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A Comprehensive Study of Silica Pools and Fluxes in Wadden Sea Salt Marshes

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Abstract As an essential nutrient for diatoms, silica plays a key role in the estuarine and coastal food web. High concentrations of dissolved silica (DSi) were found in the seepage water of tidal freshwater marshes, which were therefore assumed to contribute to the silica supply to estuarine waters in times of silica limitation. A comprehensive budget calculation for European salt marshes is presented in this study. Earlier, salt marshes were considered to have even higher silica recycling rates than tidal freshwater marshes. Between 2009 and 2011, concentrations, pools and fluxes of silica in two salt marshes at the German Wadden Sea coast were determined (in soil, pore water, aboveground vegetation, freshly deposited sediments and seepage water). Subsequently, a budget was calculated. Special emphasis was placed on the influence of grazing management on silica cycling. Our results show that the two salt marshes were sinks for silica. The average import of biogenic silica (BSi) with freshly deposited sediments (1,334 kmol km^{-2} year^{-1}) largely exceeded the DSi and BSi exports with seepage water (80 kmol km^{-2} year^{-1}). Grazing management can affect silica cycling of salt marshes by influencing hydrology and vegetation structure. Abandoned sites had larger DSi export rates than grazed sites. One third of all BSi imports occurred in only one major flooding, underlining the relevance of rare events in the silica budget of tidal marshes. This aspect has been widely neglected in earlier studies, what might have led to an underestimation of silica import rates to tidal marshes hitherto.

Keywords Silica cycling · Dissolved silica · Biogenic silica · Nutrients · Grazing management · *Elymus athericus* · Silicon · Rare events

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Introduction

Silica is an essential nutrient for diatoms and has a key function in the food web of coastal waters (Hackney et al. 2000). Depletion of dissolved silica (DSi) in early summer can lead to a limited diatom production accompanied by (partly toxic) algae blooms of non-diatom algae (Anderson et al. 2002). Human-induced alterations of nutrient ratios in coastal waters have intensified this effect during the last decades, and constructional changes like river damming have led to an enhanced biogenic silica (BSi) sedimentation in reservoirs (Dürr et al. 2011).

Tidal freshwater marshes and mesohaline marshes potentially buffer the supply of DSi to the water column during times of depletion (Norris and Hackney 1999; Hackney et al. 2000; Struyf et al. 2006). Due to frequent inundations, these ecosystems receive large amounts of biogenic silica (BSi), which partly gets buried in the marsh sediments and partly re-dissolves. In its dissolved form, silica is either taken up by plants or percolates into the soil. With a continuous stream of interstitial water, DSi seeps from the marsh soil and can be assimilated by benthic and planktonic diatoms. Although being a net sink for BSi on an annual basis, tidal freshwater marshes constitute an important additional DSi source in times of silica limitation in the estuary (Struyf et al. 2007a).

Like tidal freshwater marshes, salt marshes could contribute to the DSi export to coastal waters. Loucaides et al. (2008) showed that increased pH and salinity in seawater can lead to a fivefold enhancement of BSi solubility compared to freshwater. Furthermore, the global area covered by salt marshes is approximately five times larger than that covered by tidal freshwater marshes (Mitsch et al. 2009), and the location of salt marshes at the shoreline favours a direct supply of silica to the adjacent coastal waters. Despite this potential importance, research is limited to only a small number of studies, each of them focussing on certain aspects of silica cycling in salt marshes, such as silica in vegetation (Lanning and Eleuterius 1983; de Bakker et al. 1999; Hou et al. 2010; Querné et al. 2012), soil (Hou et al. 2008; 2010), pore water (Scudlark and Church 1989; Wang et al. 2010) or on silica fluxes (Dankers et al. 1984; Struyf et al. 2006; Vieillard et al. 2011). However, if one aims to assess the role of salt marshes in silica cycling, it is important to not solely measure concentrations, but also to estimate pools of silica and imports and exports of silica, and to finally calculate a budget from these fluxes.

A factor potentially affecting silica cycling in tidal marshes is grazing. By changing soil properties and both quality and quantity of biomass, grazing management can influence the cycling of nutrients in salt marshes (Olsen et al. 2011). European salt marshes were traditionally used as pastures for domestic grazers such as sheep and cattle. For nature conservation reasons, grazing was stopped on many salt marshes since the 1980s. The percentage of abandoned salt marsh area in the German Schleswig-Holstein National Park, for instance, increased from 7 % in 1988 to 44 % in 2006; another 7 % was moderately grazed (Esselink et al. 2009). The abandonment did not only lead to more aboveground biomass and litter accumulation, but also to a shift in species composition and, at many locations, to a reduced plant species diversity (Esselink et al. 2000). On several locations, this change in grazing management resulted in a dominance of *Elymus athericus* (Bockelmann and Neuhaus 1999). This grass species accumulates more silica in its tissue than most other salt marsh plants (de Bakker et al. 1999) and at the same time produces large amounts of biomass (Groenendijk 1984). Analogous to its capacity to sequester carbon in salt marshes (Valéry et al. 2004), it could be hypothesised that it affects silica cycling as well. To our knowledge, only one study identified the impact of grazing management on silica cycling on the ecosystem level. In annually burned grasslands, Melzer et al. (2010) found significantly larger BSi pools in soil on grazed sites than in soils on ungrazed sites.

For several terrestrial and aquatic ecosystems, silica pools contained in soil and vegetation were estimated in earlier studies (e.g. Alexandre et al. 1997; Norris and Hackney 1999; Blecker et al. 2006; Struyf et al. 2007a; Borrelli et al. 2010), but no comprehensive estimation has been carried out for salt marshes so far. With this study, we aim to (1) quantify concentrations and the size of BSi and DSi pools in two European salt marshes, (2) link these pools to silica imports and exports and (3) identify whether or not grazing has an influence on silica pools and budgets.

Methods

Study Sites

The study was conducted in two salt marshes at the coast of the Wadden Sea, a shallow depositional coastal system, stretching from the Netherlands to Denmark (Fig. 1). The Wadden Sea includes the largest coherent tidal flat area of the temperate zone (4,700 km^2) and more than 400 km^2 of salt marshes (Reise et al. 2010). Long-term mean temperature in the region is 8.2 °C (January, 0.3 °C; July, 16.2 °C), and precipitation sums up to 800 mm $year^{-1}$ (DWD 2011). The region experienced a mean sea level rise of approximately 3.6 mm $year^{-1}$ from 1971 to 2008 (Wahl et al. 2011). The coastal waters adjacent to the two salt marshes have a macrotidal regime with a tidal amplitude of 3.0–3.4 m and a mean high tide at +1.6 m Normalhöhennull (NHN) (German height reference system; BSH 2011). Both study sites are man-made landscapes, originally created by land reclamation techniques since the beginning of the twentieth century, and are now part of the Schleswig-Holstein Wadden Sea National Park in Germany, which was established in 1985. A rectangular network of main creeks, side creeks, ditches and levees still reveals the anthropogenic formation. Both study sites are still laterally expanding, have no salt marsh cliff and show a clear zonation from pioneer zone to high marsh, and most of their surface is not inundated during regular floodings. Due to these morphological characteristics, they can be considered representative for the majority of mainland salt marshes of the Wadden Sea area. Traditional land use of the two sites was sheep grazing. To investigate the impact of grazing management on silica cycling, we chose sites in which intensively grazed (>10 sheep ha^{-1}, typical for the region) and ungrazed salt marshes are located next to each other.

Lower Elevated Site, Sönke-Nissen-Koog In 1924, the polder Sönke-Nissen-Koog (SNK) (i.e. an area for land reclamation) was embanked, and after construction of sedimentation fields, the adjacent salt marsh began to develop (54°38′N, 8°50′E). The marsh now extends 1,000 m from dike to mudflats. Mean elevation of the area is 2.0 m NHN, ranging from 0.9 to 2.6 m NHN (digital elevation model retrieved from Vermessungs- und Katasterverwaltung

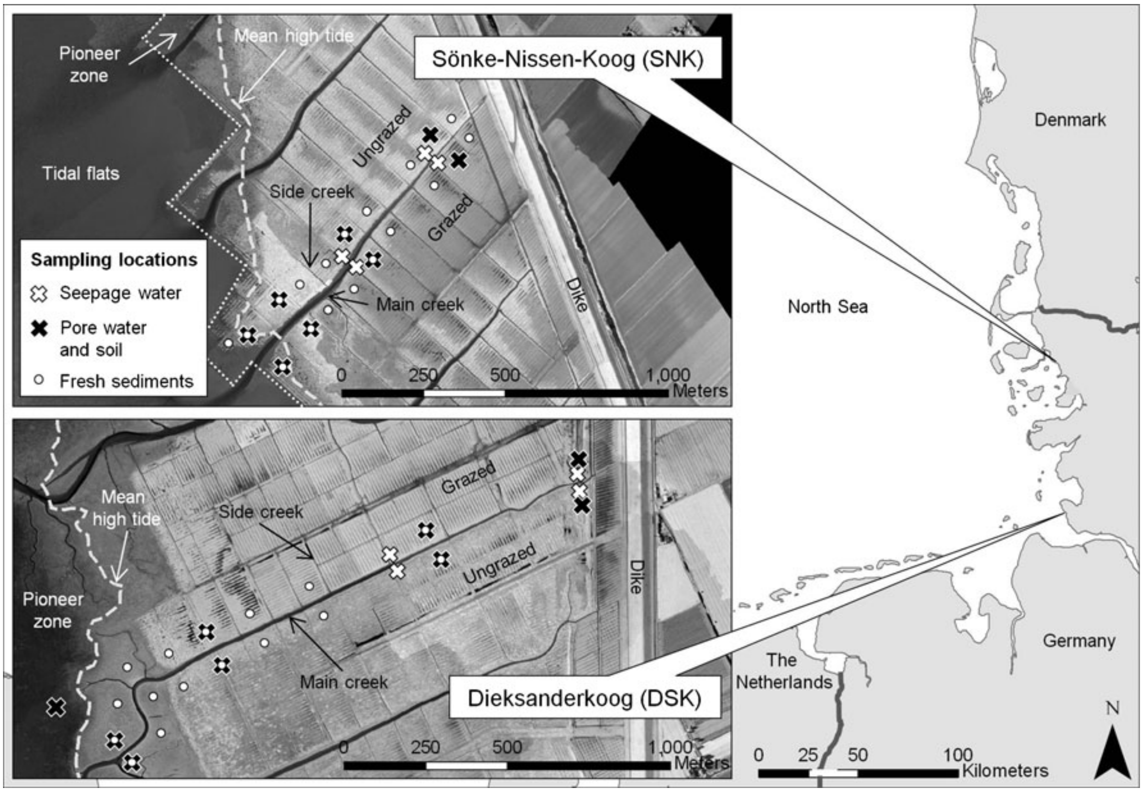

Fig. 1 Location of study sites in the German Bight. Aerial pictures of study sites with sampling locations. Base maps: Amtliche Geobasisdaten Schleswig-Holstein, © VermKatV-SH

Schleswig-Holstein). Approximately one third of the marsh surface is flooded during spring tide. Salinity of the adjacent coastal water is between 25 and 29 (winter and summer, respectively; Becker 1998). Predominant vegetation is the *Puccinellia maritima* type for the grazed site and the *E. athericus* type for the ungrazed part of the salt marsh (according to the vegetation typology of the Trilateral Monitoring and Assessment Program; Esselink et al. 2009). In the upper 60 cm of soil, 25 % of the grains are smaller than 20 μm and 65 % are smaller than 63 μm (Müller 2013).

Higher Elevated Site, Dieksanderkoog The land reclamation polder Dieksanderkoog is located north of the Elbe Estuary (53°58′N, 8°53′E). It was embanked in 1935, and high sedimentation rates led to a quick growth of the adjacent salt marsh. Even when the maintenance of sedimentation fields and ditches was stopped, the marsh continued to grow and finally reached its current extent of 2,500 m from the dike to the mudflats. With a mean elevation of 2.1 m NHN, ranging from 1.2 to 2.8 m NHN, the marsh is slightly higher elevated than SNK. Salinity of the adjacent coastal water is approximately between 14 and 22 (winter and summer, respectively; Becker 1998). The grazed part of the salt marsh is dominated by the *Festuca rubra* vegetation type; on the ungrazed site, the *E. athericus* type is dominant (Esselink et al. 2009). In the upper 60 cm of soil, 40 % of the grains are smaller than 20 μm and 75 % are smaller than 63 μm (Müller 2013).

Sampling

In January 2011, samples from seven different soil depths (3, 7, 10, 15, 20, 40, 60 cm) were taken with a soil corer (Ø 3 cm). To ensure a representative sample, four cores were taken at each sampling location (Fig. 1) within a radius of 2 m. Soil was subsequently pooled per depth. Soil bulk density samples were taken at all soil sampling locations with 100-ml steel cylinders at three depths (5, 20, 60 cm). Depth of the groundwater table and thickness of the litter layer were also determined per sampling location. In August 2009, aboveground biomass of four salt marsh plant species typical for grazed (*F. rubra*, *P. maritima*) and ungrazed conditions (*E. athericus*, *Atriplex portulacoides*) was sampled at locations where these species were dominant. As discussed by De Leeuw et al. (1990), sampling in the second half of August allows a reliable approximation of peak aboveground biomass for European salt marshes. The biomass sampling locations were in a distance of less than 250 m from the main creek. Biomass was harvested on five plots of 400 cm^2 per species and per salt marsh (40 plots in total). If other species were present in these plots, these were separated directly after sampling. Pore water was collected at neap tide in four sampling campaigns covering all seasons (spring, April 2010; summer, July 2010; autumn, November 2010; winter, January 2011). It was sampled from five different depths (3, 10, 20, 40, 60 cm) with porous 'rhizons' (© Eijkelkamp; Shotbolt 2010) connected to a 12-ml syringe under vacuum. Distance to soil sampling sites was 2 m. Freshly deposited sediments were collected with 66 circular sediment traps (see Temmerman et al. 2003) placed pairwise near the soil and pore water sampling locations (Fig. 1). Traps were built of plastic plates (Ø 19 cm) and were equipped with a floatable lid, preventing washout by rain. Traps were firmly attached to the ground with a plastic stick of 1 m length. Sediment was collected biweekly for the duration of 1 year (June 2009–May 2010). Seepage water and flood water were sampled in four side creeks per marsh simultaneously with pore water campaigns. Samples were taken hourly in the middle of the creek during ebb tide and every half an hour during flood tide. During ebb tide, discharge of the creek was measured every half an hour.

Laboratory Analysis

Pore water, seepage water and soil samples were transported to the lab at 4 °C. Conductivity and pH of pore water and seepage water were determined with standard electrodes (Multi 3500i, © WTW). For technical reasons, conductivity and pH were not measured in spring. DSi concentrations of pore water and seepage water were analysed photometrically (DR3800, © Hach Lange; Hansen and Koroleff 1999). Fresh sediments were sieved with a mesh size of 630 μm to remove macroscopic plant material. Fresh sediments and soil samples were dried at 70 °C to constant weight, and 25 mg dry material was weighed into test tubes. Subsequently, the samples were digested in 30 ml of 0.1 M Na_2CO_3 in a shaking water bath at 80 °C (Struyf et al. 2006; Clymans et al. 2011). After 3, 4 and 6 h, subsamples were taken and analysed on their BSi concentration with an ICP-OES (iCAP 6300 Duo, © Thermo Scientific). To correct for the amount of silica resulting from mineral dissolution, the silica content of the subsamples was plotted against dissolution time. The intersection point of the linear regression line through the measured values and the y-axis represents the actual BSi concentration (DeMaster 1981). Seepage water samples were filtered over 0.45-μm nitrocellulose filters within 24 h after sampling. Conductivity, pH and DSi were determined as described above. BSi on filters was determined as described for soil samples, with the only difference that subsamples were taken after 1, 2 and 3 h. Since suitable reaction time largely depends on the sampled material, this time was determined in pre-tests for both filters and soil samples. Aboveground biomass was dried to constant weight at 50 °C. Prior to photometrical measurement of BSi concentration, 25 mg biomass was digested with 10 ml 0.2 M NaOH for 2 h at 80 °C. Soil bulk density and water content were determined by weighing soil bulk density samples before and after drying to constant weight at 105 °C.

Calculation of Pools, Fluxes, Budgets

Pools of soil BSi were calculated by multiplying soil bulk density with mean BSi concentration in soil samples for the upper 60 cm. Pools of BSi in aboveground biomass were calculated by multiplying mean weight of aboveground biomass with BSi content of the analysed salt marsh plants. Pools of pore water DSi were calculated by multiplying water content with the yearly mean of DSi concentration for the upper 60 cm of soil. For pools of soil BSi and pore water DSi, data were linearly interpolated for unsampled depths. All pools were calculated per salt marsh and grazing regime. For soil BSi and pore water DSi, pools were calculated for low and high elevation zones separately, with 'low' zones being elevated lower than 2 m NHN and 'high' zones being higher than 2 m NHN.

To estimate BSi imports, sediment samples were analysed for their BSi concentration as described for soil samples (in total 126 samples). The number of samples analysed varied between 7 and 21 per marsh and season since, for some periods, only a minor amount of floodings was registered and therefore not for all seasons and trap locations the same amount of samples was available. To obtain yearly BSi import rates, the mean seasonal BSi concentration of sediments was multiplied with the sum of sediment weight recorded for each trap location in that very season. These values were summed up. Low marsh zones were represented by only two to four traps (compared to up to 16 traps for high marsh zones), and thus no statistical comparison between the zones was carried out. DSi and BSi imports via the creek water during flood tide were not quantified in this study. Even during spring tides, the water level in these salt marshes stays below the edge of the creeks we sampled. Consequently, no DSi and BSi is deposited on the marsh surface as long as no higher flood occurred. For safety reasons, sampling was only carried out when no higher flood was forecasted.

To calculate silica exports with seepage water, discharge and silica concentrations were related to the catchment area of each creek. Creek catchments were determined by using contour lines as a proxy for isopiestic lines. We assumed seepage water to leach from the soil during the whole tidal cycle, since groundwater levels were higher than mean high tide during all sampling campaigns. The time when creeks were filled with flood water was therefore not subtracted when daily export rates were calculated. Silica budgets were derived by subtracting BSi and DSi exports from BSi imports. For pools, fluxes and budgets, the reported standard deviation was calculated according to the law of error propagation. All DSi and BSi values in this study are expressed as elemental silicon Si and not as SiO_2.

Statistical Analysis

Differences in the concentration of soil BSi between the two salt marshes were analysed with a general linear model with repeated measures. A Mann–Whitney *U* test was carried out for each sampled soil depth to test for statistical differences in the concentration of pore water DSi between grazed and ungrazed sites. Seasonal differences in the concentration of pore water DSi under different dominant vegetation types (*Atriplex prostrata*, *E. athericus*, *F. rubra*, *P. maritima* and *Spartina anglica*) were analysed with a Kruskal–Wallis test. For BSi in freshly deposited sediments, *U* tests were used to test for concentration differences between the two salt marshes and between grazed and ungrazed sites, and a Kruskal–Wallis test was used to detect concentration differences between seasons. Due to a limited number of cases, no statistical analysis was carried out for pools and fluxes. Statistical significance in all tests was determined using a 95 % confidence interval with the probability $p<0.05$. All analyses were conducted with SPSS 19. The symbol '±' indicates standard deviation.

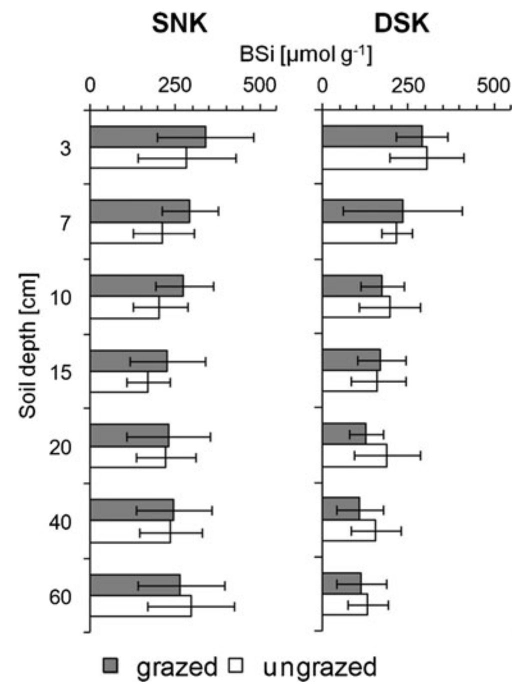

Fig. 2 Mean BSi concentration in soil samples of different depths from SNK and DSK. *Error bars* represent 1 standard deviation

Results

Concentrations: BSi in Soil

BSi concentration in the soil ranged from 40 to 519 µmol g^{-1} and was on average 213±105 µmol g^{-1} (Fig. 2). BSi was generally higher at SNK (249±104 µmol g^{-1}) than at Dieksanderkoog (DSK) (181±97 µmol g^{-1}; $F=5.11$; $N=28$; $p<0.05$; general linear model with repeated measures). Considering only samples from 40 and 60 cm depth, concentrations at SNK were even twice as high compared to DSK. The BSi depth distribution differed between the marshes: At SNK, BSi concentrations were 'u shaped' with the highest values in both the uppermost and lowest layers, whereas at DSK, values decreased with increasing depth.

There was no clear effect of grazing management: at SNK, a tendency of higher concentrations on grazed compared to ungrazed sites was observed, especially in the upper layers (Fig. 2). At DSK, the pattern was opposite, and most depths showed a tendency of higher BSi concentrations on ungrazed compared to grazed sites.

Concentrations: BSi in Aboveground Biomass

BSi concentration of typical plant species ranged from 52±14 µmol g^{-1} (*A. portulacoides*) to 429±138 µmol g^{-1} (*E. athericus*; Fig. 3). Slight but not significant differences were observed between the two study sites. All monocotyledons had higher concentrations compared to the single dicotyledon of the study (*A. portulacoides*).

Concentrations: DSi in Pore Water

DSi concentration in the pore water was on average 408±128 µmol l^{-1} and ranged from 145 to 1,039 µmol l^{-1} (Fig. 4). It was similar for SNK (420±146 µmol l^{-1}) and DSK (396±109 µmol l^{-1}). On both salt marshes, DSi concentrations increased with depth, and both marshes showed a tendency of lower values on ungrazed compared to grazed sites. The only significant differences related to management were found for DSK, where in winter pore water in 3-cm soil depth had higher DSi concentrations on ungrazed sites than on grazed sites (winter: $U=1.00$; $N=9$; $p<0.05$; Mann–Whitney *U* test).

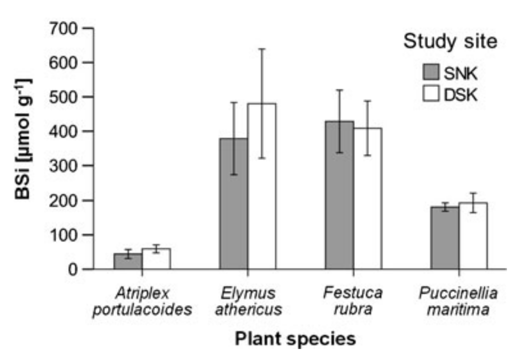

Fig. 3 Mean BSi concentration in four typical marsh plants. *Error bars* represent 1 standard deviation

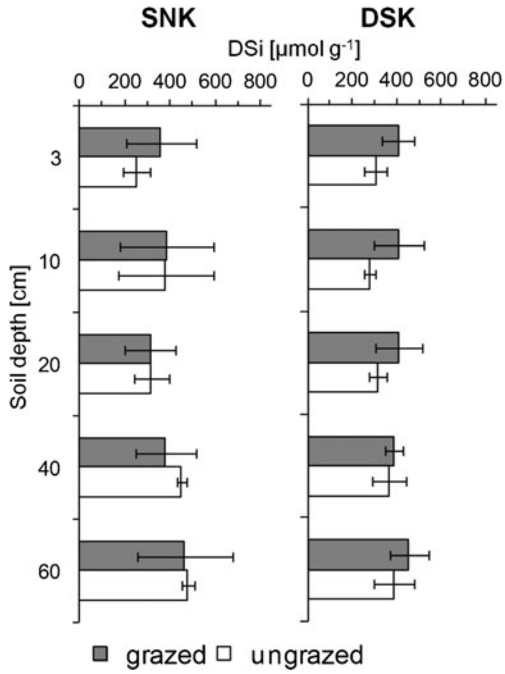

Fig. 4 Mean winter DSi concentration in pore water samples from SNK and DSK grouped for sampling depth. *Error bars* represent 1 standard deviation

In summer, all pore water samples in 3- and 10-cm depth below *E. athericus* had lower DSi concentrations than in the same depth under other dominant plant species (Fig. 5). These differences were, however, not statistically significant (3 cm, H=6.46, N=13, p=0.16; 10 cm, H=8.08, N=15, p=0.09; Kruskal–Wallis tests). In winter, the average concentration at 60-cm depth was almost equal under most dominant plant species (Fig. 5).

Pore water conductivity, as a proxy for salinity, was on average 25±14 mS cm^{-1}. Annual mean conductivity was twice as high at SNK (33±11 mS cm^{-1}) compared to DSK (17±11 mS cm^{-1}).

Concentrations: BSi in Fresh Sediments

BSi concentration in freshly deposited sediments varied from 17 to 840 µmol g^{-1} and was on average 447±206 µmol g^{-1}. Concentrations differed significantly with season (H=10.23; N=126; p<0.05; Kruskal–Wallis test); highest values were found in summer (on average 517±217 µmol g^{-1}) and lowest in spring (on average 395±202 µmol g^{-1}). BSi concentration was not significantly different in samples taken at SNK or DSK (U=1,931, N=126, p=0.84; Mann–Whitney U test) or under different grazing management (U=1,810, N=126, p=0.41; Mann–Whitney U test).

Pools: BSi in Soil

The spatial distribution of silica pools in the upper 60 cm of soil differed between the two salt marshes (Table 1). At SNK, independently from the management, the largest pools of soil BSi were found in the high elevated zones. At DSK, this pattern was opposite and pools were higher in the low elevated zones. Except for the high elevated zone at SNK, ungrazed sites had always larger pools of soil BSi than grazed sites.

Pools: BSi in Aboveground Biomass

Aboveground biomass weighed between 202±91 g m^{-2} (DSK, grazed site) and 2,443±1,103 g m^{-2} (DSK, ungrazed site) and had an average weight of 1,047±1,084 g m^{-2}. Largest silica pools in aboveground biomass were observed on ungrazed sites (Table 1). The biomass BSi pool made up between 0.04 and 0.58 % of the soil BSi pool.

Pools: DSi in Pore Water

No large variation was observed in the size of the DSi pool in the pore water in the upper 60 cm of soil (Table 1). It made up between 0.09 and 0.20 % of the soil BSi pool.

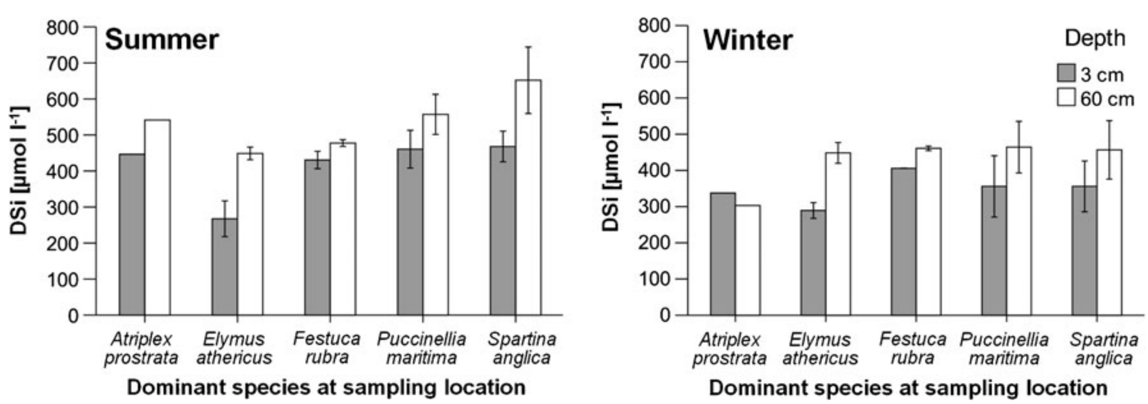

Fig. 5 Mean DSi concentration in pore water samples under dominant plant species, averaged for both SNK and DSK. *Error bars* represent 1 standard deviation

Table 1 Pools, fluxes and budgets of silica in SNK and DSK. The reported standard deviation is calculated according to the law of error propagation from the standard deviations of the input parameters. Silica imports via flood water and silica pools in belowground biomass were not determined; see 'Methods' and 'Discussion' sections for further information

Salt marsh	SNK				DSK			
Grazing management	Grazed		Ungrazed		Grazed		Ungrazed	
Elevation (high, >2 m NN; low, <2 m NN)	High	Low	High	Low	High	Low	High	Low
Pools [kmol Si km^{-2}]								
Soil (BSi)	171,360±34,180	84,990	151,690±47,110	138,500	90,170±31,000	117,900±8,750	114,300±53,700	139,900
Aboveground biomass (BSi)	76±53		274±256		61±38		660±671	
Pore water (DSi)	147±20	171±13	140±9	172±25	128±10	136±10	108±12	134±13
Fluxes [kmol Si km^{-2} year^{-1}]								
Imports with fresh sediments (BSi)	1,051±602	4,266±389	696±173	2,598±567	185±58	943±171	144±33	758±377
Exports with seepage water (DSi)	76±53		108±47		16±19		84±65	
Exports with seepage water (BSi)	14±12		13±8		1±2		4±3	
Budgets [kmol Si km^{-2} year^{-1}]								
Imports - Exports	962±604	4,176±393	475±173	2,477±569	186±61	926±172	55±73	670±382

Fluxes: Imports

Yearly sedimentation rates were on average 2.2±0.5 kg m^{-2} year^{-1} with maximum values observed for spring and autumn (Fig. 6), when storm events caused high inundations. Due to a flooding event in spring, the standard deviation is large in this season. If that outlier would be removed, the sum of sediments would be 0.3 instead of 1.3 kg m^{-2} per 3-month period. However, since episodic events are part of the dynamic nature of a salt marsh, outliers were not excluded from the data set. More sediment was deposited at the lower elevated SNK (3.6±0.9 kg m^{-2} year^{-1}) than at the higher elevated DSK (1.0±0.3 kg m^{-2} year^{-1}).

Sedimentation appeared to be the driving factor influencing BSi imports. Higher BSi imports were observed for SNK compared to DSK and in the low elevated zone compared to the high elevated zone (Table 1). On average, BSi imports were 1,316±1,019 kmol Si km^{-2} year^{-1} (Table 1).

Fluxes: Exports

Mean discharge of seepage water was between 28 (DSK, grazed site) and 265 l m^{-2} year^{-1} (SNK, ungrazed site). DSi and BSi concentrations in the seepage water were on average 338±112 and 49±42 µmol l^{-1}, respectively (as a comparison: DSi and BSi concentrations in the flood water were on average 90±69 and 54±34 µmol l^{-1}, respectively). DSi exports via the seepage water were on average 72±59 kmol km^{-2} year^{-1} (Table 1). BSi exports made up 11 % of this value. Compared to DSK, SNK had higher exports of both DSi and BSi. At the latter marsh, average DSi exports from ungrazed sites exceeded those from grazed sites by 40 %; on DSK, it was 440 %.

Fluxes: Budgets

BSi imports with sediments exceeded DSi exports with seepage water by far (Table 1). The net silica import at both

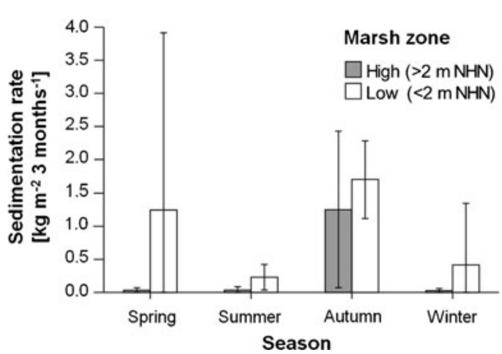

Fig. 6 Mean seasonal sedimentation rate between June 2009 and May 2010 per marsh zone, averaged for both study areas. Spring: Mar.–May; summer: Jun.–Aug.; autumn; Sep.–Nov.; winter; Dec.–Feb. *Error bars* represent standard deviation

salt marshes was on average 1,334±736 kmol km^{-2} year^{-1}. At SNK, imports were up to two orders of magnitude larger than exports, whereas at DSK, the difference between imports and exports was less pronounced.

Discussion

An integrated study about the role of salt marshes in coastal silica cycling, considering concentrations, pools and budgets as well as the different compartments in a marsh system (soil, aboveground biomass, pore water, fresh sediments and seepage water) was carried out. The salt marshes investigated here were clear sinks for silica. Due to the large amount of stored BSi, the sites have the potential to become efficient net sources of silica in the future. Grazing management had an effect on BSi pools in aboveground vegetation and on DSi exports, but its overall impact on the role of salt marshes in silica cycling appears limited.

Concentrations

Soil BSi concentrations of the studied sites were lower than in many other terrestrial soils, but in the range of values from most other tidal marsh systems (Table 2). In contrast to this study, a recent budget study of silica pools and fluxes in two North American salt marshes (Carey and Fulweiler 2013) identified exceptionally high soil BSi concentrations of up to 4,586 µmol g^{-1}. The latter high value is interesting as pore water DSi concentrations in the same marshes did not show comparably elevated values, but are in the same range as found for other tidal marshes. Thus, both settings (here and in the study of Carey and Fulweiler 2013) might give the span of BSi concentrations to be expected in salt marshes.

Pore water DSi concentrations were relatively high compared to other tidal marshes (Table 2). Comparably high concentrations were earlier mainly reported for groundwater and river water in volcanic soils (Miretzki et al. 2001). BSi concentrations in the aboveground dry biomass were at the lower end of values reported to be typical for 'dryland' grasses (1–3 wt%, equivalent to 360–1,070 µmol g^{-1}; Epstein 1994).

The 'u-shaped' depth distribution of soil BSi at SNK (Fig. 2) resembles patterns described for rain forest soils (Alexandre et al. 1997) and a tidal freshwater marsh (Struyf et al. 2007a). Alexandre et al. (1997) ascribed lower values in the root zone to plant uptake of DSi and consequently increased equilibrium-driven weathering of soil BSi (Farmer et al. 2005). Struyf et al. (2007a) mentioned high BSi imports and subsequent burial in the early marsh development as a reason for higher concentrations in deep soil layers. Also, grain size was discussed as an explanation for BSi distribution in the soil profile (Hou et al. 2008). For our study sites, a combination of these explanations could be considered. On the one hand, plants like *E. athericus*

Table 2 BSi concentrations in the soil of tidal marshes and of different grassland ecosystems and DSi concentrations in the pore water of tidal marshes

Ecosystem	μmol g^{-1}		Reference
BSi concentrations in the soil	Range	Average	
Mesohaline marsh, North Carolina	140–180		Norris and Hackney (1999)
Tidal freshwater marshes, Belgium	110–390		Struyf et al. (2005a); Struyf et al. (2007a)
Vegetated intertidal flats at Yangtze Estuary, China	240–420		Hou et al. (2008)
Vegetated intertidal flats at Chongming Island, Yangtze Estuary, China	305–801		Hou et al. (2010)
2 salt marshes at Narragansett Bay, Rhode Island, USA, upper 30 cm	107–4,586		Carey and Fulweiler (2013)
2 salt marshes at the Wadden Sea coast, Germany	40–519	213	This study
Salt marsh, Het Zwin, Belgium (summer)	3–380	199	This study, attachment
Terrestrial soils, worldwide	40–1,070		Sommer et al. (2006), citing several authors
Mixed and tall grass steppe, North America	40–1,600		Blecker et al. (2006)
Mesic grassland, Argentina	2,100–4,450		Borelli et al. (2010)
Mesic grassland, Kansas	610–2,640		Melzer et al. (2010)
Pasture, Sweden	33–201		Clymans et al. (2011)
	μmol l^{-1}		
DSi concentrations in the pore water	Range	Average	
Salt marsh, South Carolina	250–749	516	Gardner (1975)
Salt marsh, Great Marsh, Delaware, upper 60 cm (spring)	100–520		Scudlark and Church (1989)
Salt marsh, Great Marsh, Delaware, upper 40 cm (autumn)	110–1,000		Scudlark and Church (1989)
Mesohaline marsh, North Carolina, upper 30 cm (June–September)		295	Norris and Hackney (1999)
Mesohaline marsh, North Carolina, upper 30 cm (January–May)		198	Norris and Hackney (1999)
10 salt marshes at the Oosterschelde	51–554		de Bakker et al. (1999)
Tidal freshwater marsh, Tielrode, Belgium, upper 30 cm (summer)	500–600		Struyf et al. (2005b)
Tidal freshwater marsh, Tielrode, Belgium, upper 30 cm (winter)	350–410		Struyf et al. (2005b)
Salt marshes at Yangtze Estuary and Hangzhou Bay, China	50–250		Wang et al. (2010)
Salt marsh in the Bay of Brest, France	40–260		Querné et al. (2012)
2 salt marshes at Narragansett Bay, Rhode Island, USA, upper 30 cm	8–309		Carey and Fulweiler (2013)
2 salt marshes at the Wadden Sea coast, Germany	150–1,040	408	This study
Salt marsh, Het Zwin, Belgium (summer)	80–530	301	This study, attachment

and *F. rubra* with high silica concentrations (Lanning and Eleuterius 1983) might have led to decreased BSi concentrations in the root zone. On the other hand, fast sedimentation in the early marsh development might have led to the burial of soil layers enriched in BSi. Finally, at DSK, where BSi concentrations were generally lower compared to SNK, the percentage of small grain sizes was lower too.

It has previously been hypothesised that salt marshes might be very active silica recyclers (Hackney et al. 2000; Struyf et al. 2007a), since high salinity of seawater can enhance dissolution rates of BSi (Loucaides et al. 2008). For instance, a study on the silica efflux from tidal marshes along the salinity gradient in the same area identified increased DSi concentrations for brackish marshes and salt marshes (Weiss et al. 2013). Although the elevated DSi concentrations in the pore water support this hypothesis at a first glance, it is not certain whether the concentrations were indeed mainly salinity driven. One indication that other mechanisms act on DSi concentrations is the fact that electrical conductivity of pore water was higher at SNK than at DSK, whereas DSi concentrations in the pore water did not differ between the two marshes. Further factors such as temperature, pH, hydrology, catchment lithology, tidal regime, season and silica imports can affect DSi concentrations as well (e.g. Gerard et al. 2002; Loucaides et al. 2008; Struyf and Conley 2009; Hartmann et al. 2010; Weiss et al. 2013).

Pools

The overall silica pools of our study sites appeared to be medium to large compared to comparable ecosystems (Table 1). By far, the largest of the three investigated pools was observed as BSi in the upper 60 cm of soil, ranging from 85,000 to 171,400 kmol km^{-2}. Struyf et al. (2005b) reported 54,000 kmol km^{-2} for the upper 30 cm of a tidal freshwater marsh, and Blecker et al. (2006) calculated 30,000 to 240,000 kmol km^{-2} for the upper 50 cm of grassland soils along a climatic gradient. It can be assumed that the silica pool in Wadden Sea salt marshes is far larger than calculated for the upper 60 cm in this study. On average, 10–12 m of marine sediments, potentially rich in BSi, were deposited on top of the Pleistocene sand layer in Wadden Sea salt marshes during the Holocene (Freund and Streif 2000).

Compared to soils, silica pools in biomass and pore water were up to four orders of magnitude smaller. The BSi pool in aboveground biomass was between 61 and 660 kmol km^{-2}, which is even higher than silica generally recycled by plants on a yearly base (10 to 270 kmol km^{-2}) as it was reported by Cornelis et al. (2011; citing several authors). Biomass accumulation and hence size of BSi pools differ between salt marshes and tidal freshwater marshes. For a *Phragmites australis*-dominated site, Struyf et al. (2005b) calculated aboveground pools of up to 3,000 kmol km^{-2}. This value is in the same order of magnitude as BSi pools in rain forest vegetation (Lucas et al. 1993) with the essential difference that aboveground biomass of *P. australis* decays to nearly 100 % in winter (Struyf et al. 2007b), leading to very short silica turnover times. The size of the DSi pool in the pore water of our sites was in the same order of magnitude as the BSi pool in aboveground biomass. If vegetation is considered as being an important silica pool in budget calculations (as it was done by Blecker et al. 2006), pore water should consequently be included in such calculations as well.

The BSi pool in belowground biomass was not measured, but can be estimated. For this purpose, it is assumed that the BSi concentration in the belowground biomass corresponds to one third of the concentration in the aboveground biomass, as described for several grass species by Webb and Longstaffe (2000) and Querné et al. (2012). Kiehl et al. (2001) determined belowground biomass at SNK to be on average 2,340± 260 g m^{-2} in the upper 50 cm of soil. Using these data, a BSi pool in belowground biomass of 160±150 kmol km^{-2} can be estimated. This value is within the range of the aboveground biomass. Carey and Fulweiler (2013), however, reported an elevated aboveground vegetation to root BSi concentration ratio (on average 1:1.3), which underlines the fact that the ratio is likely to be both species and site depending and should be measured in future budget studies.

Fluxes

BSi imports to the study sites were one order of magnitude larger than DSi exports, causing an accumulation of silica in the marshes. As outlined in the ‘Methods’ section, imports via the creek water were not considered in this study as the flood water normally does not inundate the marsh surface. This is mainly because the salt marshes are relatively highly elevated. For younger, lower elevated salt marshes, the import via the creek water might well be of importance and should be considered in the budget.

Gross exports of DSi with seepage water of 16–108 kmol Si km^{-2} year^{-1} were slightly larger than export rates measured for terrestrial grasslands in North America (1–39 kmol Si km^{-2} year^{-1}; Blecker et al. 2006). However, since imports to these systems were only atmospheric, these systems were net sources, exporting up to 32 kmol Si km^{-2} year^{-1}. In contrast to our sites, also salt marshes in the Netherlands, Delaware and France were reported to be net exporters of silica (net export rates of 110, 170 and 340 kmol Si km^{-2} year^{-1}, respectively; Dankers et al. 1984; Scudlark and Church 1989; Struyf et al. 2006). These results are, however, not directly comparable to results of this study: Only DSi and BSi fluxes via the flood and seepage water were considered, and no sediment BSi influxes using sediment traps were considered.

This methodological difference would cause an underestimation of DSi and BSi imports in referenced studies, since no measurements during heavy storm tides have been conducted. In addition, for shrinking salt marshes, also BSi exports via physical erosion might affect the silica budget significantly. Thus, an overarching determination of the question whether a salt marsh acts as a source or a sink for silica, sedimentation and erosion processes needs to be considered where sediment-related fluxes are significant.

Even though salt marshes are BSi-accumulating systems, they still deliver significant amounts of DSi to the adjacent nearshore coastal system, which especially in summer could help diatoms to overcome DSi shortage. While the effect is probably only local, it could be relevant since diatoms play a key role in the productivity of the adjacent tidal flat ecosystem (Admiraal 1977). Thus, the additional DSi supply from salt marshes could be important for the nearshore coastal food web in the coastal zone. When stable isotope analyses showed that the high productivity of estuaries is not linked to plant production in tidal marshes (Haines 1976; Kang et al. 2003), silica exports were hypothesised to be the missing link between tidal marshes and productivity in adjacent water bodies (Hackney et al. 2000). The absence of studies quantifying this marsh–nearshore water body DSi fluxes calls for a series of new experiments.

Storm Surges and Tidal Regime

BSi imports were strongly driven by storm tides. During one major flooding in October 2009 for instance, 36 % of all sediments recorded for the whole study period were deposited. The BSi concentration of these sediments was slightly lower than the autumn average but still higher than the yearly average. This single occurrence underlines the importance of rare events for the import of sediments (McKee and Cherry 2009) and the soil BSi pool.

To assess whether the sedimentation rates reported here are representative, accretion rates can be calculated by setting the imported mass of sediment per unit area in relation to soil bulk density at the sampling locations. The resulting accretion rate of on average +2 mm year^{-1} is below the +6 mm year^{-1} that Stock (2011) and Suchrow et al. (2012) reported for adjacent study areas. The conclusion that BSi imports are most likely underestimated in this study seems reasonable given the fact that an untypical low number of floodings were observed during the study period. Water levels of 1 m>MHT were reached six times and water levels of 1.5 m>MHT only once. In the last decade, these water levels were reached 12 and 3 times per year, respectively (calculated from a water gauge Cuxhaven, near DSK; WSV 2012). Based on the episodic nature of sedimentation events, it seems to be necessary to conduct long-term measurements on accretion rates in addition to sediment trap measurements to estimate better BSi imports into marshes and to quantify the role of rare events on the silica-flux dynamics in marshes.

Tidal freshwater marshes in the Scheldt estuary (at location Notelaar; Struyf et al. 2007a) had smaller net BSi imports than the salt marshes investigated here, even though their gross imports were 30 % larger. At Tielrode, a tidal freshwater marsh of 5 km distance to Notelaar, Struyf et al. (2005a) measured DSi exports in seepage water of 200 to 13,000 kmol km^{-2} year^{-1}. We assume that differences in hydrology are the reason for both the large variation within the Scheldt dataset as well as the large difference to our values. Whereas the tidal freshwater marshes were completely flooded during each spring tide, our salt marsh sites were only entirely inundated during storm tides. Consequently, the discharge values reported by Struyf et al. (2005a) were on average 15,000 l m^{-2} year^{-1}, equivalent to the 20-fold amount of annual rainfall. Since regionally representative salt marshes were chosen for this study, it can be assumed that our findings apply to many salt marshes of the Wadden Sea region and close a relevant gap in the available data inventory.

Marsh Maturity

Silica budgets in this study differed considerably with elevation. BSi imports were far higher in the low (<2 m NHN) than in the high (>2 m NHN) marsh zone, and they were higher at SNK compared to DSK. Modelling of BSi burial rates in tidal freshwater marshes confirmed that due to larger sediment inputs, in a low elevated young marsh, nearly all freshly deposited BSi got buried. In a higher elevated older marsh, this was true for less than half of the BSi (Struyf et al. 2007a). According to the concept of 'marsh maturity', a salt marsh functions as a sink for nutrients as long as it is low in elevation and therefore 'flood dominated' or 'immature' (Boorman 1999; Hazelden and Boorman 1999). With increasing age and elevation, the marsh would turn from a sink to a source since inundation frequency and the import of sediments and organic matter decrease on this now 'ebb-dominated' or 'mature' marsh, allowing for the leaching of nutrients to the adjacent coastal water.

In the present study, the higher elevated DSK gets flooded less often than the lower elevated SNK and can be considered as being more 'mature'. At DSK, soil BSi concentration in the deepest soil layers (40 and 60 cm) was only half of the values measured for SNK (126±115 compared to 260±68 μmol g^{-1}). One explanation could be that BSi concentrations have always been lower. However, this appears unlikely considering that no significant difference in BSi concentrations of fresh sediments between the two marshes could be found. It is more likely that dissolution and leaching of BSi have already led to a partial depletion of the overall silica pool at DSK, and the pool has not been refilled by imports to the same extent. This hypothesis is supported by data on the soil BSi concentration of an even less often flooded salt marsh in Belgium (Appendix). In this marsh, average BSi concentration in 40- and 60-cm depth was only 79±56 μmol g^{-1}. Although both DSK and SNK are sinks for silica at present, with increasing maturity, the marshes might turn from a sink to a source. In theory, this could earlier be the case for DSK, because it is already more mature and has lower soil BSi concentrations and lower BSi imports. However, a rising sea level could also lead to a backward development towards immature marshes with again high sediment and BSi imports (Hazelden and Boorman 1999).

Grazing Management

Although vegetation composition changed considerably since the abandonment of grazing (Stock et al. 2005), no congruent differences in BSi concentrations of soil and aboveground biomass were observed between grazed and ungrazed sites. At SNK, ungrazed sites had slightly higher soil BSi concentrations; at DSK, the opposite was the case. However, these differences were generally not significant and variation was high. The silica-accumulating grass *E. athericus*, which was dominant on all ungrazed sites, is known for its high biomass production (Valéry et al. 2004). It could have been expected that BSi concentrations were lower on *E. athericus*-dominated sites, because high silica uptake rates might cause the abovementioned equilibrium-driven BSi dissolution in soils. However, probably the time of abandonment was not long enough to observe a significant reduction of soil BSi on ungrazed sites. Solely pore water DSi showed significant differences related to grazing management. In winter, pore water DSi concentrations in upper soil layers were decreased under ungrazed conditions. With increasing depth, the differences between the differently managed sites vanished almost completely, probably because biological activity is lower in deeper soil layers.

Concerning the pools, grazing management only had an influence on BSi pools in vegetation. Larger stands of biomass on ungrazed sites led to larger pools. However, given the fact that BSi pools in the soil were two orders of magnitude larger, the differences between BSi pools in biomass of grazed and ungrazed sites were negligible. It should further be noted that only standing biomass and litter was harvested and the amount of biomass consumed by grazing animals was not accounted for. The effect of grazing could have led to an increased biomass turnover and therefore quicker mineralisation of phytoliths on the grazed site. Furthermore, during the digestion process, the plant tissue around grass phytoliths is removed, presumably accelerating the dissolution of BSi as it was found for the removal of organic coatings from diatom frustules (Bidle and Azam 1999).

BSi imports appeared to be much larger for grazed compared to ungrazed sites. However, this difference could be an artefact of the applied sampling method. While sediment traps are an adequate measure to evaluate the amount and distribution of sediments within a homogeneous stand of vegetation, it can be questioned if their application is appropriate if vegetation structure differs between sampling locations. Vegetation is known to sieve sediments from the inundation water (Christiansen et al. 2000). The high and dense stands of *E. athericus* on the ungrazed sites could hence reduce the amount of sediment that reaches the trap. Another factor influencing sedimentation rates is the elevation of a site. At SNK, elevation of traps on the grazed site were on average 5 cm lower than traps on the ungrazed site, what might have led to more frequent inundations and consequently more sedimentation. At DSK, elevation of traps on the grazed site was 1 cm lower compared to the ungrazed site.

DSi exports were largest on ungrazed sites. Aboveground biomass and a thick litter layer can lead to retention of precipitation and inundation water (Facelli and Pickett 1991). As a consequence, soils on these sites were flushed better, what might have enhanced desilication (dissolution and leaching of silica during ageing of soils; Sommer et al. 2006). With advanced desilication, BSi concentrations in the soil could be expected to drop. We did not observe decreased concentrations of BSi in ungrazed sites. The dense and tall vegetation might lead to increased trapping of BSi during inundation, compensating for possible losses. It can therefore be concluded that the abandonment of grazing did not yet have an effect on the overall silica budgets. However, assuming the marshes would reach a more mature state with decreased tidal influence, the leaching of BSi can be expected to be enhanced on ungrazed sites.

Conclusion

Both salt marshes were sinks for silica. Even though a considerable amount of DSi was exported with the seepage water, BSi imports with freshly deposited sediments strongly exceeded this value. Most of the BSi was imported during storm tides. Neglecting these rare events may have led to a vast underestimation of BSi import rates in earlier studies on silica budgets in tidal marshes. In future budget studies, BSi import rates should hence be considered. The marshes differ in their level of maturity, which might influence their role in silica cycling: as seen for other nutrients, mature salt marshes can turn from a sink to a source of silica. However, data on the influence of maturity on silica fluxes are widely missing. We found different effects of grazing management on the silica budget of the sites. On the one hand, silica exports were enhanced on ungrazed sites, where litter and vegetation led to a longer retention time of rain and inundation water. On the other hand, tall vegetation can increase sedimentation and therefore silica imports. Little is known about the role of grazing animals in silica cycling. In future studies, the fate of BSi in the digestive tract of large and small herbivores should be considered as well as the implications of grazing management for the local and global silica cycling.

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Appendix

Table 3 Mean pore water DSi concentration, conductivity and pH and soil BSi concentrations of an ungrazed Belgian salt marsh ('Het Zwin' near Knokke-Heist, 51°22′N, 3°22′E), sampled in a supplemental sampling campaign on 9 August 2011. Sampling locations A and B were located next to two different creeks in a distance of about 400 m to each other. Sampling and analysis were carried out as described in this study

Soil depth (cm)	Pore water						Soil	
	DSi concentration (μmol l^{-1})		Conductivity (mS cm^{-1})		pH		BSi concentration (μmol g^{-1})	
	Mean	*N*	Mean	*N*	Mean	*N*	Mean	*N*
3	273±181	4	29±4	4	7.48±0.2	3	350±34	4
7							292±57	4
10	222±126	4	45±6	4	7.37±0.07	3	213±96	4
15							188±36	4
20	286±193	4	47±5	3	7.24±0.12	3	192±71	4
40	266±95	4	48±3	4	7.48±0.07	4	87±78	4
60	381±104	4	47±3	4	7.32±0.12	4	71±31	4

N number of samples, ± standard deviation

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