

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

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Abstract

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

Compared with our extensive knowledge concerning N and P processing in the aquatic continuum of watersheds, rivers, lakes, and estuaries, the transport and cycling of silicon has been significantly less well studied (Conley et al.

2000). In contrast to N and P, with large human inputs, anthropogenic input of Si to estuarine systems is negligible. However, the ratio of dissolved Si (DSi) to nitrogen and phosphorus that eventually reaches coastal waters through estuaries greatly affects eutrophication in the coastal zone. High anthropogenic inputs of N and P can induce DSi limitation in diatoms and cause a succession of the phytoplankton community to nondiatom species (Schelske et al. 1983; Lancelot 1995; Smayda 1997), which are less available to higher trophic levels (e.g., *Phaeocystis* sp., *Gonyaulax* sp., *Chrysochromulina* sp.). Apart from this negative effect on estuarine and coastal food webs, enhanced nondiatom phytoplankton production can have several other negative consequences, including increased water turbidity, anoxic conditions, and the appearance of toxic algal blooms (Gazeau et al. 2004).

Within estuarine ecosystems, tidal marshes and wetlands are important processors and sinks for nutrients, sediments, and pollutants. However, intertidal systems have often been neglected in terms of their functioning within the estuarine Si cycle. Vegetated intertidal systems, often characterized by large standing stocks of biomass, can contain a large amount of biogenic silica (BSi; Norris and Hackney 1999; Conley

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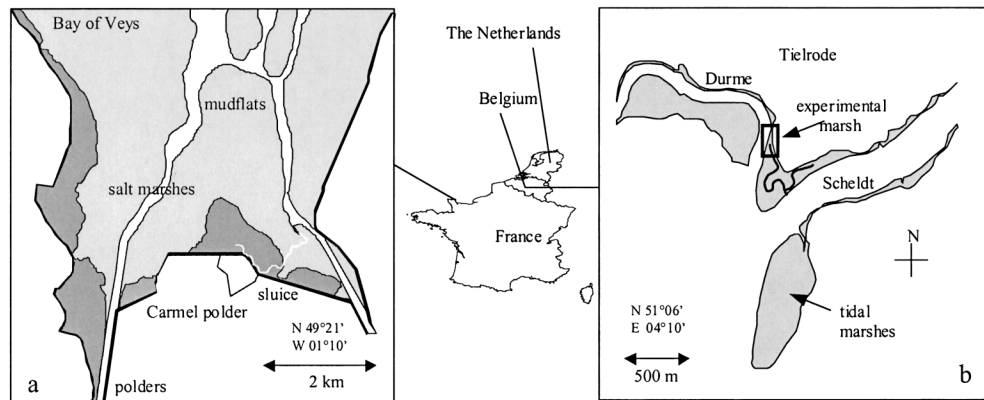


Fig. 1. (a) Location of Carmel Polder in northwestern France ($49^{\circ}21'N$, $1^{\circ}10'W$). (b) Location of the Tielrode marsh along the Scheldt estuary near the confluence of the Durme and the Scheldt ($51^{\circ}06'N$, $4^{\circ}10'E$). The study area is the northern part of a larger marsh system.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

2002; Struyf et al. 2005b). They act as efficient traps for BSi, and BSi and DSi are stored in concentrations above levels found in adjacent estuarine waters (Hackney et al. 2000).

Although marsh habitats are a major sink for BSi, DSi is exported from tidal freshwater marshes to nearby estuarine waters, indicating that tidal marshes could be important sites for Si recycling within estuaries (Struyf et al. 2005). A continuous supply of DSi from marsh recycling could be essential for autochthonous diatom communities and, as a result, be of vital importance in estuarine food webs, for which production by diatoms is an important energy source (Sullivan and Moncreiff 1990).

Despite the high potential of marshes to be buffer systems within the estuarine Si cycle, supplying DSi to estuarine waters in periods of low DSi availability, the exchange of BSi and DSi between intertidal marshes and tidal waters has only been studied for one freshwater marsh and only in spring (Struyf et al. 2005). To our knowledge, no complete flux studies have been conducted in saltwater or brackish marshes, and information is lacking on the seasonal variation in Si exchange between marshes and estuaries. The flux could differ significantly over the seasons: in summer and spring, diatom production in the estuary can increase BSi concentrations through uptake of DSi and consequently decrease the DSi concentration.

In this study, BSi and DSi fluxes were determined for a freshwater and a saltwater tidal marsh. Six full tidal cycles were studied in each area to quantify the BSi recycling capacity of marshes in different seasons. For the first time, whole-tidal marsh ecosystem functioning within estuarine Si cycling was quantified over a range of ambient DSi concentrations. The observed fluxes indicate that tidal marshes might play an important role in enhancing internal BSi recycling in estuarine waters, especially in spring and summer when DSi concentrations decrease because of diatom production.

Materials and methods

Study sites—We compared Si exchange at a freshwater marsh near Tielrode (Fig. 1b) in the Scheldt estuary (Bel-

gium) with the recently formed salt marsh of the Carmel Polder (France; Fig. 1a). Six complete tidal cycle studies were conducted at the freshwater marsh: two in May 2002 (two cycles, Struyf et al. 2005), and one in September 2003, October 2003, January 2004, and February 2004. The salt marsh was studied during February and July 2004, and three tidal exchange studies were conducted during both periods. Both sites were chosen because of their isolated nature, with only one connection to the surrounding estuarine waters, allowing for accurate construction of water balances. The study sites were characterized by representative European tidal saltwater and freshwater marsh vegetation (see following).

Tielrode: The Scheldt estuary, located in northern Belgium (Flanders) and the southwest of the Netherlands, has a history of extensive anthropogenic pollution (Wollast 1988; Van Damme et al. 2005). Average yearly discharge in the freshwater region is between 25 and $75 \text{ m}^3 \text{ s}^{-1}$ (Struyf et al. 2004). The estuary is known as highly eutrophic and receives large inputs of inorganic nutrients from nonpoint as well as point sources (Heip 1988; Soetaert et al. 2006). 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 along the Scheldt is approximately 4,500,000 m^2 on a total of 30,000,000 m^2 of tidal marshes.

Our mass balance studies were conducted in a fresh tidal marsh near Tielrode at the confluence of Durme and Scheldt (Fig. 1b). The tidal amplitude in the Scheldt near Tielrode is 5.5 m on average. The total area of this marsh is approximately 100,000 m^2 . Mass balance studies were conducted in a study area of 3,477 m^2 , flanked by dikes at the western and eastern side, which received water through one creek from the south. Perpendicular to the entrance creek, there was no isolation by a dike. Here, artificial isolation by wooden screens ensured water could only enter the isolated study area through the creek at high tide and not over marsh edges and surface. All major vegetation types characterizing freshwater marshes along the Scheldt (i.e., pure *Phragmites aus-*

tralis vegetation; tall herb vegetation dominated by *Urtica dioica*, *Impatiens glandulifera*, and *Epilobium hirsutum*; a mixed reed–tall herb vegetation; and a *Salix* shrub and tree vegetation) were present in the study area. Groundwater input from the surrounding polders to the marsh upper sediment layers does not occur because the marsh surface is several meters above the surrounding polder surface. A detailed description of the site is available in Gribsholt et al. (2005).

Carmel Polder: The saltwater Carmel Polder is located in the Bay of Veys in northwestern France (Fig. 1a). It is a polyhaline (salinity 18–30) macrotidal bay with a tidal amplitude averaging 7 m. The polder is now directly connected to the sea after a storm broke the tidal gate in 1990. Water flows in and out of the polder only through this gate (diameter 1 m). Fifty-eight thousand square meters are now flooded tidally. About 17,000 m² of the total 300,000 m² of the polder is covered with salt marsh vegetation. The dominant species are *Salicornia europaea*, *Spergularia marina*, and *Puccinellia maritima*. An area of about 41,000 m² in the southern half of the polder represents a shallow impoundment with no rooted vegetation. The level of this shallow impoundment rises with seawater inflows. The daily variations in the impoundment have a maximal amplitude of 20 cm, and monthly, the level can vary up to 60 cm. The water in this shallow impoundment is never totally drained. Water flows into the polder at almost every tide, except during the lowest neap tides. The difference between the total flooded surface and the surface of 41,000 m² of the impoundment is the total flooded vegetation-covered surface. A detailed description of the polder is provided in Dausse et al. (2005).

Water balances—Tielrode: Water velocities were continuously measured in the center of the creek just below the surface and near the bottom (OTT-mills or Valeport® EMF [electromagnetic flowmeter], model 801) every minute. Simultaneously, lateral velocity profiles were carried out continuously at the creek surface (10 lateral measurement points) with a second EMF. During the 2003 and 2004 cycles, water velocities were available for every lateral measurement point approximately every 1–2 min. In 2002, lateral velocity measurements were less frequent (approximately every 6 min). Here, a simple flow model was developed predicting the ratio of water velocity at any width segment to the water velocity in the center of the creek with the use of water height, the ratio to the highest water height observed during the tidal cycle, or both as predictors (robust linear regression; Rousseeuw and Yohai 1984). The ingoing and outgoing tides were fitted separately.

Discharged volumes were calculated by multiplying flow velocity and cross surface in over 40 lateral subsections every minute during bulk tidal phase and every hour during seepage water phase. Bulk tidal phase is here defined as the period of approximately 3 h during which large amounts of water flow in and out the marsh through the creek (around high water in the main river, incoming bulk phase is ~75 min, outgoing bulk phase is ~105 min). The seepage water phase was defined as the period after the bulk tide when no decrease in water level was observed for 30 min. Seepage

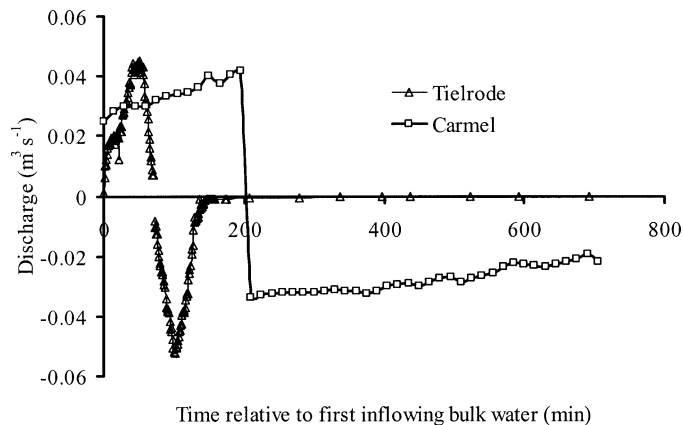


Fig. 2. Water discharge through the main creek at Tielrode (12 September 2003) and through the sluice at Carmel Polder (17 February 2004). Both show flow patterns representative for all of the tidal cycles studied.

water is exported out of the marsh between two bulk tidal phases, when tide in the main river is approaching low tide or rising to the threshold water level at which water starts flowing into the marsh (= bulk tide). The seepage water is mainly water leaving the sediments. Flow velocities were low and stable during the 9-h seepage water phase for all campaigns (as in Fig. 2). Accuracy of water balances was evaluated with the use of water volume estimates from a digital terrain model.

Carmel Polder: Discharge was measured directly every minute with an ISCO® Doppler area velocity flow sensor mounted at the bottom of the rectangular-shaped entrance sluice. In contrast to the Tielrode marsh, water flowed out at a continuous flow rate during the whole outgoing tide. There was no real seepage water phase, and water outflow was mostly surface drainage during the whole ebb stage (Fig. 2).

Silica sampling and analysis—At Tielrode, water samples were collected every 15 min during bulk tidal phase and every hour in seepage water, whereas hourly sampling was conducted during the entire tidal cycle at Carmel Polder. DSi, BSi, and suspended solids were analyzed from each sample. For BSi analysis, three 30-ml subsamples were filtered from a well-mixed total sample of 200 ml onto 0.45- μ polycarbonate filters. BSi was extracted from the filters in a 0.1 mol L⁻¹ Na₂CO₃ solution at 80°C. Subsamples were taken at 80, 120, and 160 min. Blank extractions revealed insignificant (<0.2 mg L⁻¹) DSi release from filters or chemicals. BSi was calculated by extrapolating the linear line through the three extraction points in a time-extracted silica plot (DeMaster 1981). DSi, both from extractions and in the water phase, was analyzed on a Thermo Iris® inductively coupled plasma (ICP) spectrophotometer. All Si concentrations (mg Si L⁻¹) are corrected for salt contributions at the marine site. Suspended solids were determined gravimetrically after filtration on Whatman GF/F filters.

Silica and suspended matter transport was calculated by multiplying discharge with measured concentrations contin-

Table 1. The exchanged water volumes during all tidal cycles at Tielrode and Carmel Polder. Water heights are for Tielrode (m above mean low sea level; TAW, Belgian national tidal reference) and Carmel Polder (m above lowest astronomical tide). Exchanged water volumes are given for the different tidal phases. Water balance is percentage compared with inflowing bulk (+ = import, - = export). The geographic information systems (GIS) estimate of flooding volume is indicated for Tielrode.

| | Date | Water height (m) | Bulk in (m ³) | Bulk out (m ³) | Seepage (m ³) | Water balance (% import/export) | GIS (m ³) |
|------------------------|-------------|------------------|---------------------------|----------------------------|---------------------------|---------------------------------|-----------------------|
| Tielrode freshwater | 26 May 2002 | 5.97 | 1,700 | -1,642 | -61 | -0.2 | 1,800 |
| | 30 May 2002 | 5.89 | 1,376 | -1,305 | -65 | 0.4 | 1,500 |
| | 12 Sep 2003 | 5.75 | 667 | -641 | -42 | -2.4 | 986 |
| | 10 Oct 2003 | 5.95 | 1,466 | -1,380 | -95 | -0.6 | 1,725 |
| | 29 Jan 2004 | 6.09 | 1,557 | -1,584 | -55 | -5.3 | 2,249 |
| | 26 Feb 2004 | 6.08 | 1,763 | -1,560 | -48 | 8.8 | 2,212 |
| Carmel saltwater | 17 Feb 2004 | 5.35 | 425 | -853 | — | -100.7 | — |
| | 22 Feb 2004 | 6.60 | 1,218 | -1,221 | — | -0.2 | — |
| | 25 Feb 2004 | 6.00 | 1,272 | -1,132 | — | 11.0 | — |
| | 28 Jul 2004 | 5.15 | 233 | -670 | — | -187.6 | — |
| | 31 Jul 2004 | 6.00 | 656 | -836 | — | -27.4 | — |
| | 01 Aug 2004 | 6.55 | 910 | -660 | — | 27.5 | — |

uously throughout the tidal cycles. Weighted average Si concentrations per tidal cycle phase (bulk incoming, bulk outgoing, and seepage) were calculated as the ratio of total amount of transported BSi or DSi and the amount of water discharged during a particular tidal phase. A comparison of suspended matter transport during ebb and flood was used to estimate the suspended matter deposition on the marsh surface.

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

Results

Water balances—Calculated water budgets were nearly closed during four of six tidal cycles at the freshwater marsh (Tielrode; Table 1). Highest high water levels (in meters, height over mean sea level at low tide [TAW] = Belgian Ordnance Level) were observed in January and February 2004. Export of water (-5.3%) and import (8.8%) were observed at these tidal cycles, respectively. Calculations of the total volume of water covering the study area from a digital terrain model with the use of maximum water levels validate the water balances (Table 1). The whole marsh was flooded during all six tidal cycles studied.

At Carmel Polder, water balances were mostly characterized by significant import or export of water (Table 1). There was a large discrepancy between incoming and outgoing water at lower tides (up to -188%), with more water leaving the area than entering. The flooded surfaces during winter tides were between 51,000 and 53,000 m². During the July cycles, 39,000, 42,000 and 43,000 m² were flooded on 28 July, 31 July and 1 August 2004, respectively. Si exchange per square meter at the Carmel Polder was based on these

observed flooded surfaces (and not the complete polder area). More salt marsh vegetation was inundated during the winter cycles than during summer, and no saltwater marsh vegetation was submerged on 28 July 2004.

BSi and DSi concentrations—At Tielrode, DSi (Fig. 3a) and BSi (Fig. 3b) concentrations showed opposite patterns as a function of season. Highest BSi concentrations were observed in late summer-early fall, and DSi concentrations were concurrently at their lowest. Inflowing DSi concentrations were between 2.1 and 7.0 mg Si L⁻¹. Within tides, there was very little difference in DSi concentrations between incoming and outgoing bulk. In the seepage water, DSi concentrations increased to ~9 mg Si L⁻¹ for all cycles. Inflowing BSi concentrations varied between 0.7 and 3.6 mg Si L⁻¹. BSi was always highest in inflowing bulk water, dropped by ~30% during all cycles in outgoing bulk water, and dropped to low concentrations (0–0.5 mg Si L⁻¹) in seepage water.

At Carmel Polder, inflowing DSi concentrations were low compared with Tielrode and varied seasonally between 1.0 and 3.5 mg Si L⁻¹. In the absence of a seepage water phase, DSi concentrations increased during all tidal cycles in outgoing bulk water (Fig. 3c). In summer, the relative increase in DSi concentration was high compared with winter. Incoming BSi concentrations at Carmel Polder were around 0.5 mg Si L⁻¹ in both winter and summer, with the exception of 2.1 mg Si L⁻¹ measured on 22 February 2004 (Fig. 3d). BSi decreased during outgoing water in winter (~0.4 mg Si L⁻¹, 0.9 mg Si L⁻¹ on 22 February 2004). In summer there was little difference between inflowing and outflowing BSi.

Balance uncertainties—Freshwater: A proper estimate of uncertainty associated with the balance calculations is important for the interpretation of the Si exchange rates (Table 2). At the freshwater site, uncertainty can come both from the errors associated with the balance calculation and from the error inherent in the noncontinuous measurement of Si and water velocities at all depths and lateral points. The stan-

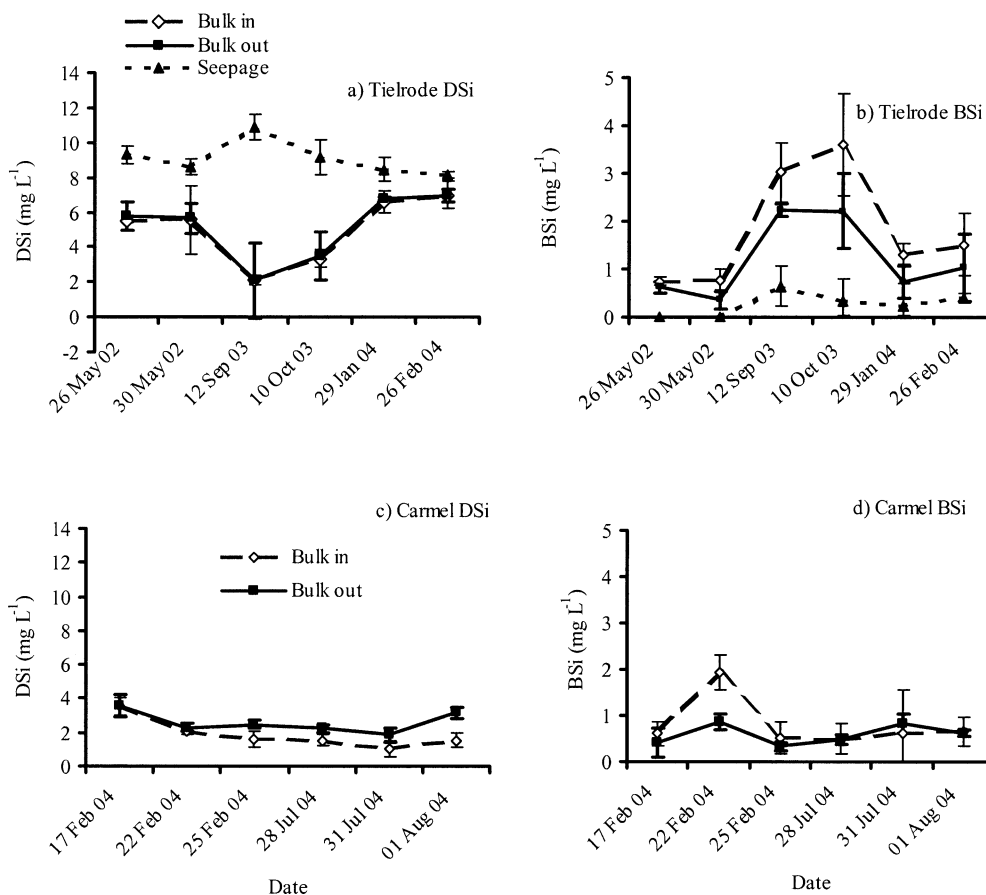


Fig. 3. DSi and BSi concentrations in the inundating water at (a,b) the Tielrode freshwater marsh and (c,d) the saltwater Carmel Polder for the six exchange studies at both locations. Results for bulk inflow, bulk outflow, and seepage water at Tielrode and for bulk inflow and bulk outflow at Carmel Polder, are presented. BSi and DSi plots have different scales.

dard errors associated with ICP measurements of DSi concentration (0.01 mg L^{-1}) and EMF measurements (0.02 m s^{-1}) were small, and DSi concentrations were stable during both bulk tides and seepage. The error on the DSi balances resulting from the calculation itself was always $<3\%$ (of the

relative balance; i.e., if we calculated 0% export, the uncertainty interval resulting from calculation is between 3% import and 3% export). For BSi, we assumed a standard error of 1 mg L^{-1} to reflect the higher uncertainty associated with BSi measurements. This error also corresponds to the max-

Table 2. The percent import (+) and export (-) and the exchange per square meter per tidal cycle of BSi and DSi during all tidal cycles at Tielrode and Carmel Polder. All mass balances were corrected with the water balance to allow comparison and for correcting balance errors in freshwater. An uncertainty range is given for all percent mass balances.

| Location | Date | DSi exchange | | | BSi exchange | | |
|------------------------|-------------|--------------|------------------|--------------------|--------------|----------------|--------------------|
| | | % | Uncertainty | mg m^{-2} | % | Uncertainty | mg m^{-2} |
| Tielrode freshwater | 26 May 2002 | -6.1 | -1.6 to -9.1 | -164.9 | 19.1 | 12.1 to 26.1 | 69.1 |
| | 30 May 2002 | -4.2 | -0.3 to -7.2 | -93.3 | 55.7 | 48.7 to 62.7 | 170.7 |
| | 12 Sep 2003 | -23.4 | -16.8 to -26.4 | -96.5 | 29.9 | 22.8 to 37.0 | 173.2 |
| | 10 Oct 2003 | -15.4 | -10.1 to -18.4 | -216.0 | 42.1 | 35.0 to 49.2 | 639.2 |
| | 29 Jan 2004 | -3.0 | 0.6 to -6.0 | -90.2 | 47.3 | 40.2 to 54.4 | 278.0 |
| | 26 Feb 2004 | -0.2 | 3.2 to -3.2 | -5.7 | 29.9 | 22.8 to 37.0 | 229.8 |
| Carmel saltwater | 17 Feb 2004 | -2.0 | -1.0 to -3.0 | -0.6 | 64.6 | 28.6 to 110.6 | 3.2 |
| | 22 Feb 2004 | -10.1 | -9.1 to -11.1 | -5.0 | 55.4 | 47.4 to 63.4 | 25.5 |
| | 25 Feb 2004 | -47.6 | -46.6 to -48.6 | -19.0 | 32.3 | 4.3 to 50.3 | 4.1 |
| | 28 Jul 2004 | -123.8 | -121.8 to -125.8 | -11.4 | 12.8 | -44.2 to 69.8 | 0.3 |
| | 31 Jul 2004 | -101.7 | -100.7 to -102.7 | -16.2 | -39.8 | -65.8 to -13.8 | -3.0 |
| | 01 Aug 2004 | -78.7 | -79.7 to -77.7 | -25.4 | 2.8 | -17.2 to 22.8 | 0.4 |

imal standard deviation in BSi concentrations during a single tidal phase. The resulting calculation error on the BSi balances was always <7%.

We added a conservative tracer (Br^-) to the floodwater both in May 2002 and September 2003 during tides in which no Si was sampled to verify our ability to accurately construct the water balance (see Gribsholt et al. [2005] for details). Both tracer additions indicated a near closed water budget. This is supported by the visual observation that no significant pools of water were left on the marsh surface after bulk tide. All water budgets were therefore assumed balanced, and conservative correction of the silica balances with the calculated water balance was assumed to correct the silica balances for errors in calculated water budgets.

In addition, the geographic information system (GIS), terrain model estimates of water volume were used to estimate the possible over- or underestimation of water balances. During both tides studied in May 2002, the GIS estimate was 6% and 8% ($\sim 100 \text{ m}^3$) higher than ingoing and outgoing water, respectively (Table 1). This difference could be explained by the volume of vegetation and litter, which was not accounted for in the GIS budget. In 2003 and 2004, the discrepancies between GIS and calculated water balances were larger, especially at the highest tides (between 259 and 692 m^3 , a 15% and 31% underestimation, respectively), as already indicated by the bromide balance (see previous paragraph). The maximal underestimation of the exchanged water volume in the conservative water balance was thus 31%. We applied this maximal underestimation of the water balance of 31% to all silica balances and added the uncertainty resulting from the calculation errors ($\pm 3\%$ DSi, $\pm 7\%$ BSi; see earlier in this section), which resulted in the uncertainty range presented in Table 2. These ranges indicate that the calculated fluxes are, in general, a good indication of the real fluxes, and error on the balances is relatively small.

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

Silica balances—All mass balances were rendered conservative by correction for import or export of water to allow comparison and as a correction for errors in the freshwater balance (see *Silica sampling and analysis*). In freshwater, rendering conservative only had a small effect on the winter cycles because of the observed imbalance between ingoing and outgoing tides in winter. At Carmel Polder, effects were larger during the lowest tides (one each season) because of the larger imbalances observed between incoming and outgoing tides (Table 1). Uncertainty to the balances was high (>30% on average) for BSi in salt water because of the relatively high error estimate for BSi compared with the low observed BSi concentrations and small differences in BSi

concentrations (on average, $<0.3 \text{ mg Si L}^{-1}$) between ingoing and outgoing water volume.

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

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

The inverse relationship between percentage export of DSi from the marsh sites and DSi concentration in the inundating water was consistent (Fig. 4a). At Tielrode (freshwater), a significant linear relationship was also observed between tidal height and percent export ($F_{1,4} = 8.42$, $p = 0.044$, $r^2 = 0.68$; Fig. 4b), but the relationship between export and inundating DSi was much stronger ($r^2 = 0.97$; Fig. 4a). At Carmel Polder (salt water), no consistent linear relationship between DSi export and tidal height was observed (Fig. 4b).

Percent export of DSi was highest when inundation concentration was lowest (Fig. 4a). At the freshwater Tielrode marsh, the negative relationship was significantly linear. A similar significant linear relationship was not observed at saltwater Carmel Polder ($p = 0.08$). At Carmel Polder, inundating DSi concentrations were much lower than at Tielrode. Percent export increased more rapidly with lower inundating DSi concentrations than at Tielrode. Results obtained from both Carmel Polder and Tielrode span a wide range of inundating DSi concentrations. Combined results from both areas show a logarithmic relationship between inundating DSi and percent export of DSi (Fig. 4a). The highest import of BSi per square meter was observed when the estimates of deposition of suspended solids were maximal, suggesting import of BSi with suspended solids (Fig. 5).

Discussion

A consistent export of DSi was observed from both tidal marshes investigated in this study. In both systems, highest relative export of DSi was observed at low DSi concentrations in the inundating water. At the saltwater site, the percent export of DSi was independent of the tidal height. At Tielrode, a significant relation between tidal height and percent export was observed, but this relationship was only driven by the low tidal height during the September cycle. Excluding this tidal cycle, no significant relationship was observed. As a result of the minor influence of tidal height on percent export of DSi, a larger exchange per square meter occurred at highest water levels. This explains why, despite

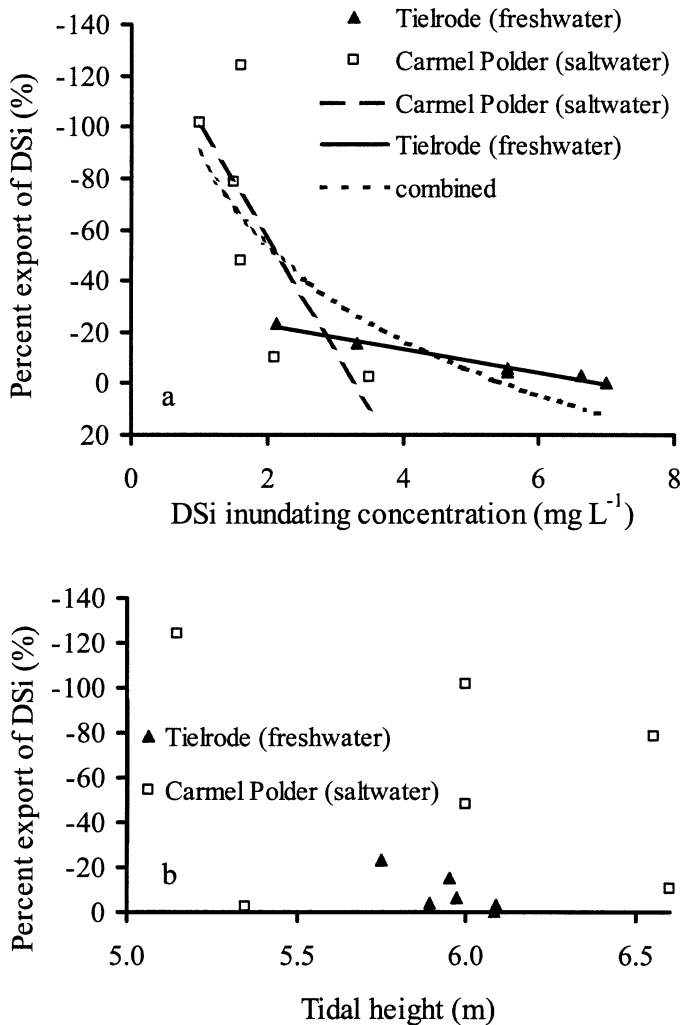


Fig. 4. (a) Percent export of DSi from the Tielrode (freshwater) and Carmel Polder (saltwater) wetlands in relation to the inundating DSi concentration (linear regressions for Tielrode: $F_{1,4} = 144$, $r^2 = 0.97$, $p < 0.001$; and Carmel Polder $F_{1,4} = 5.61$, $r^2 = 0.58$, $p = 0.08$). Combined data sets result in a logarithmic relation ($F_{1,10} = 18.2$, $r^2 = 0.64$, $p < 0.002$). (b) Percent export of DSi versus tidal height (m above mean low sea level).

the very low inundation concentration during the September 2003 Tielrode cycle (2.2 mg Si L^{-1} , the lowest observed), exchange per square meter was relatively low. Low water height resulted in $\sim 35\%$ of the marsh only being inundated with shallow water ($< 9 \text{ cm}$).

In contrast to the export of DSi observed, the freshwater marsh at Tielrode was subject to BSi deposition year round, whereas at the saltwater Carmel Polder, BSi was only imported in winter. It was the amount of suspended matter imported that mainly controlled the imported BSi load into the freshwater marsh. The low exchanged water volumes at the saltwater site and larger surface compared with the freshwater site resulted in much lower BSi deposition per squared meter here.

Marsh BSi import and DSi export seem to be intricately dependent on each other. Marshes have been shown to accumulate large quantities of BSi, stored in sediments, plants,

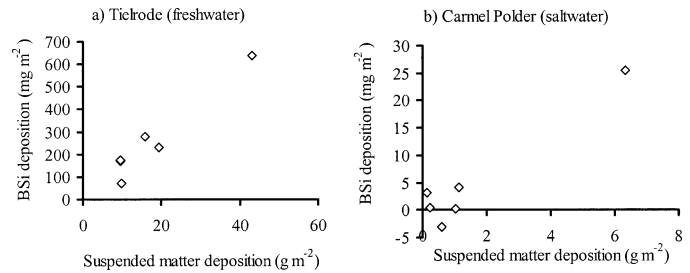


Fig. 5. Import of BSi per square meter versus estimated surface-averaged import of suspended matter at (a) freshwater marsh Tielrode and (b) saltwater marsh Carmel Polder. The BSi import scale differs for Carmel Polder and Tielrode.

and pore water (Norris and Hackney 1999; Struyf et al. 2005b). Deposition of BSi, imported during flood tides in both the saltwater (only in winter) and freshwater marsh, could be an important factor controlling this accumulation. The BSi-rich sediments deposited in the marsh can contribute directly to the observed export of DSi. At the Tielrode freshwater marsh, the concentration of BSi in the imported suspended matter during this study was about twice the concentration found in the surficial (0–1 cm) sediment layer covering the marsh (Struyf et al. 2005b). Furthermore, it has been observed that BSi concentration in the marsh sediments decreases with increasing depth and age in marsh sediment cores in the Tielrode marsh (Struyf et al. 2005b). Sediment BSi dissolves to DSi in the marsh pore water. The freshwater marsh sediments are hence characterized by pore-water DSi concentrations that clearly exceed the concentrations of DSi found in nearby estuarine waters (Hackney et al. 2000). At the studied freshwater site, pore-water concentrations in summer were as high as 16 mg L^{-1} , clearly exceeding the observed floodwater concentrations between 2.1 and 7 mg L^{-1} at this study. Marshes act as leaky dams, slowly releasing the pore water between two tidal floodings as seepage water when pore water is refreshed (Hackney et al. 2000). Most export of DSi ($+90\%$ during five of six tidal cycles) observed from the freshwater marsh in Tielrode was directly attributable to the DSi-enriched seepage water that has been in contact with marsh pore water and is largely uncoupled from bulk surface-water flows.

The role of higher plants growing in the marsh also cannot be neglected in DSi export. Higher plants take up DSi from pore water and deposit the DSi in cell wall structures known as opal phytoliths (Piperno 1988). BSi remains in the plant until dissolution after plant decay. At the freshwater site, dissolution of BSi from decomposing *Phragmites australis* litter could contribute significantly (up to 50%) to the total amount of DSi exported from the marsh (Struyf et al. 2005b). Porewater concentrations were significantly higher in *Phragmites* vegetation compared with other vegetation, indicating that the contribution of litter to DSi recycling could also pass through the seepage water.

A major difference between the sites was the absence of a seepage water phase at the saltwater site. At the saltwater site, export flow of water is buffered by drainage from the never fully drained impoundment, keeping export flow at a continuously higher level compared with the freshwater site.

Although no seepage water phase as such existed at the saltwater Carmel Polder, similar export patterns of DSi as in the freshwater marsh were observed. Between high tides, water drained from the sediments into the shallow impoundment and the creeks. This drainage leads to higher DSi concentrations in the outflowing water, and as observed in Tielrode, the percent increase was highest when the inundation concentration was lowest. The absence of a seepage water phase might explain why DSi exchange per square meter was much lower at Carmel Polder compared with Tielrode.

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

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

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

Low exchanged water volumes per square meter at the saltwater site could result in high percent export at the saltwater polder compared with the freshwater because of the relatively much higher available reaction surface for DSi dissolution to floodwater. Furthermore, vegetation type and age is completely different between both sites; the saltwater site has not yet evolved into a fully vegetation-covered marsh, and large parts remain unvegetated. Whereas Si in vegetation, sediment, and pore water has been intensively studied in the Tielrode freshwater marsh site (Struyf et al. 2005b), little or nothing is known about the total stocks of Si within the saltwater polder or saltwater marshes in general. It was

therefore not possible to expand conclusions about sediment and vegetation contribution to freshwater marsh Si cycling to the saltwater site.

The obtained results do, however, clearly suggest that tidal marshes, both saltwater and freshwater, can play important roles in the self-regulatory capacity of the estuarine systems with regard to DSi availability. DSi concentrations can drop $<0.4 \text{ mg Si L}^{-1}$ in summer months in the freshwater part of the Scheldt estuary. According to the relationship observed between percent DSi export and inundating DSi concentration in the freshwater, export of DSi from the marsh could exceed import by around 30% (or even more if the combined relationship from both sites is considered), and exchange per square meter could rise $>400 \text{ mg m}^{-2}$ per tidal cycle. This is about four times higher than previous estimates on the basis of observations in May only (Struyf et al. 2005). Total monthly discharge of DSi in the main river channel in months with DSi concentrations $<0.4 \text{ mg Si L}^{-1}$ can drop as low as 10,000 kg. With a total area of freshwater marshes along the Scheldt estuary of about 4,500,000 m^2 (however, this area is expected to increase significantly in future years according to nature development plans), only six tidal cycles in a summer month, each exporting $\sim 400 \text{ mg m}^{-2}$, are sufficient to recycle 10,000 kg of DSi.

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

Restoration of tidal wetlands has been based on the observed relationship between tidal marshes and production of economically valuable fish and invertebrates (Hackney et al. 2000). Tidal marsh plant production and uptake in the detrital food chain have been suggested as an explanation for this link—plant detritus being the energetic source for secondary consumers (Teal 1962; Odum and De La Cruz 1967; Odum 2000). Hackney et al. (2000) hypothesized that the ability of tidal marshes to sequester and enhance internal cycling of Si could provide an alternative explanation for the observed link between tidal marsh production and secondary production in the coastal zone. Our results support the importance of this hypothesis, which relates Si stockage and recycling in tidal areas to secondary production. However, the scale of the importance of biogeochemical processing of Si by marsh habitats remains as of yet unknown. Our results suggest that Si retention and processing by tidal marsh systems might be an important, though overlooked, component in continental and global biogeochemical cycling of Si. Integrated research at other marsh sites, combining both quantification of BSi stocked in marsh systems and quantification of DSi/BSi processing, are necessary to allow us to advance from local, small-scale ecosystem conclusions toward quantifying the importance of Si processing in tidal inundated areas on a continental and even global scale.

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