *Salix* sp. sites)

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 modeled depth profiles.

Discussion

Our modeled results suggest 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 elevation equilibrium with mean high water level. Although the modeled depth gradient of BSi content in marsh sediments underestimated the observed BSi content in both the upper and lower parts of the sampled cores (possible explanations are discussed below), the modeled results demonstrate the mechanisms which underlie the functional changes in the marsh' role in estuarine Si cycling as the marsh develops.

Dynamics of BSi deposition and retention in freshwater tidal marshes

At the beginning of marsh development, the elevation of the *P. australis* marsh was far below mean high water level (Fig. 7c). High sedimentation rates resulted in 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 slowed down (e.g. Allen and Rae 1988; Temmerman et al. 2004). Sedimentation rates directly control the deposition of BSi, as indicated by the observed short-term correlation. Import of BSi into tidal marshes on a shorter time scale of a single tidal cycle has also been correlated to suspended matter import (Struyf et al. 2006). 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 early 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 the marsh sediments, becoming unavailable for recycling to DSi (Fig. 9a).

Sedimentation rate decreased with marsh elevation; deposited sediments were subject to BSi dissolution to pore water (and export with ebb water) for a longer time-period, which resulted in a gradual decrease in BSi burial efficiency. Buried BSi concentrations in the sediment decrease concurrently. Since the 1960s both the *P. australis* and *Salix* sp. marsh have been in equilibrium with the linearly rising mean high water level. Sedimentation rate is relatively constant since (Fig. 7c; Temmerman et al. 2003a). Sediments deposited during the early years of equilibrium are now approximately 50 cm under the marsh surface and considered buried. The results indicate that around 40% of the BSi deposited on a marsh in elevation equilibrium with mean high water is ultimately buried. From modeled results, we can conclude that 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.

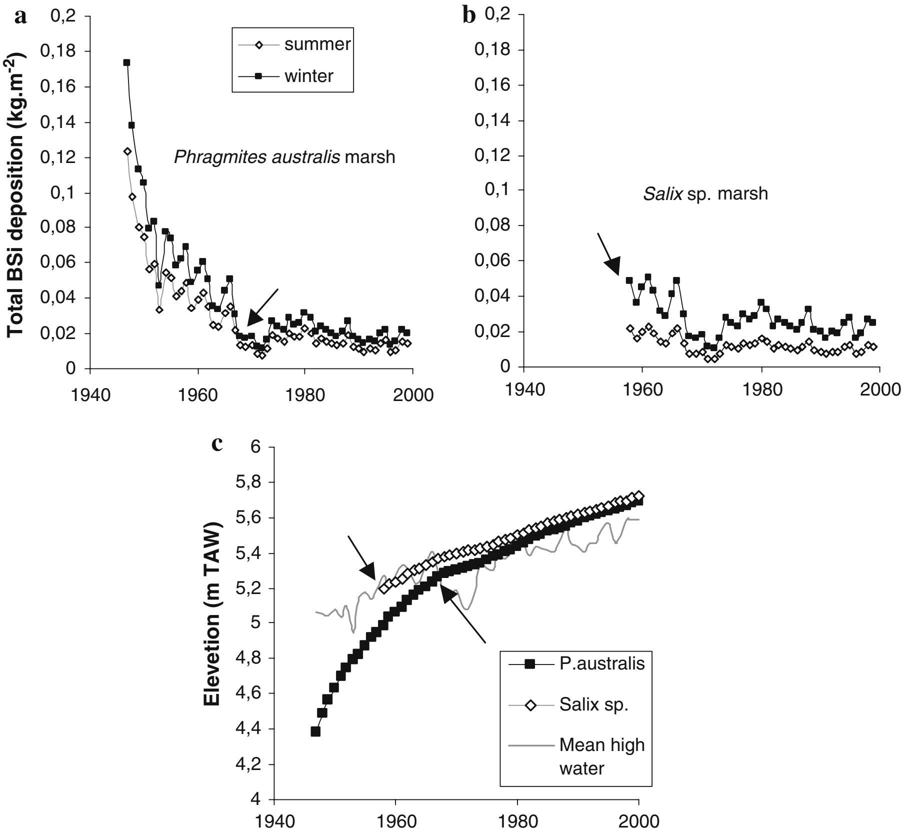

Fig. 7 Modeled BSi deposition on the *Phragmites australis* (**a**) and the *Salix* marsh (**b**) in winter and summer through the history of the sites. Marsh elevation evolution in comparison to mean high water level (**c**). Arrows indicate beginning of equilibrium stage of marsh elevation with mean high water. Water level in m TAW (= Belgian Ordnance Level, corresponding to height over mean sea level at low tide)

Model assumptions and consequences

Our model assumes that once buried below 50 cm depth, BSi is no longer recycled and ultimately exported from the marsh as DSi (based on the constant BSi concentration in sediment cores below this depth). However, below 50 cm depth, the fairly constant BSi value in the sampled cores (~2.5 mg g^{-1}) was low compared to the modeled BSi content at these depths (~4 mg g^{-1}). This suggests that we might underestimate recycling by excluding it below 50 cm. Diffusion of pore water DSi from deeper layers to the upper 50 cm of sediment pore water could occur, and could be compensated for by additional BSi dissolution at deeper sediment layers. The absolute values of reconstructed and observed BSi content also differ, especially in the upper and lower sediment layers within the *P. australis* core. This could be explained by the high spatial variability observed in BSi content of marsh sediments (Struyf et al. 2005b). Both spatial and temporal variability in BSi in imported suspended matter could result in the scatter observed in the sampled marsh cores. Autochtonous marsh diatom development (not included in the model and consequently assumed absent) could explain why the modeled BSi profile strongly underestimated the BSi concentration in the upper sediment layers. 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*, which contains over 90% of BSi stored in vegetation along the freshwater tidal Scheldt, see Struyf et al. 2005b) are known to accumulate vast quantities of BSi in the

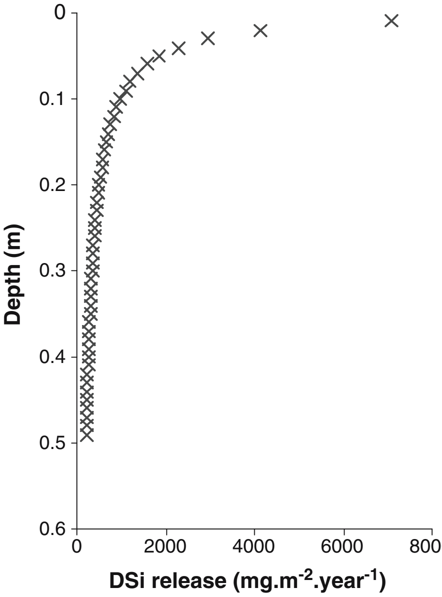

Fig. 8 The modeled DSi release from the sediment at different depth layers, according to the observed exponential decrease of BSi concentration in the cores (see Fig. 6)

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 several ecosystem Si balances (Conley 2002). Recent work on *Phragmites australis* decomposition however suggests that BSi recycling from *Phragmites* phytoliths in the Scheldt tidal marshes is almost 100% within 1 year (Struyf et al. submitted). At such high recycling rates, phytoliths could not significantly contribute to BSi burial in the marsh sediments.

Autochtonous diatom growth could also explain the underestimation of BSi concentration in the deepest sediment layers. However, low modeled BSi concentrations here could also be explained by an overestimation of dissolution rate during the early marsh development. Dissolution rates have been modeled from the gradient observed in the upper 50 cm of sampled sediments; the model consequently assumes that

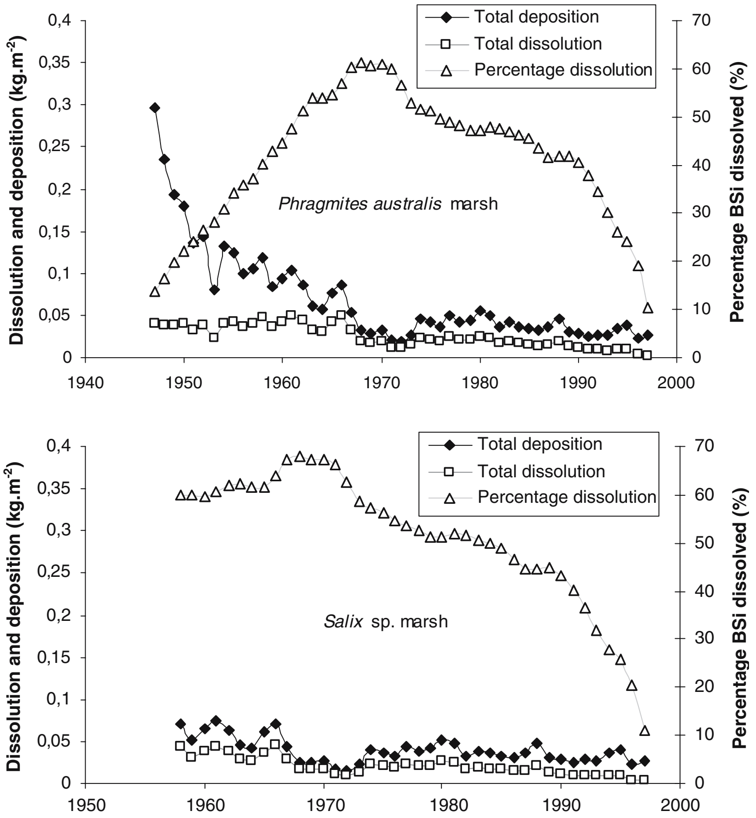

Fig. 9 Modeled recycling efficiency for BSi in deposited sediments for both marsh sites. The total yearly deposition of BSi on both marsh sites (top *Phragmites australis* site, down *Salix* sp. site) throughout their history is indicated, and compared to the total amount of DSi that was recycled up to the year 2000 from these deposited sediments

dissolution rates were similar during all stages of marsh development. DSi flux rates on tidal mudflats (Mortimer et al. 1998; Asmus et al. 2000) have however been observed both in and out of the sediment in European temperate estuaries; 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). In the early stages of marsh development, influx of DSi into the marsh sediments could have occurred instead of export.

Regional and global implications

Scheldt freshwater tidal marshes have already been shown to be net sinks for Si in the estuarine environment, by comparing import of BSi and export of DSi during single tidal cycles (Struyf et al. 2005a, 2006). This is in agreement with the 40% burial of BSi 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} (Struyf et al. 2006) and a yearly average water discharge of 47 $m^3 s^{-1}$ (Struyf et al. 2004), yearly about 2,600 tons of BSi are discharged through the freshwater reaches of the Scheldt. Our deposition data, both modeled and observed, show that annually about 40 g BSi m^{-2} are deposited on the marsh surface. With approximately 450 ha of freshwater marshes along the Scheldt, 180 tons of BSi would be deposited every year on freshwater marshes along the Scheldt, 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 modeled 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. However, in contrast to freshwater marshes, BSi dynamics in tidal brackish and saltwater marshes are still 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 and D'Elia 1984). In order to compare BSi retention in marshes of different salinity, data from marshes situated at different places along the salinity gradient, are needed.

The recent progress achieved in the study of silica cycling in tidal marshes has stressed the importance of these habitats in the global biogeochemical cycle (e.g. Norris and Hackney 1999; Struyf et al. 2006). The DSi recycling capacity of tidal marshes, resulting from the ability to accumulate BSi, was recently 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 experimental results have supported this hypothesis (Struyf et al. 2006). 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) will result in increasing BSi concentrations relative to DSi concentrations and consequently enhance the retention of Si in tidal marshes, and the amount of Si which is eventually transported to the coastal area will decrease. On the other hand, the reduction of tidal habitat through human activities (embankment, polderisation) could result in enhanced Si transport towards the sea. Burial of BSi in tidal marshes will decrease because of reduced tidal marsh surface, while a reduction in water retention time and higher discharge will reduce diatom growth (Muylaert et al. 2001; Struyf et al. 2004) and consequently reduce BSi concentrations in estuaries and BSi burial efficiency on marsh habitat. For the moment, our quantitative knowledge of Si dynamics in tidal habitat is too limited to estimate the relative importance of both human enhancement (eutrophication) and reduction (reduced tidal area) of Si retention 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. On the other hand, the reduced tidal habitat area will have decreased the buffer function of these areas in the prevention of DSi limitation, a function which became increasingly important due to the high human input of both N and P into the system.

To even further complicate the quantification of human influence, marshes are very sensitive to environmental changes, such as sea-level rise (Van Wijnen and Bakker 2001; Adam 2002; Temmerman et al. 2004). Increased flooding can degrade marshes to bare tidal mudflats, which could drastically increase BSi retention in estuaries while at the same time reducing their DSi recycling efficiency. It is clear that more research is needed to relate the local scale ecosystem conclusions provided here 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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