

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

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ABSTRACT: To date, estuarine ecosystem research has mostly neglected silica cycling in freshwater intertidal marshes. 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. Of the live plants, *P. australis* contained the most BSi (accumulating from 6 to 55 mg g⁻¹). Dead shoots of *P. australis* had the highest 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 a much lower BSi content. Except for *P. australis* rhizomes (<15 mg g⁻¹) underground biomass contained low amounts of BSi (<6 mg g⁻¹). Sediment BSi content decreased from the surface (9 to 10 mg g⁻¹) to deeper layers (5 to 7 mg g⁻¹). There was seasonal variation in sediment BSi. Dissolved Si in porewater was highest in summer (ca. 600 µM) and lowest in winter (ca. 400 µM). *P. australis* vegetation (aboveground and roots) contained up to 126 g m⁻² BSi, while the upper 30 cm of sediment accumulated up to 1500 g m⁻², making sediment the largest BSi reservoir in the marsh. We conclude that *P. australis* wetlands could be an essential, but unrecognised, sink for BSi in the biogeochemical cycling of Si.

KEY WORDS: Biogenic silica · Freshwater marsh · Estuary · *Phragmites australis* · Eutrophication · *Impatiens glandulifera* · Sediment

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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 in influencing the occurrence of eutrophication problems 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 it 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 to be important Si stocks and processors in estuarine systems. In North Carolina, a study of silica in mesohaline marsh sediments, vegetation and porewater clearly revealed these intertidal habitats to constitute large

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reservoirs of silica (Norris & Hackney 1999). Moreover, it was shown how a freshwater marsh (Schelde estuary, Belgium) acted as an important DSi recycler in the estuarine environment (Struyf et al. 2005).

Marshes have a high DSi recycling capacity, since they act as efficient biogenic silica (BSi) traps, concentrating Si at levels above those 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's life cycle and only released to the environment after the plant's decay. 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).

The main source of biogenic silica in sediments is plant phytoliths and diatom shells, deposited on the sediments at flood tide along with suspended matter. Plant phytoliths can also be deposited on the marsh sediments after vegetation decays. BSi dissolution occurs when porewater comes into contact with this sediment BSi in between tidal flooding events, resulting in high porewater DSi concentrations in marshes.

Despite the importance of silica 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. In addition, 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 for grassland ecosystems, to quantify the role of the terrestrial cycle in the global biogeochemical cycle of Si and the transport of Si by 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 *P. australis*-dominated freshwater marsh systems have focused on C- or N-cycling (Meyerson et al. 2000, Soetaert et al. 2004). *P. australis* has great potential as a nutrient sink, because of its high productivity and dense clonal growth, and because dead culms can remain standing for 2 or more years before collapsing. We

performed a year-long (approximately 2 mo intervals) study of silica content in porewater, sediment and vegetation, in order to gain a complete picture of the amounts of silica stored in the freshwater marsh ecosystem and to explore seasonal variability in Si storage.

MATERIALS AND METHODS

Study site. The Schelde estuary (Fig. 1), in northern Belgium (Flanders) and SW Netherlands, has a history of extensive anthropogenic pollution (Wollast 1988, Boderie et al. 1993, Baeyens 1998, Van Damme et al. 2005). It is extremely eutrophic, and receives large inputs of inorganic nutrients from non-point as well as point sources (Heip 1988). Tidal influence reaches inland as far as Gent, 155 km from the mouth of the estuary. A full gradient from salt to fresh tidal water is present along the estuary. A large freshwater tidal area characterises the Schelde, situated approximately between Gent (at Km 155, i.e. 155 km upstream of the estuarine mouth) and Temse (Km 100). The total surface area of freshwater marshes along the Schelde is approximately 450 ha. The study area was a freshwater marsh near Tielrode, at the confluence of Durme and Schelde. The total area of the study site was about 3500 m². All major vegetation types, characterising the freshwater marshes along the Schelde (i.e. pure *Phragmites australis* vegetation, tall-herb vegetation dominated by *Urtica dioica*, *Impatiens glandulifera* and *Epilobium hirsutum*, a mixed reed-tall-herb vegetation, and a *Salix* sp. shrubs and tree vegetation), were present in the study area.

Sampling. Vegetation: Aboveground vegetation samples were taken approximately every 2 mo from June 2002 until May 2003 for 4 target herbaceous

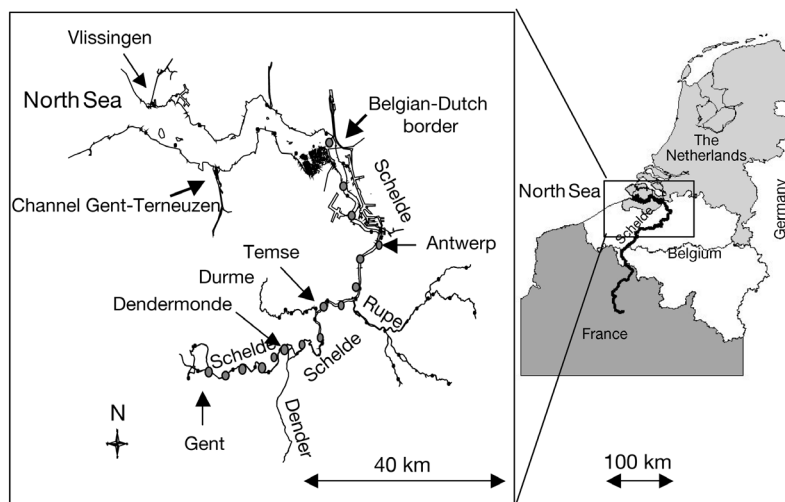


Fig. 1. Schelde estuary and tributaries. The study site is situated at Temse

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 (but standing) shoots and decomposing litter during winter. *Salix* sp. leaves 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 into leaves 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, 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 1 mixed sample. Underground biomass was separated into 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 m⁻²) was studied in 48 vegetation plots of 1 m², 12 in

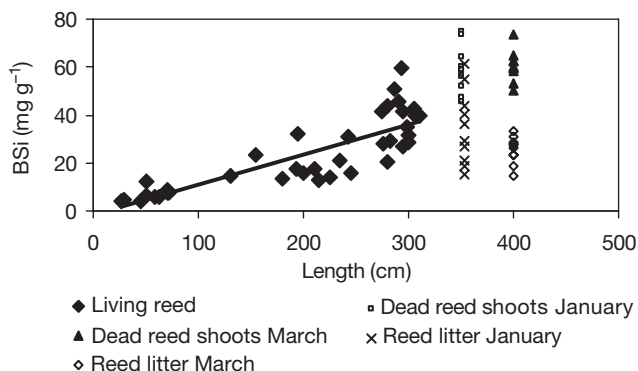


Fig. 2. *Phragmites australis*. BSi content of plant tissue throughout different life-cycle stages: shoot length used as age indicator. Dead plants and litter given an imaginary length higher than that of any living individuals to indicate they comprise last stages of life cycle. Dead plants omitted from regression

each vegetation type. Combined with individual plant weights, these data were used for marsh biomass estimates.

Sediment 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 subsampled at 4 different depths (0 to 1, 1 to 10, 10 to 20 and 20 to 30 cm) and pooled per depth per vegetation type. Roots and litter were removed manually from the sediment. Porewater was sampled in

Table 1. Mean (\bar{x} , mg g⁻¹ dry wt) biogenic silica (BSi) content of different plant species in Tielrode marsh, Schelde estuary, in different seasons. n: no. of individuals; SD: standard deviation; -: no data

Species	Jun 2002			Sep 2002			Nov 2002			Jan 2003			Mar 2003			May 2003		
	\bar{x}	SD	n	\bar{x}	SD	n	\bar{x}	SD	n	\bar{x}	SD	n	\bar{x}	SD	n	\bar{x}	SD	n
<i>Phragmites australis</i>																		
Entire plant	16.6	3.4	10	40.6	6.3	10	55.0	14.8	10	59.2	9.7	10	60.5	6.3	10	6.7	2.6	10
Shoots	25.4	6.8	5	42.1	6.7	5	49.3	2.9	5	59.2	9.7	10	60.5	6.3	10	7.6	2.2	5
Leaves	9.4	2.6	5	26.6	4.5	5	32.1	6.3	5	-	-	-	-	-	-	5.0	1.0	5
Dead shoot	51.1	26.5	10	72.2	14.4	10	51.3	18.9	5	59.2	9.7	10	60.5	6.3	10	-	-	-
Litter	-	-	-	-	-	-	-	-	-	34.7	15.4	10	25.5	5.5	10	-	-	-
<i>Epilobium hirsutum</i>																		
Entire plant	0.5	0.2	5	1.5	0.6	5	1.2	0.1	5	5.5	1.0	5	3.6	1.9	5	2.6	0.5	5
<i>Impatiens glandulifera</i>																		
Entire plant	0.4	0.2	10	2.5	2.0	10	1.1	0.5	10	6.8	2.8	10	8.0	1.4	10	2.3	1.0	10
Shoots	0.2	0.1	5	1.1	0.1	5	1.1	0.5	10	6.8	2.8	10	8.0	1.4	10	2.6	1.6	5
Leaves	0.3	0.1	5	0.6	0.1	5	-	-	-	-	-	-	-	-	-	1.0	0.3	5
<i>Urtica dioica</i>																		
Entire plant	4.2	1.5	10	7.7	1.2	10	8.6	1.8	10	8.5	2.3	10	-	-	-	5.2	1.1	10
Shoots	1.1	0.4	5	4.9	1.4	5	4.8	1.0	5	8.5	2.3	10	-	-	-	2.3	0.9	5
Leaves	5.4	1.4	5	9.2	1.6	5	11.1	2.8	5	-	-	-	-	-	-	6.3	0.7	5
<i>Salix</i> sp.																		
Leaves	0.5	0.3	5	1.2	0.1	5	1.1	0.4	5	-	-	-	-	-	-	-	-	-
Twigs	-	-	-	1.9	1.0	5	0.5	0.2	5	0.6	0.1	5	0.4	0.1	5	-	-	-

January, March, May, July and October 2003. Porewater samples were taken at 12 different sampling points, 3 in each vegetation type, using Eijkelkamp polymeric rhizons (diameter 2.5×1.4 mm). Subsamples were taken at 0 to 10, 10 to 20 and 20 to 30 cm depth.

Analysis. After sampling, plant samples were oven-dried for 3 d at 75°C , after which dry weight of individual plants was determined. Subsequently, samples were ground and sieved through $300 \mu\text{m}$ mesh. To

extract BSi, 25 mg of sieved plant material was incubated for 4 h in $0.1 \text{ M Na}_2\text{CO}_3$ (DeMaster 1981). Sediment was oven-dried for 3 d at 75°C , always within 24 h of sampling. BSi was extracted from the sediment (25 mg) in a $0.1 \text{ M Na}_2\text{CO}_3$ solution at 80°C . Subsamples were taken after 150, 210 and 270 min. BSi was calculated by linear extrapolation through the 3 extraction points in a time-extracted silica plot (DeMaster 1981). Dissolved silica was analysed spectrophotometrically on an IRIS ICP (Inductively Coupled Plasma Spectrophotometer).

RESULTS

Vegetation

Phragmites australis was the greatest plant BSi accumulator (Table 1). Throughout the growth season, silica was accumulated linearly in its tissue, from $6.7 \text{ mg BSi g}^{-1}$ in May to 55.0 mg g^{-1} in November ($F_{1,37} = 87.89$, $R^2 = 0.7037$, $p < 0.00001$) (Fig. 2, Table 1). Shoot length was used as age indicator. In January and March, shoot length of standing dead shoots and decomposing reed litter on the marsh surface was thus considered at a constantly high imaginary level, a level higher than that in any living reed plants. Thus, dead plants in Fig. 2 are indicated as being 'older' than living plants. Accumulation patterns were similar in leaves and shoots. Shoots contained more BSi than leaves (Wilcoxon signed-rank test $n = 20$, $p < 0.0001$). Dead shoots contained the most BSi (Table 1, Fig. 2). They were present year-round, and their silica content was at a similar high level throughout the year (51.1 mg g^{-1} in June to 72.2 mg g^{-1} in September 2002). Decomposing litter on the marsh floor contained about half of the BSi present in the dead shoots (Table 1, Fig. 2). The BSi content of the litter decreased between January and March 2003 (34.7 and 25.5 mg g^{-1} respectively).

Impatiens glandulifera (monthly average 0.4 to $2.5 \text{ mg BSi g}^{-1}$), *Urtica dioica* (monthly average 4.2 to 8.6 mg g^{-1}) and *Epilobium hirsutum* (monthly average 0.5 to 2.6 mg g^{-1}) contained less silica than *Phragmites australis* (Table 1). During the early growth season, the BSi content of *I. glandulifera* was slightly higher than later in its life cycle (Fig. 3a). Accumulation of silica in its tissue during the main growth season was less apparent than in *P. australis*, although again the highest BSi contents were mostly found in the oldest plants. No significant linear accumulation pattern was found. The amorphous silica content of *I. glandulifera* litter (6.8 to $8.0 \text{ mg BSi g}^{-1}$) was 1 order of magnitude higher than the silica content of live plants (Fig. 3a). The accumulation pattern was very similar for *E. hirsutum*, with

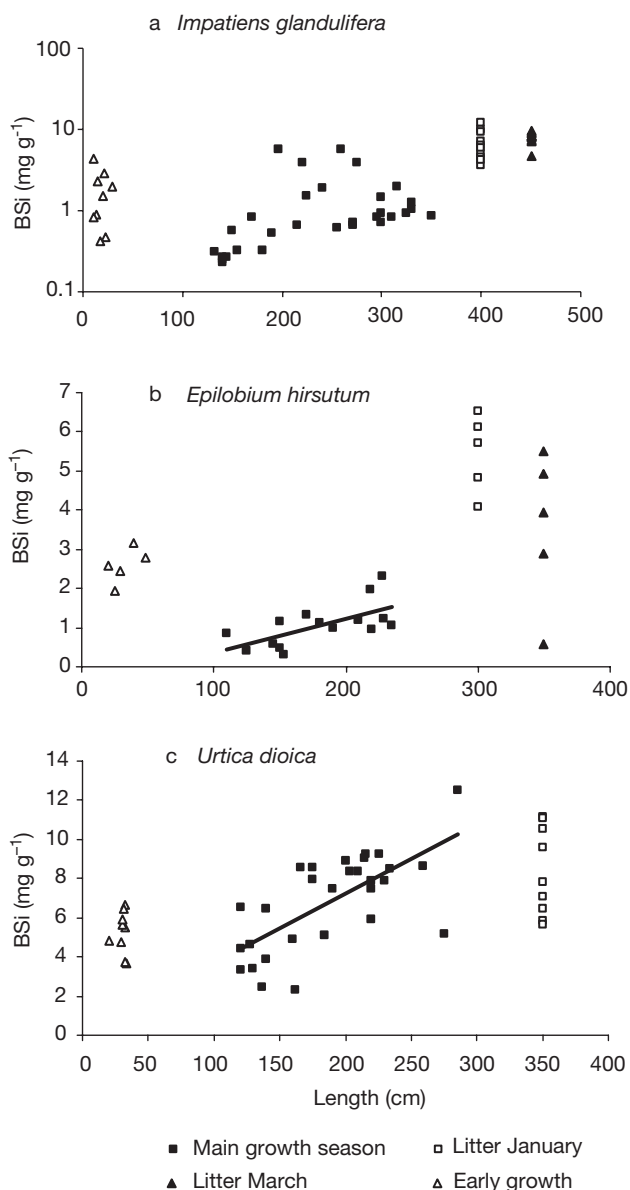


Fig. 3. BSi content throughout different life-cycle stages. *Impatiens glandulifera*, *Epilobium hirsutum* and *Urtica dioica*: shoot length used as age indicator. Litter given an imaginary length higher than that of any living individuals, to indicate it is formed in last life-cycle stage. Litter omitted from regressions

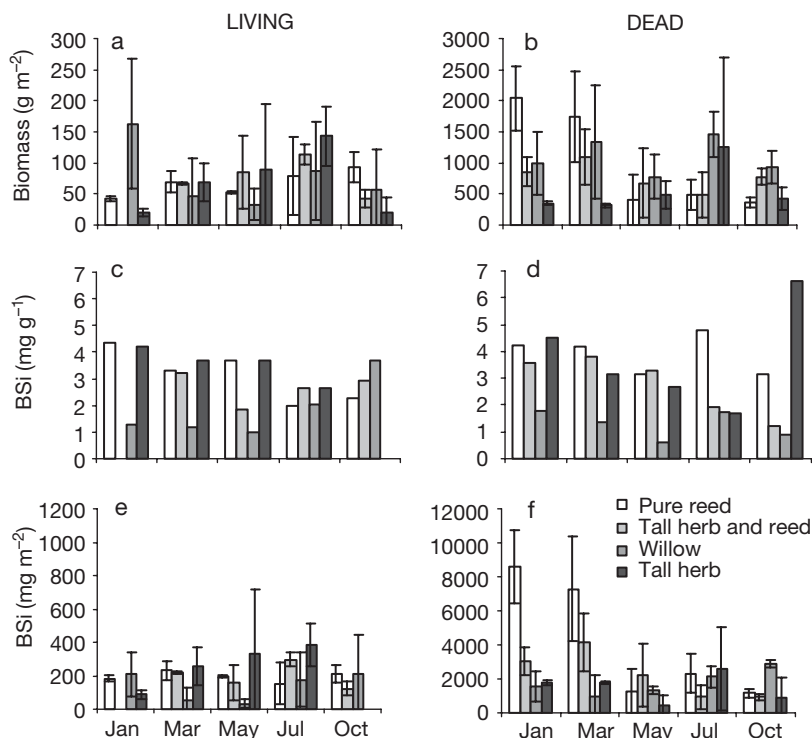


Fig. 4. (a,b) Underground biomass, (c,d) BSi content per unit dry weight of underground biomass and (e,f) underground biomass associated BSi per surface unit in upper 30 cm of sediment under 4 different vegetation types throughout 2003

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

Dead underground biomass was generally highest in winter (Fig. 4b). Living non-rhizome root biomass was mostly highest in summer (Fig. 4a). Dead underground biomass was much higher (about 10-fold) than living (non-rhizome) biomass. The BSi content of both dead and living (non-rhizome) underground biomass (Fig. 4c,d) was between 1 and 5 mg g⁻¹. Generally, lowest values were found in the *Salix* sp. vegetation, and highest values in the *Phragmites australis* vegetation. The total amount of Si stored in the dead underground biomass was much higher (1 order of magnitude) than in the non-rhizomeous roots. It was highest in winter (Fig. 4e,f).

Rhizomes of *Phragmites australis* (Fig. 5) contained more BSi than the other underground biomass. The BSi content of rhizomes was highest in winter (15 mg g⁻¹) and lowest in late summer and early autumn (8 mg g⁻¹).

On an areal basis, *Phragmites australis* was the biggest BSi sink in the marsh in all 4 vegetation types, containing up to 85 g BSi m⁻² in its aboveground vegetation (Table 2a). The other plant species and underground non-rhizomeous biomass contributed far minor amounts to sinks (Table 2). Based on a biomass estimate of 2500 g m⁻² (Schierup 1978, Asaeda & Karunaratne 2000), rhizomes could accumulate on average 30 g BSi m⁻².

Sediment and porewater

The BSi content of the sediment under pure *Phragmites australis* vegetation was generally higher than under the other vegetation types (Fig. 6). The whole marsh-averaged BSi content in the marsh sediment (Fig. 7) was similar during all monitored months. A 2-way ANOVA with depth, and month as class variables showed a significant depth gradient of sediment BSi content ($F_{3,60} = 10.11$, $p < 0.0001$). The highest BSi content was in the upper sediment layers (0 to 1 cm: 9.5 mg g⁻¹), gradually decreasing in the deeper sediment layers (1 to 10 cm: 8.7 mg g⁻¹; 10 to 20 cm: 7.5 mg g⁻¹, 20 to 30 cm: 6 mg g⁻¹) (Fig. 6). The BSi content of the 20 to 30 cm layer was about two-thirds that of the upper 10 cm. Only in January 2003 did the upper cm of sediment contain less BSi than the deeper layers. No consistent seasonal variation was observed. On areal (m²) basis, sediment was the biggest BSi sink in the marsh, containing on, an average annual basis, 1500 g m⁻² BSi in the top 30 cm (Table 2b).

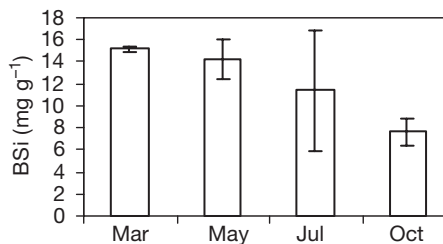


Fig. 5. *Phragmites australis*. BSi content of rhizomes throughout 2003

Table 2. BSi (g m^{-2}) content of different marsh sinks. (a) BSi content of target plant species and underground biomass in different vegetation types; (b) BSi content of sediment and porewater. For sediments, calculation based on sediment bulk density of 0.74 g cm^{-3} (Van de Moortel & Deckers unpubl. data). *P. a.*: *Phragmites australis*; *I. g.*: *Impatiens glandulifera*; *U. d.*: *Urtica dioica*; *E. h.*: *Epilobium hirsutum*; ds: dead shoots

a		Vegetation type			
Species	<i>P. a.</i>	<i>P. a./tall herb</i>	<i>Salix</i> sp.	Tall herb	
<i>P. a.</i>	85 ± 39	45 ± 22	5 ± 9	18 ± 21	
<i>P. a.</i> – ds	11 ± 7	5 ± 4	0	0.5 ± 1.4	
<i>I. g.</i>	0	0.5 ± 0.7	0.6 ± 0.8	1.7 ± 2.5	
<i>U. d.</i>	0	0.1 ± 0.3	0.9 ± 0.8	0.6 ± 0.6	
<i>E. h.</i>	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	
Rhizomes	30 ^a				
b					
Depth (cm)	Sediment	Porewater			
0–1	64 ± 23	0.8 ± 0.1			
1–10	533 ± 220				
10–20	511 ± 183	0.9 ± 0.1			
20–30	429 ± 146	0.9 ± 0.1			

^aBased on 2500 g m^{-2} biomass estimate (Asaeda & Karunaratne 2000)

Average DSi concentration for all vegetation types in the porewater (Fig. 8) was highest in summer (500 to 600 μM) and lowest in winter (350 to 410 μM). DSi content of the porewater gradually increased from January to July, decreasing again between July and October. The *Phragmites australis* vegetation had higher porewater DSi concentrations (Fig. 8). A 3-way ANOVA with depth, time and vegetation type as class

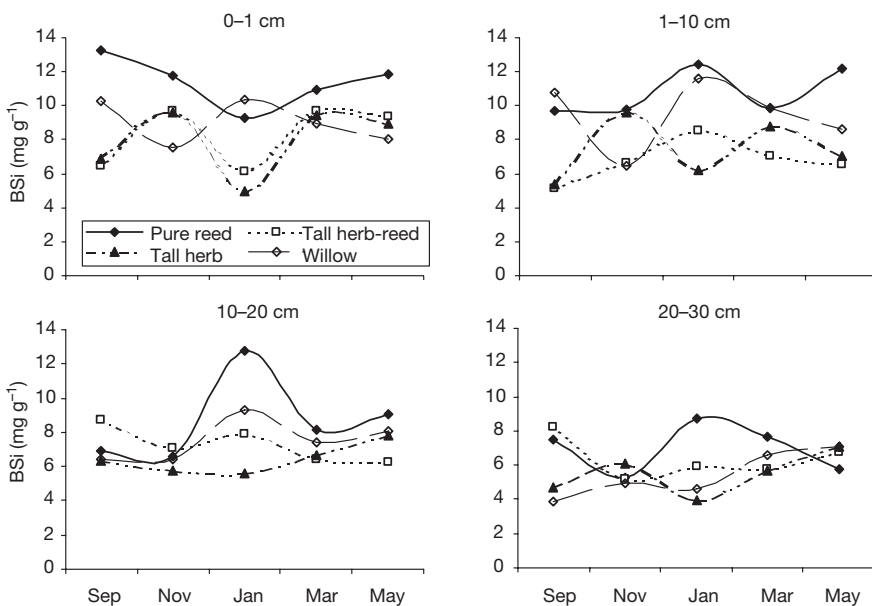


Fig. 6. Sediment BSi concentration in different sediment layers throughout 2003, showing variability observed for the different vegetation types

variables showed significant time ($F_{4,22} = 20.96$, $p < 0.000001$) and vegetation type ($F_{3,22} = 13.57$, $p < 0.0001$) differences in porewater concentrations. No significant depth gradient was observed. Porewater contained around 3 g BSi m^{-2} in the top 30 cm (Table 2).

DISCUSSION

Of the plant species studied, *Phragmites australis* accumulated the most BSi. Wetland grasses in general are known silicon accumulators, taking up DSi faster than would be expected from non-selective uptake of DSi with water (Raven 2003). Silicon accumulators contain large amounts of Si relative to their dry weight ($>10 \text{ mg g}^{-1}$; Ma et al. 2001).

Generally, monocotyledons (e.g. *Phragmites australis*) contain more BSi in their tissues than dicotyledons. Indeed, in the present study, *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 (Si content $<5 \text{ mg g}^{-1}$; Ma et al. 2001). The Urticales comprise an intermediate category between accumulators and non-accumulators (Ma et al. 2001). The relatively high BSi content of *Urtica dioica* (between 5 and 10 mg g^{-1}) was also in accordance with this. Differential strategies related to DSi

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

Phragmites australis accumulated BSi in its tissue linearly

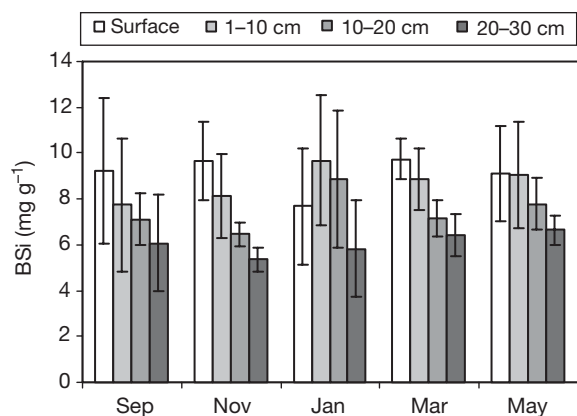


Fig. 7. Marsh-averaged sediment BSi concentration in different sediment layers ('surface' = 0 to 1 cm), in 2003

throughout the entire growth season. Linear accumulation of BSi was also observed in *Epilobium hirsutum* and *Urtica dioica*, but in contrast to *P. australis*, in these species accumulation was only linear from a certain shoot length onwards. Young plants (<50 cm shoot length) of *Impatiens glandulifera*, *E. hirsutum* and *U. dioica* all had a relatively high BSi content. These accumulation patterns reflect the ability of marsh vegetation to act as a silica sink in tidal wetlands, immobilising the Si until decomposition occurs.

Delayed accumulation in *Impatiens glandulifera* and *Epilobium hirsutum* could result from these species actively excluding Si from the plant tissues. Silica is deposited at major sites of transpirational water loss, 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 contents. In *Urtica dioica*, delayed accumulation may also result from retrans-

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

Dead *Phragmites australis* shoots had higher BSi contents than 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 the 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 *Phragmites australis* rhizomes. This is in contrast to the results of a study 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 environment-related. Very few studies have focused on this issue as yet. Sangster (1982) also found Si deposits in the rhizomes of *P. australis* clones which differed from the other 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 in BSi content of rhizomes at our study site. Seasonal variability due to retranslocation of BSi is most unlikely, as Si is immobilised after deposition in the aboveground biomass.

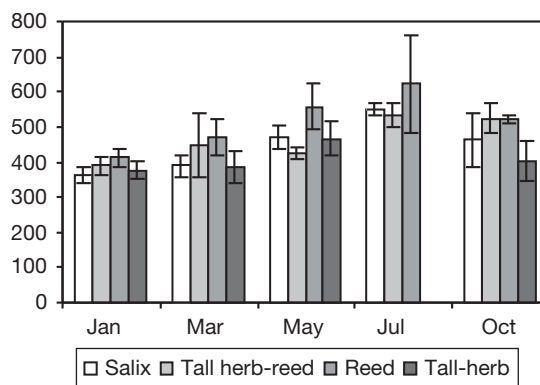
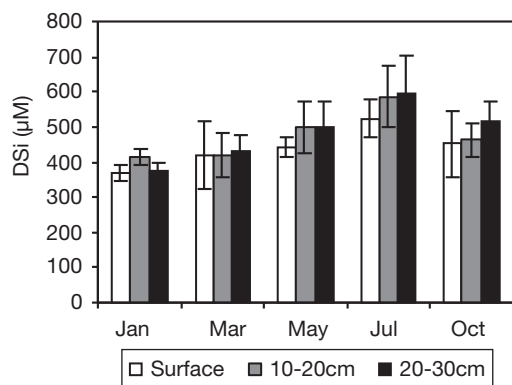


Fig. 8. Marsh-averaged DSi concentration in sediment porewater at different depths ('surface' = 0 to 10 cm) in 2003

BSi in marsh sediments is mostly attributable to BSi imported during flooding, BSi produced by benthic autochthonous marsh diatoms, and plant phytoliths buried after plant decay. 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, the total amounts of BSi stored in the freshwater marsh sediments were much higher than those in the mesohaline tidal marsh (597 vs. 82 g m⁻² in the upper 10 cm), because of higher bulk density of the sediment in our study site. A clear depth gradient was apparent at our site, with BSi content highest in the upper layers. This depth gradient reflects the capacity of freshwater marsh sediments to act as an important DSi source for the estuarine ecosystem in periods of DSi depletion. This recycling capacity was previously shown during a tidal ecosystem-exchange study in the same freshwater marsh (Struyf et al. 2005). The older sediment, which is buried deeper in the marsh, has lost a substantial part (about one-third) of its amorphous silica through dissolution of DSi in the porewater. The porewater is drained from the tidal marsh at flood tides, and recycled DSi is thus resupplied to the estuarine system.

No clear seasonal variation in 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 m²) would, according to the measured BSi concentrations, contain around 5.3 t (±2.0) of BSi. The export of DSi from the same marsh system to the main channel was previously reported to be around 100 to 200 kg each year (Struyf et al. 2005). 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 *Phragmites australis* vegetation generally contained more BSi than sediments under other vegetation types. This could indicate that along with BSi import to the marsh from the main river channel at high tide, burial of *P. australis* phytoliths could also contribute to BSi accumulation in the marsh sediments.

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 for a mesohaline tidal marsh (Norris & Hackney 1999). Dissolution of BSi in the porewater is enhanced by higher temperature and bacterial activity. High porewater DSi concentrations in summer further add to the DSi recycling capacity of the marsh. Based on a porewater volume of 67% (Van de Moortel & Deckers unpubl. data), the total amount of DSi stored in the

studied freshwater marsh is around 10 kg. Compared to the yearly DSi export of around 100 to 200 kg, it is clear that porewater drainage is capable of being the driving force for DSi export to the main river channel.

Using aboveground *Phragmites australis* and tall-herb biomass production data for different vegetation types (Struyf unpubl. data), it was possible to estimate the total BSi stored in aboveground vegetation in freshwater marshes. The total area of freshwater marshes along the Schelde 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 *Phragmites 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; thus these vegetation types were left out of extrapolation. At peak biomass in September, aboveground herbaceous vegetation contained about 75 to 130 t of BSi, 70 to 125 t of which were stored in *P. australis*. In our extrapolations, aboveground tree biomass (*Salix* sp.) was not incorporated, due to lack of data about biomass production of *Salix* sp. along the Schelde. However, *Salix* sp. contained very low amounts of BSi compared to *P. australis*. Low BSi contents in roots were reflected in only 5 to 10 t of BSi stored in non-rhizomeous roots in the upper 30 cm. BSi in *P. australis* rhizomes would account for about 10 to 20 t 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 Schelde contained 90 to 160 t of BSi. The upper 30 cm of sediment along the freshwater Schelde estuary was estimated to contain 4000 to 9000 t 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. Nevertheless, the export of DSi from freshwater tidal marshes to the adjacent estuarine waters was estimated to be around 100 to 200 t yearly in the Schelde freshwater (Struyf et al. 2005), with this export contributing significantly to DSi availability in nearby coastal waters in summer and spring months. Given the high turnover of reed and tall-herb vegetation 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 the vegetation compared to the sediment.

For another freshwater marsh along the Schelde estuary, we recently modelled the sequestration of BSi in the sediment through a combination of short-term year-round sediment-trap data with a long-term sedimentation model (Struyf et al. unpubl. data). We found that 40% of the BSi imported with tidal floodwater was

ultimately buried in the marsh sediments, with the remaining 60% being recycled as DSi. About 7% of the yearly discharge of BSi through the freshwater estuary was estimated to be deposited in freshwater marshes ($40 \text{ g m}^{-2} \text{ yr}^{-1}$) (Struyf et al. unpubl. data). This clearly shows that the marsh sediments not only represent a very large BSi stock among estuarine waters, but that this stock is also subject to significant exchange processes with nearby coastal waters. Freshwater tidal marshes comprise huge reservoirs of BSi, available for recycling as 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 that in the mesohaline marsh study (597 vs. 82 g m^{-2}), and in the *Phragmites australis* vegetation, the BSi content was about 10-fold greater than the content of the mesohaline *Juncus roemerianus* and *Spartina alterniflora* vegetation (85 vs. 7.1 g m^{-2}). The BSi stocks in the aboveground *P. australis* vegetation were comparable to those found in an Amazon rain forest ($83.4 \text{ g BSi m}^{-2}$) (Lucas et al. 1993), while the BSi in the upper 30 cm of sediment was comparable to the phytolith content of the soil of an equatorial rain forest in the Congo (1124 g m^{-2}) (Alexandre et al. 1997). BSi in the aboveground biomass was much higher compared to that of a deciduous forest ($\sim 18 \text{ g BSi m}^{-2}$) (Bartoli 1983) and a coniferous forest ($\sim 9 \text{ g BSi m}^{-2}$) (Bartoli 1983). Around 80% of the reed is deposited yearly as litter on the marsh floor (E. Struyf pers. obs.). The yearly litterfall deposition of BSi in the reed wetland is much higher than in forest ecosystems (*P. australis*: $68 \text{ g BSi m}^{-2} \text{ yr}^{-1}$; forest systems 0.5 to $4.1 \text{ g BSi m}^{-2} \text{ yr}^{-1}$), and we observed that surface litter contained only half the BSi found in standing dead shoots. As *P. australis* is one of the most widely distributed species on Earth (Soetaert et al. 2004), reeds may not only be a largely ignored, highly recyclable sink of BSi in estuarine systems, but also in the global biogeochemical cycle of Si, for which the important role of terrestrial fixation of BSi in plants has only recently been recognised (Conley 2002).

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