

Management effects on
ecosystem functions
of salt marshes:

silica cycling and
sedimentation processes



Dissertation

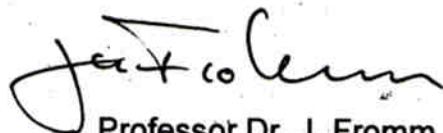
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Summary

Salt marshes are productive ecosystems in the transition zone between land and sea. They develop at shallow coasts, where currents slow down and allow suspended sediments to settle or organic material to accumulate. Salt marshes fulfil a variety of ecosystem functions, which can be grouped into regulation, habitat, production and information functions. They provide, for instance, a rich habitat for a great diversity of plants, invertebrates, birds, fish and mammals, and because they attenuate waves, they play an important role in coastal defence. In the Wadden Sea area, along the Dutch, German and Danish coasts, salt marshes have been subjected to far-reaching human alterations. Since the early Middle Ages, the majority of natural marshes has been embanked and turned into farmland. Today, nearly all existing salt marshes on the mainland have been anthropogenically created and traditionally grazed by cattle and sheep. Due to a shift in nature conservation aims, grazing and artificial drainage was stopped in many salt marshes at the Wadden Sea during recent decades. At some locations in the Wadden Sea and at European estuaries, former tidal marshes were even de-embanked to reintroduce natural dynamics to the systems. This development has considerably changed plant species composition of salt marshes, and it is very likely that it affects ecosystem functions. Silica cycling and sedimentation processes were earlier identified to be ecosystem functions of great importance in salt marshes. It was, for instance, hypothesised that their high salinities would render salt marshes very efficient silica recyclers, and sedimentation is a necessary process to ensure the resistance of salt marshes to sea-level rise. The aim of this thesis was to assess the role of salt marshes in coastal silica cycling, to characterise sedimentation processes in salt marshes and to analyse the influence of grazing and restoration management on these two ecosystem functions.

Chapter 1 comprises a general introduction to salt marshes, the Wadden Sea, silica cycling and sedimentation processes. The subsequent chapters address the study objectives in the form of three first-author and three second-author manuscripts, each with a different focus. **Chapter 8** summarises the findings of the thesis.

As an essential nutrient for diatoms, silica plays a key role in the estuarine and coastal food web. In times of silica limitation, seepage water from tidal freshwater marshes supplies a significant amount of dissolved silica (DSi) to the estuary. Salt

marshes were assumed to have even higher silica recycling rates than freshwater systems. In **chapter 2**, export rates of DSi and biogenic silica (BSi) from two salt marshes in the Schleswig-Holstein Wadden Sea National Park, Germany, are presented. Seepage water from salt marshes was highly enriched in DSi; concentrations were between 1.7 times (spring) and 7.6 times higher than in flood water. On average, $72 \pm 59 \text{ kmol km}^{-2} \text{ yr}^{-1}$ DSi and $8 \pm 9 \text{ kmol km}^{-2} \text{ yr}^{-1}$ BSi leached to the adjacent coastal waters from two investigated salt marshes. Exports from ungrazed sites were twice as high as exports from grazed sites. Although DSi concentrations in the seepage water were higher on grazed (mean $289 \pm 38 \mu\text{M l}^{-1}$) than on ungrazed sites (mean $169 \pm 66 \mu\text{M l}^{-1}$), higher discharge from the latter sites was driving the differences in export rates. Concentration differences between grazed and ungrazed sites were assumed to be related to silica uptake by benthic diatoms.

Chapter 3 presents an estimation of all silica containing compartments and a budget calculation for the same two salt marshes. Pools of silica were determined in soil, pore water, aboveground vegetation; fluxes were determined in freshly deposited sediments, flood and seepage water. Our results show that both sites were clear sinks for silica. The average BSi import with freshly deposited sediments ($1,334 \pm 1,019 \text{ kmol km}^{-2} \text{ yr}^{-1}$) largely exceeded the abovementioned DSi and BSi export with seepage water. Next to exports, the vegetation BSi pool was affected by grazing as well. Mainly due to a larger standing stock of biomass, BSi pools on ungrazed sites ($467 \pm 464 \text{ kmol km}^{-2}$) exceeded those on grazed ($68 \pm 45 \text{ kmol km}^{-2}$) sites by far. The study revealed that silica cycling is tightly connected to sedimentation processes. One third of all BSi was imported with sediment that was deposited during only one major flooding event. Such rare events have been widely omitted in most silica budgets of tidal marshes so far.

In **chapter 4**, the scope is extended to salt marsh sites on the European scale. DSi fluxes from five sites were extrapolated to salt marshes bordering three European sea basins. Results were compared to riverine DSi exports to the same basins. On a regional scale, DSi export from salt marshes seemed of minor importance compared to riverine DSi exports. The total DSi flux from salt marshes equalled only 0.5% of the annual and 2.1% of the summer riverine export in the study area. Locally, however, salt marshes may contribute substantially to the supply of DSi to coastal waters. The mean DSi export per km^2 from salt marshes was 5.7 times as high as DSi export per km^2 from European rivers.

Tidal marsh management not only includes grazing, but can also imply re-introducing the tidal regime to formerly embanked sites. The effect of such a measure on the size of the vegetation BSi pool in a tidal freshwater marsh is presented in **chapter 5**. Species-based cover-biomass relationships were determined, and BSi was analysed for all plant species. During the first six years of colonisation by tidal freshwater marsh species, the BSi pool in the aboveground biomass increased from 40 to 230 kmol km^{-2} , equalling the size of the vegetation BSi pool in salt marshes. Our results indicate that young tidal freshwater marshes have a high potential to quickly build up a large veg-

etation BSi pool, mostly due to colonisation by species that have both high BSi concentrations and high biomass production (e.g. *Phragmites australis*). However, the BSi pool in this study site was still one order of magnitude smaller than the vegetation BSi pool in a reference tidal freshwater marsh with a nearly closed *P. australis* cover.

Interactions between silica and plant communities influence both local and global ecological processes, and the effects reach far through higher levels of ecological organisation. In **chapter 6**, it is reviewed how local vegetation can affect silica fluxes on the watershed scale. From spring to estuary, examples are provided of the importance of linking local processes to large-scale fluxes in different ecosystems along the river continuum. For tidal wetlands, for instance, the role of silica in abating current and future environmental threats to estuaries is discussed. Plants that are able to utilise silica to increase their resistance against various stressors could be favoured in terms of resisting sea level rise, stronger currents, increasing salinities, chemical contaminants or introduced pathogens.

Currently, coastal and estuarine systems are threatened by a rising sea level. A number of studies already dealt with the question to which extent sedimentation processes in salt marshes contribute to keep pace with this development. In these investigations, salt marsh management has hardly ever been considered. Grazing by livestock might influence accretion rates directly, by increasing soil compaction through trampling, and indirectly, by reducing vegetation structure and thus decreasing sediment deposition rates. In **chapter 7**, it was tested whether accretion rates were lower in grazed compared to ungrazed salt marshes. In four study sites along the mainland coast of the Wadden Sea, ^{137}Cs radionuclide dating and soil compaction measurements were carried out. The effect of livestock grazing on accretion rates, sediment deposition rates and compaction was assessed as well as the effect of abiotic factors. Accretion rates were on average 11.6 mm yr^{-1} during the recent decades. Neither accretion rates nor sediment deposition rates were significantly different between grazing treatments, but decreased with distance to the marsh edge (i.e. the sediment source). Although we found clear evidence for soil compaction by livestock grazing, this factor did not determine accretion rates. Instead, a possible effect of livestock grazing on accretion rate was superimposed by abiotic factors. We conclude that grazing might be a relevant factor, which could not be detected in our approach due to a limited sample size. Grazing management is an up to now overlooked factor in determining accretion and spatial distribution of sediments in salt marshes. Particularly in the face of sea-level rise, it needs further, multi-factorial investigation and should be included in models predicting marsh development.

Overall, the results of this thesis indicate that silica cycling and sedimentation processes in salt marshes are tightly connected on both small and large scale. Due to their large extent, high salinity and strong tidal influence, salt marshes take an active part in coastal silica cycling. They have high DSi exports per km^2 and are discharging significant amounts of DSi to the coastal zone. At the same time, they are importing

large amounts of BSi with deposited sediments. Sedimentation processes play an important role in vertical growth of salt marshes, which is especially relevant against the background of a rising sea level. The current accretion rates indicate that most salt marshes in the Wadden Sea are not threatened by inundation in the near future. However, feedback processes between sea-level rise, marsh morphology and salt marsh vegetation necessitate a continuous monitoring of vertical marsh growth. In this context, significantly higher compaction rates on grazed sites, indicating an influence of livestock grazing, suggest that the effect of salt marsh management might be a relevant factor for future marsh development. It should hence be further studied.

Zusammenfassung

Salzmarschen entwickeln sich an flachen Küsten im Übergangsbereich zwischen Land und Meer, an denen strömungsberuhigte Zonen die Sedimentation von Partikeln und die Akkumulation von organischer Substanz zulassen. Salzmarschen erfüllen eine Reihe wichtiger Ökosystemfunktionen: Sie bieten einer Reihe von hochspezialisierten Pflanzen und Tieren Lebensraum und fungieren als effiziente Nährstoffspeicher. Im Vorland von Deichen übernehmen sie zudem eine bedeutende Rolle im Küstenschutz, da sie bei Sturmfluten die Wellenenergie mindern. Im Wattenmeer, entlang der niederländischen, deutschen und dänischen Küste, waren und sind diese Vordeichsflächen weitreichenden anthropogenen Einflüssen ausgesetzt. Seit dem frühen Mittelalter wurde ein Großteil der natürlich gewachsenen Salzmarschen eingedeicht und in landwirtschaftliche Nutzflächen umgewandelt. Nahezu alle heute vorhandenen Salzmarschen an der Festlandsküste sind durch sedimentationsfördernde Maßnahmen entstanden und wurden seit jeher intensiv mit Schafen oder Rindern beweidet. Aus Naturschutzgründen hat sich seit den 1980er Jahren ihre Nutzung stark verändert: Die traditionelle Beweidung wurde in großen Teilen aufgegeben oder deren Intensität verringert. Zudem wurde in den nun brachliegenden Flächen die künstliche Entwässerung eingestellt. An einigen Stellen im Wattenmeer und an den europäischen Ästuaren ist auch die Deichlinie zurückgesetzt worden, um den natürlichen Prozessen in Salz- und Süßwassermarschen wieder mehr Raum zu geben.

Der Wandel im Management der Marschen hatte weitreichende Veränderungen beispielsweise der Pflanzengemeinschaften zur Folge, mit mutmaßlichen Auswirkungen auch auf die Ökosystemfunktionen. Der Siliziumkreislauf und die Sedimentationsprozesse wurden in früheren Studien als besonders wichtige Prozesse in Salzmarschen beschrieben. Beispielsweise wurde vermutet, dass Salzmarschen aufgrund ihrer hohen Salinität effiziente Siliziumrecycler sein könnten, und eine ausreichende Sedimentation ist die Voraussetzung für ein Weiterbestehen der Marsch in Zeiten des steigenden Meeresspiegels. Diese Dissertation befasst sich daher mit der Frage, welche Rolle Salzmarschen tatsächlich im Siliziumkreislauf spielen, charakterisiert die Sedimentationsprozesse in Salzmarschen und untersucht den Einfluss des Managements auf diese beiden Ökosystemfunktionen. **Kapitel 1** führt in die zugrunde liegenden Faktoren und Prozesse ein. Vorgestellt werden das Ökosystem Salzmarsch, das Wattenmeer, der Siliziumkreislauf und die Sedimentationsprozesse in Salzmarschen. Jeweils mit einem

unterschiedlichen Schwerpunkt widmen sich die nachfolgenden sechs Kapitel der Fragestellung. Sie sind in Zusammenarbeit mit anderen Autoren entstanden. **Kapitel 8** führt die Ergebnisse in einer Synthese zusammen.

Als ein essentieller Nährstoff für Kieselalgen erfüllt Silizium eine wichtige Funktion im Nahrungsnetz von Ästuaren und Küstengewässern. Unter anderem kann ein ausreichender Gehalt gelösten Siliziums Eutrophierungserscheinungen wie toxischen Algenblüten entgegen wirken. Für Süßwassermarschen ist bereits nachgewiesen, dass in ihnen biogenes Silizium (BSi) zu gelöstem Silizium (DSi) recycelt wird und sie damit zur Siliziumversorgung in Ästuaren beitragen. In früheren Studien wurde vermutet, dass Salzmarschen im Vergleich zu Süßwassermarschen noch effizientere Siliziumlieferanten für die Küstenzone sein könnten. In **Kapitel 2** wurden daher DSi- und BSi-Exportraten aus zwei Salzmarschen im Nationalpark Schleswig-Holsteinisches Wattenmeer ermittelt. In vier saisonalen Messkampagnen wurden Exportraten von im Mittel $72 \pm 59 \text{ kmol km}^{-2} \text{ yr}^{-1}$ DSi und $8 \pm 9 \text{ kmol km}^{-2} \text{ yr}^{-1}$ BSi festgestellt. Unbeweidete Flächen wiesen doppelt so hohe Exportraten auf wie beweidete Flächen. Zwar waren die DSi-Konzentrationen im Sickerwasser beweideter Flächen in der Regel höher als im Sickerwasser unbeweideter Flächen (im Mittel $289 \pm 38 \mu\text{M l}^{-1}$ und $169 \pm 66 \mu\text{M l}^{-1}$), doch überlagerten größere Abflussraten auf unbeweideten Flächen diesen Effekt. Durch die dichte Biomasse- und Streuauflage auf diesen Flächen läuft das Regen- und Überflutungswasser verzögert ab und hat daher mehr Zeit, Silizium aus dem Boden zu lösen. Als Grund für den Unterschied in den DSi-Konzentrationen der beiden Beweidungsstufen wurde eine stärkere Kieselalgenbesiedlung in den Prieln der beweideten Fläche diskutiert.

In **Kapitel 3** wird in der ersten umfassenden Bilanz für europäische Salzmarschen die Größe aller Siliziumkompartimente präsentiert und die Importe und Exporte der beiden Untersuchungsgebiete bilanziert. Die Siliziumpools im Boden, im Porenwasser und in der oberirdischen Vegetation wurden ebenso quantifiziert wie die Siliziumflüsse in frisch abgelagerten Sedimenten und im Flut- und Sickerwasser. Beide Salzmarschen stellten deutliche Siliziumsenken dar, was ein Vergleich der BSi-Importe ($1.334 \pm 1.019 \text{ kmol km}^{-2} \text{ yr}^{-1}$) mit den oben genannten DSi- und BSi-Exporten ergab. Neben den Exporten wurde auch das BSi-Pool in der oberirdischen Biomasse stark durch das Management beeinflusst. Aufgrund der durch die Beweidung verringerten Biomasse fällt der Siliziumpool der Vegetation in den beweideten Flächen deutlich geringer aus als in den unbeweideten (im Mittel $68 \pm 45 \text{ kmol km}^{-2}$ und $467 \pm 464 \text{ kmol km}^{-2}$). Die Ergebnisse unterstreichen die enge Kopplung von Siliziumhaushalt und Sedimentationsprozessen: Ein Drittel der jährlichen BSi-Importe wurde während einer einzelnen Sturmflut eingetragen. In der Vergangenheit haben sich Bilanzierungen von Siliziumflüssen in Salzmarschen überwiegend auf Stoffflüsse in den Prieln gestützt und Einzelereignisse wie Sturmfluten nicht berücksichtigt. Daher muss davon ausgegangen werden, dass bisherige Untersuchungen den Siliziumeintrag in Salzmarschen unterschätzen.

Im **Kapitel 4** wird die Untersuchung auf die europäische Ebene ausgeweitet. DSi-Exporte aus fünf Salzmarschen wurden auf sämtliche Salzmarschenflächen entlang von drei europäischen Meereseinzugsgebieten extrapoliert und mit denen von Flüssen verglichen. Auf regionaler Skala hatten die DSi-Exporte aus Salzmarschen nur einen geringen Anteil am Gesamtexport. Ihre Austräge beliefen sich auf etwa 0,5% des jährlichen und 2,1% des sommerlichen DSi-Exports aus Flüssen. Auf lokaler Ebene könnten sie jedoch für angrenzende Ökosysteme eine weit höhere Relevanz besitzen. So war der DSi-Export pro km² aus Salzmarschen 5,7-mal so hoch wie aus Flusseinzugsgebieten des gleichen Untersuchungsgebiets.

Das Management in Marschen umfasst nicht nur die Beweidung, es schließt teilweise auch die Wiederherstellung des Tideregimes in ehemals eingedeichten Marschflächen ein. Die Auswirkung einer solchen Renaturierungsmaßnahme auf die Größe des BSi-Pools in der oberirdischen Biomasse wird in **Kapitel 5** exemplarisch für eine Süßwassermarsch dargestellt. Hierfür wurde eine effiziente, nicht-destruktive Methode entwickelt, die zunächst die Beziehung zwischen dem Deckungsgrad einer Pflanzenart und ihrer Biomasse ermittelt. Nachdem auch der BSi-Gehalt jeder Art ermittelt wurde, konnte aufgrund von Vegetationskartierungen die Entwicklung des BSi-Pools über die Zeit nachvollzogen werden. Während der Wiederbesiedlung der Fläche durch typische Süßwasserarten vergrößerte sich über die ersten sechs Jahre der Pool von 40 auf 230 kmol km⁻². Damit erreichte er bereits die Größenordnung des BSi-Pools in der Vegetation in Salzmarschen (siehe Kapitel 3). Auch wenn der BSi-Pool in der Vegetation der renaturierten Marsch nur zehnte desjenigen einer natürlichen Süßwassermarsch aufwies, dokumentiert die Auswertung doch eine erhebliche Akkumulationsgeschwindigkeit von reaktivem Silizium in der oberirdischen Biomasse. Dies ist in erster Linie auf Pflanzenarten mit hohem Biomasseaufkommen bei gleichzeitig hohen Siliziumgehalten zurückzuführen (z. B. *Phragmites australis*).

Die Interaktion zwischen Silizium und Pflanzengemeinschaften beeinflusst sowohl lokale als auch regionale ökologische Prozesse. Ihre Effekte reichen weit hinauf in höhere Ebenen ökologischer Organisation. Ein Review verschafft in **Kapitel 6** einen Überblick darüber, in welcher Weise die lokale Vegetation auf Siliziumströme in Flusssystemen Einfluss nimmt. Von der Quelle bis zur Mündung werden Beispiele diskutiert, die die Relevanz lokaler Prozesse für Siliziumflüsse verdeutlichen. Für Marschen wird erörtert, ob die Akkumulation von Silizium in Pflanzen dazu beitragen kann, die Resilienz des Ökosystems gegenüber zukünftigen Umweltveränderungen zu erhöhen. Pflanzen, die in der Lage sind, Silizium zu ihrem Vorteil zu nutzen, könnten widerstandsfähiger gegenüber Stressoren wie dem steigendem Meeresspiegel, stärkeren Strömungen, erhöhtem Salzgehalt, Schadstoffen und Krankheitserregern sein.

Weltweit sind Küstenökosysteme durch den steigenden Meeresspiegel gefährdet. Eine Reihe von Studien hat sich in der Vergangenheit bereits damit auseinandergesetzt, in welchem Umfang Sedimentationsprozesse in Salzmarschen dazu beitragen, das Fortbestehen der Marschen zu sichern. In diesen Untersuchungen wurde jedoch das Management der Salzmarschen in der Regel nicht betrachtet. Dabei könnte die Bewei-

dung durch Nutztiere direkt (durch eine Verdichtung des Bodens) oder indirekt (durch Reduzierung der „sedimentfangenden“ Vegetation) die Akkretion, d. h. das vertikale Höhenwachstum, der Marschen beeinflussen. In **Kapitel 7** wurde überprüft, ob die Akkretions- und Sedimentdepositionsraten auf beweideten Salzmarschen geringer sind als auf unbeweideten. In vier Untersuchungsgebieten entlang der Wattenmeerküste wurden mit Hilfe einer geochronologischen Methode (^{137}Cs -Datierung) und durch die Bestimmung der Lagerungsdichte Akkretionsraten, Sedimentdepositionsraten und die Bodenverdichtung ermittelt. Im Mittel betrug die Akkretionsrate in den vergangenen Dekaden $11,6 \text{ mm yr}^{-1}$. Sowohl Akkretions- als auch Sedimentdepositionsrate unterschieden sich auf unbeweideten und beweideten Flächen nicht signifikant, obgleich der Boden auf letzteren deutlich stärker verdichtet war. Ein möglicher Effekt der Beweidung wurde stattdessen von anderen Faktoren überlagert, etwa der Entfernung zur Marschkante, also der Sedimentquelle. Die Ergebnisse legen nahe, dass der Einfluss der Beweidung ein durchaus relevanter Faktor sein könnte, in der gemeinsamen Betrachtung mit abiotischen Faktoren und einer gleichzeitig geringen Stichprobengröße aber nicht ermittelt werden kann.

Die in dieser Dissertation vereinten Untersuchungen veranschaulichen die enge Verzahnung von Siliziumkreislauf und Sedimentationsprozessen in Salzmarschen. Durch ihre große Flächenausdehnung, den hohen Salzgehalt und starken Tideeinfluss haben Salzmarschen einen beträchtlichen Anteil am Siliziumkreislauf der Küstengewässer. Sie weisen hohe DSi-Exportraten pro km^2 auf und exportieren das ganze Jahr über DSi in die Küstengewässer. Gleichzeitig bilden sie natürliche Senken für partikuläres Silizium in Form von BSi, das mit dem Sediment auf der Marschoberfläche abgelagert wird. Das vertikale Höhenwachstum der Vorlandflächen wird maßgeblich durch Sedimentationsprozesse bestimmt. In Anbetracht des steigenden Meeresspiegels ist die Analyse dieser Prozesse auch für Erhalt und Schutz der Küstengebiete von zunehmender Bedeutung. Die im Rahmen der Dissertation berechneten Akkretionsraten deuten darauf hin, dass das vertikale Höhenwachstum der meisten Salzmarschen im Wattenmeer ausreicht, um mit dem Anstieg des Meeresspiegels in näherer Zukunft schrittzuhalten. Da die Akkretionsraten jedoch komplexen Rückkopplungsprozessen zwischen Marschvegetation, -morphologie und Überflutungsregime unterliegen, ist ein kontinuierliches Monitoring angezeigt. In diesem Zusammenhang markiert die ermittelte, signifikant höhere Bodendichte der beweideten Flächen einen Einfluss des Managements. Die Auswirkung der Beweidung auf das vertikale Höhenwachstum sollte in zukünftigen Untersuchungen in höherer räumlicher Auflösung betrachtet werden.

1

Introduction

1.1 Salt marshes

1.1.1 Typology and hydrology

Salt marshes are ecosystems of the temperate zone that developed in shallow intertidal areas at the transition zone between land and sea. Plants and animals colonising salt marshes are adapted to frequent flooding and high salinities. As sedimentary ecosystems, salt marshes developed through the deposition of sediments, and in the long term only continuous sedimentation ensures their further existence. In Europe, salt marshes spread over at least 2,300 km² (Dijkema 1987); 400 km² are situated at the Wadden Sea coast (Reise et al. 2010). Globally, salt marshes are estimated to cover between 22,000 and 400,000 km² (McLeod et al. 2011; Fig. 1.1). In tropical and subtropical regions, similar physical settings are generally colonised by mangroves (Reise et al. 2010), but also salt marsh-mangroves ecotones occur (Friess et al. 2011).

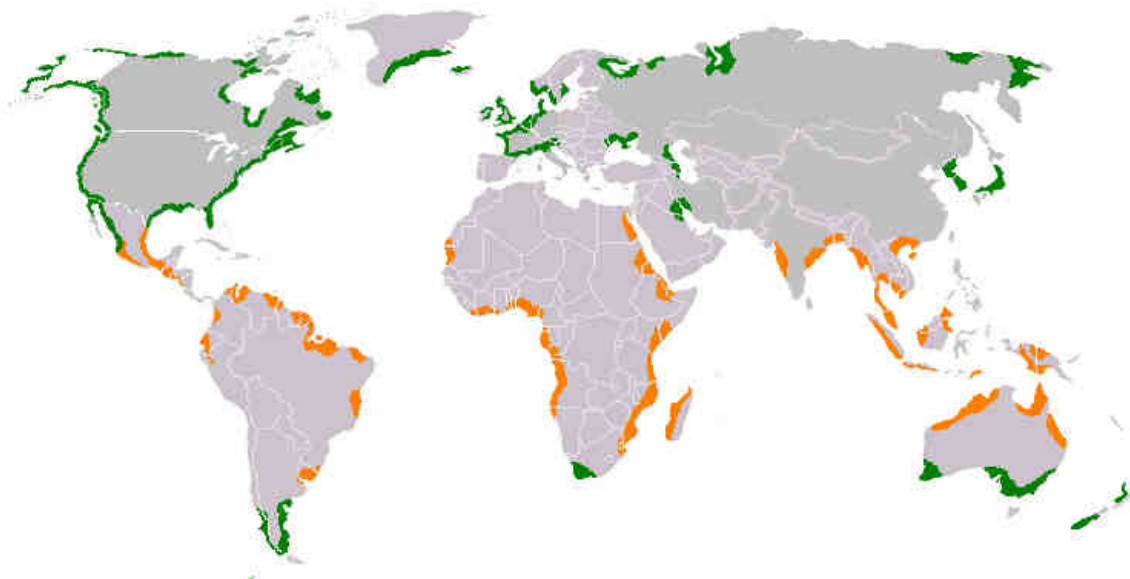


Fig. 1.1: Global distribution of salt marshes (dark gray) and mangroves (light grey; source: Wikimedia commons).

A first comprehensive classification of European coastal systems and salt marshes was proposed by Shepard (1963) and further developed by Dijkema (1987). This typology divides salt marsh systems into groups based on substrate origin, main geological driving forces, geomorphology and ecology. Salt marshes with allochthonous substrate (deposited by marine or fluvial transport) are distinguished from systems with autochthonous substrate (isostatic emergence of the seafloor). Only 3% of all European coastal salt marshes can be assigned to this latter group. Allochthonous marshes are further divided into salt marshes at rocky, fluvial sedimentary or marine sedimentary shores. Marine sedimentary shores include 65% of all European coastal salt marshes, and 'foreland salt marshes' clearly dominate this group (Dijkema 1987). Foreland salt marshes can be found in front of flat alluvial plains, where mainly clay-rich sediments settled under sheltered conditions. Often, this salt marsh type developed in or in front of man-made sedimentation fields and drainage structures (Dijkema 1987).

Another classification was suggested by Doody (2008), who distinguished salt marshes according to their geographical location. In this typology, most European salt marshes could be assigned to the group of 'open coasts or plain beach salt marshes', but also many 'estuary salt marshes' and 'barrier island salt marshes' exist. Doody (2008) further discriminates between different developmental stages of salt marshes. He described salt marshes as: 'accreting' if sedimentation continues and the marsh surface is relatively quickly rising; 'semi-stable' if times of accretion are in dynamic equilibrium with times of erosion; and as 'eroding' if the salt marsh area is decreasing over time.

Hydrological conditions in salt marshes are tightly linked to their tidal regime and to the sediments deposited. A typical back barrier salt marsh in Denmark for instance consists of 40-45% clay (predominantly illite, with varying percentages of kaolinite, chlorite and smectite), 40-55% silt and, depending on the exposition to storm surges, 5-15% sand (Bartholdy 1997). The dominance of small grain sizes (an example of a clay particle can be seen in Fig. 1.2) causes a reduced soil porosity and water conductivity. Consequently, inundation water penetrates slowly into the soil. Even 5 days after a storm surge of more than 2 m above mean high tide (MHT), only the upper 2-3 cm of the salt marsh soil at the Wadden Sea coast were saturated with water (F. Müller, personal observation). Ground water levels in salt marshes are generally high and can reach up to the surface in the lowest parts of the marshes.

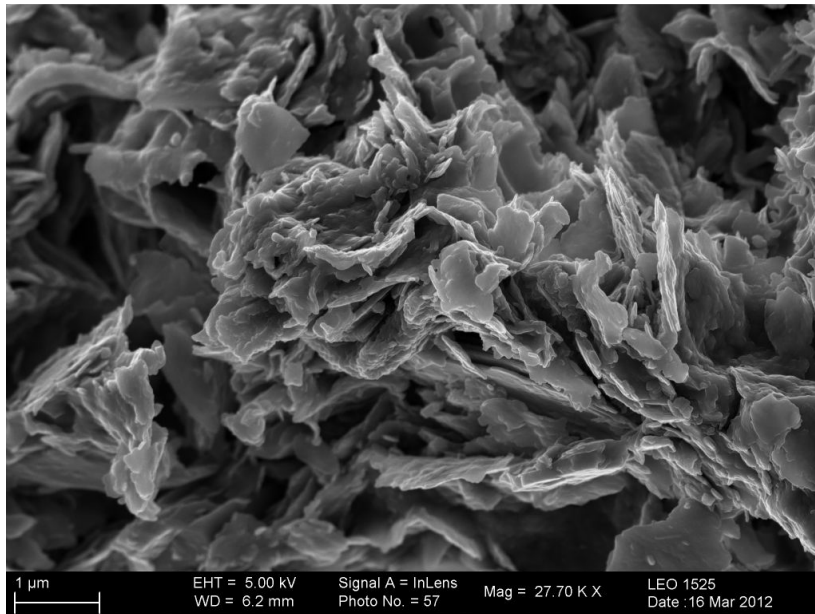


Fig. 1.2: Raster electron microscope image of clay particles in salt marsh sediments from Dieksan-derkoog.

1.1.1 Vegetation and zonation

The tidal regime induces environmental stress of frequent inundations and high salinities that leads to a zonation of the salt marsh vegetation (Fig. 1.3). Plants of the daily flooded pioneer zone are adapted to flooding and anoxic conditions in the soil and grow up to 40 cm below MHT (Bakker et al. 2005). At the Wadden Sea coast, a typical pioneer species is *Salicornia europaea*. In the beginning of the last century *Spartina anglica* was introduced to the system to enhance sediment deposition in the pioneer zone (Lambert 1964). The adjacent low marsh is flooded 100-400 times a year, mainly at spring tides (Bakker et al. 2005). The plant communities in the low marsh typically contain *Atriplex portulacoides*, *Puccinellia maritima*, *Aster tripolium* and *Suaeda maritima* (Esselink et al. 2000). The high marsh is inundated less than 100 times a year and some locations are only flooded during storm tides (Bakker et al. 2005). High marsh vegetation is often dominated by *Elymus athericus*, but also *Agrostis stolonifera*, *Atriplex prostrata* and *Festuca rubra* frequently occur in this part of the marsh (Andresen et al. 1990; Suchrow et al. 2010).

Salt marshes are dynamic habitats and their vegetation is subject to succession. Plants in the pioneer zone stabilise muddy sediments and enhance the settlement of new material. The marsh surface is consequently rising and low marsh plants establish and start to dominate. If sediment supply to the marsh is sufficient, this process will continue until high marsh plants increase in cover and replace low marsh plants. This ageing process of vegetation communities is called ‘progressive succession’, and the order of plants occurring generally corresponds to the above mentioned zonation of a salt marsh (de Leeuw et al. 1993). If sediment supply is limited and sea level is rising faster than the marsh is accreting, vegetation development can also be reversed. This process is called ‘retrogressive succession’, in which plant communities of

high marshes will retreat and low marsh plant species will become more abundant (Bakker 1985). This process can also be induced by intensive grazing (Kiehl et al. 1996).

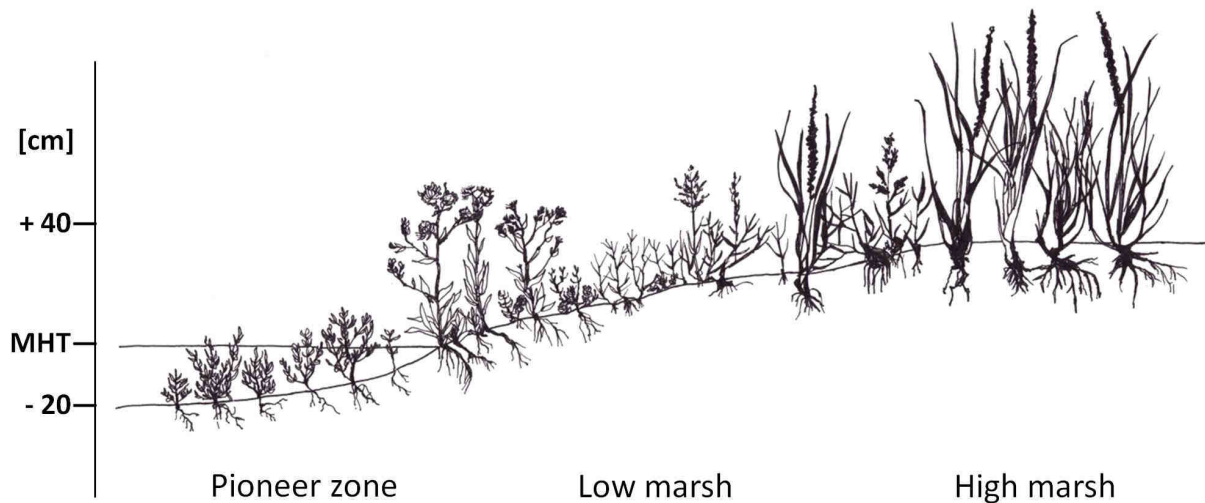


Fig. 1.3: Typical zonation of salt marsh vegetation: pioneer zone (from 40 cm below MHT to MHT); low marsh (from MHT to 20 cm above MHT); high marsh (from 20 cm above MHT; modified by S. Jung after Ellenberg 1996).

1.1.2 Ecosystem functions and services

Salt marshes are often considered to be especially valuable wetland habitats because they fulfil various ecosystem functions and services (Costanza et al. 1989). According to the TEEB report, ecosystem functions can be defined as a “subset of the interactions between ecosystem structure and processes that underpin the capacity to provide goods and services” (TEEB 2010). They can be grouped into four main categories: regulation, habitat, production and information functions (Fig. 1.4; de Groot et al. 2010). In salt marshes, regulation functions include sedimentation processes and the formation of new soil, nutrient regulation and flood protection. Habitat functions indicate that a salt marsh serves as a nursery or a refuge for plant and animal species. Information functions include the system’s relevance in science and education and in providing aesthetic and historic information. Finally, the fact that salt marshes are among the most productive ecosystems of the world (Mitsch and Gosselink 2000) emphasises the importance of their production functions, which include primary productivity as well as the provision of genetic resources (de Groot et al. 2002).

In contrast to ecosystem functions, ecosystem services address only the benefits that humans derive from the system. The TEEB report divides ecosystem services into four main groups: provisioning, regulating, habitat and cultural and amenity services (de Groot et al. 2010), mainly following a former classification given by the Millennium Ecosystem Assessment (2005). Slightly different classifications were given by Costanza et al. (1997), Pimentel et al. (1997) and Hein et al. (2006) and the discussion about definitions and classifications continues to this day (de Groot et al. 2010). Coastal systems provide large quantities of ecosystem services (UNEP 2006). Salt

marshes for instance supply food (e.g. meat, fish), flood protection (e.g. attenuation), aesthetic recreation (e.g. tourism, bird watching) and nutrient cycling (e.g. denitrification; Gedan et al. 2009). Supply of dissolved silica from salt marshes was assumed to be a very important ecosystem service, but so far, only little is known about silica pools in salt marshes and the processes related to silica exports (Struyf et al. 2006, 2007a). Sedimentation, another central ecosystem service of salt marshes, has extensively been studied, but mainly in relation to abiotic influencing factors and rarely, for instance, in relation to salt marsh management.

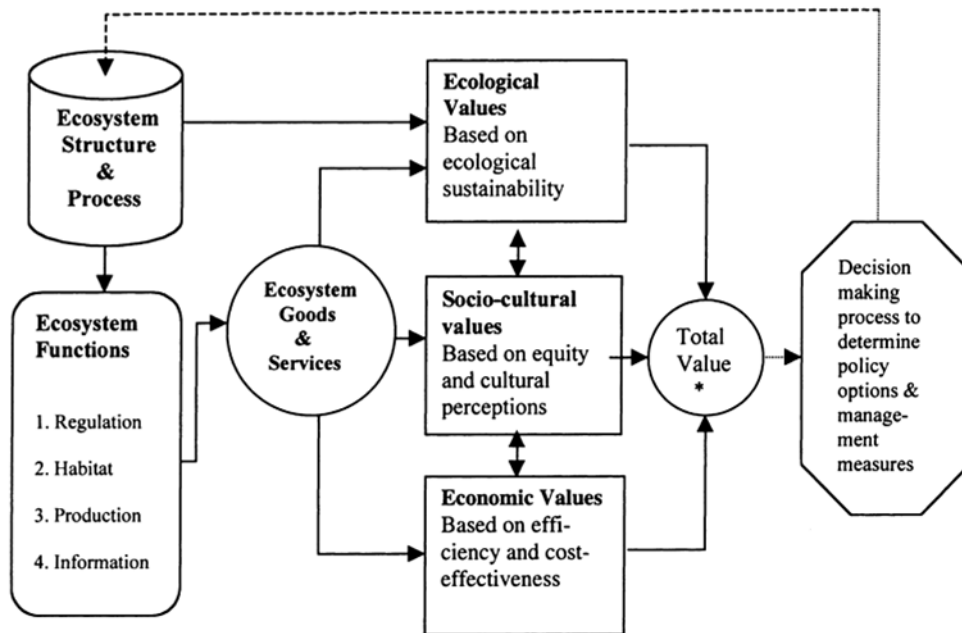


Fig. 1.4: Model of ecosystem functions, goods and services and their relationship to ecological, socio-cultural and economic values of ecosystems (from de Groot et al. 2002).

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1.1.3 Management

Salt marshes in the Wadden Sea were traditionally used as pastures for domestic grazers such as sheep and cattle (Bakker et al. 1993). Doody (2008) distinguished five different classes of grazing pressure. These classes range from: ‘overgrazed’ conditions with destroyed vegetation canopy and bare soil; through ‘heavily grazed’ sites with a stock density of up to 6.5 sheep/ha (whole year grazing) or 9-10 sheep/ha (summer grazing); to ‘abandoned, formerly grazed’ marshes with no grazing influence whatsoever. As intermediate categories, ‘moderately grazed’ and ‘historically ungrazed/light grazed’ conditions are listed. In this thesis, only two categories will be used to underline the contrast between ‘intensively grazed’ (in short ‘grazed’) and ‘ungrazed’ sites. In this context, the term ‘grazed’ always refers to an intensive grazing pressure of at least 10 sheep/ha (Kiehl et al. 1996). The second category, ‘ungrazed’ sites, includes salt marshes that were grazed for decades but have been abandoned since the late 1980s or early 1990s.

Grazing affects both abiotic and biotic conditions in salt marshes and largely determines their vegetation composition (Bakker 1985). Trampling on the soil surface for instance, induces soil compaction that can lead to water logging and longer retention times of pore and ground water (Andresen et al. 1990; Esselink et al. 2000; Tate et al. 2004). This altered soil hydrology can cause increased salinities (Yu and Chmura 2010), elevated pH-values (Binkley 2003) and generally modify the cycling of nutrients (Olsen et al. 2011) and decomposition rates in the soil (Schrama et al. 2012). Under grazing, plant species composition consequently shifts towards species less sensitive to soil compaction and higher salinities (Esselink et al. 2000). Furthermore, growth of belowground biomass is often enhanced (Kiehl et al. 2001). Plant species able to quickly regenerate aboveground parts are favoured by grazing as well as small-sized and light-demanding species (Bakker et al. 1985; Scherfrose 1993). From this selective pressure, plants of the low marsh zone often benefit and retrogressive succession is initiated (Bakker 1985). In general, vegetation composition developing under grazing is poor in species and structural diversity (Kiehl et al. 1996). In the low marsh zone, retrogressive succession leads to a dominance of *Puccinellia maritima* instead of *Atriplex portulacoides*, and in the high marsh zone, *Festuca rubra* is the typical dominant species in grazed areas (Bakker 1985; Esselink et al. 2000).

Due to nature conservation management, grazing was stopped in many salt marshes at the Wadden Sea during recent decades. The conservation aim was to allow for the re-establishment of natural dynamics in the ecosystem. As a consequence of the abandonment of grazing, vegetation diversity increased in many areas (Kiehl 1997). Species composition shifted back to species sensitive to grazing, water logging and high soil salinities. Progressive succession was initiated, and the proportion of tall species, typical for the high marsh, increased (Esselink et al. 2000). Their abundance was accompanied by a growing standing stock of aboveground biomass and consequently by higher litter accumulation (Andresen et al. 1990). Together with grazing, the maintenance of the drainage systems was stopped at most locations (Esselink et

al. 2002). The purpose of the drainage system was to quickly discharge the inundation water, to increase soil aeration and to prevent the formation of irregular creeks and pans in the salt marsh (Esselink et al. 1998). In the long term, a reduced drainage can lead to water logging and could again favour plant species of the low marsh. Furthermore, it can cause more variation in surface elevation and in vegetation composition (Esselink et al. 2000). In salt marshes in Friesland at the Dutch Wadden Sea coast, former drainage ditches quickly silted up. Here, it takes days to discharge the water after inundation, leading to low marsh conditions even in relatively high elevated parts of the marsh (S. Nolte, personal communication).

After some years, the cessation of grazing resulted in a reduction of species diversity (Esselink et al. 2000) and in monospecific stands of plants such as *Elymus athericus* and *Atriplex portulacoides* (Bockelmann and Neuhaus 1999; Bakker et al. 2003). Although this was not the case for all salt marshes (Schröder et al. 2002; Bos et al. 2002), nature conservation agencies in the Netherlands started to reintroduce grazing to the system (Bakker et al. 1985). This shift in nature conservation norms and values was accompanied by an extended scientific debate over the advantages and disadvantages of grazing in salt marshes (e.g. Bakker et al. 1985; Kiehl et al. 1996; Esselink et al. 2000; Schröder et al. 2002; Bakker et al. 2003). Today, the primary management objective for Denmark and the Netherlands is to maintain general biodiversity at a high level, whereas legislation in Germany aims at natural development of the area (Esselink et al. 2009). This is reflected by the percentage of ungrazed salt-marsh area, which is 20% in the Netherlands, 35% in Denmark, 50% in Schleswig-Holstein and nearly 70% in Lower-Saxony and Hamburg (surveyed within the Trilateral Monitoring and Assessment Program (TMAP) between 2002 and 2008; Esselink et al. 2009). Even if the undisturbed course of natural processes is by law the declared prime objective in Germany (Esselink et al. 2009), there is still ongoing discussion about the reintroduction of grazing. Whereas Schröder et al. (2002) concluded that the abandonment of grazing did not lead to large-scale monodominance of single plant species; Scherfrose (1993) advised to reintroduce grazing at least in some parts of the high marsh zone to induce retrogressive succession.

1.1.4 Environmental threats

Although salt marshes have proven to be comparably resilient to external influences in the past, they are facing various future threats (Gedan et al. 2009; Esselink et al. 2009). For instance, invasive plant species endanger vegetation composition in salt marsh systems. In North America, a European haplotype of *Phragmites australis* is invading tidal marshes and threatening local species composition (Meyerson et al. 2000). In European salt marshes, the native invasive grass *Elymus athericus* benefits from the cessation of grazing (de Bakker et al. 1999; Pétilion et al. 2005; Bockelmann et al. 2011) and in Chinese salt marshes, *Spartina alterniflora* is spreading (An et al. 2007). Also introduced animal species can cause damage, as seen in North American marshes, where burrowing activity of the isopod *Sphaeroma quoyanum* enhanced marsh edge erosion (Talley et al. 2001).

Hydrological alterations mainly occurred in the past but their effects continue until today. Ditching for soil drainage and mosquito control has been the most severe alteration of hydrology in salt marshes (Gedan et al. 2009). In many abandoned salt marshes, strong tidal currents keep the ditches open and their drainage effect persists. The competitive success of invading high marsh species such as *E. athericus* in salt marshes and *P. australis* in freshwater and brackish marshes has been related to the well drained conditions (Esselink et al. 2009; Gedan et al. 2011) Also the decreasing number of ponds on the salt marsh surface was explained by drainage (Gedan et al. 2009).

Eutrophication and environmental pollution are further factors potentially altering competitive hierarchies of salt marsh plant species (Levine et al. 1998). Since most salt marsh plants are nitrogen (N) limited under natural conditions, anthropogenically elevated N levels favour large aboveground biomass producers such as *E. athericus* and *P. australis* and enable them to outcompete smaller plants in competition for light (Rozema et al. 2000). Even though environmental regulations are more and more restrictive worldwide, chemical pollutants are still considered to be a major threat to estuarine and coastal wetlands (Tate 2002). Detrimental to their status and function, salt marshes accumulate pollutants and nutrients in the marsh soil (Gedan et al. 2011).

Furthermore, alterations of consumer control can affect the salt marsh ecosystem. In the early years of tidal marsh ecology, it was assumed that development and functioning of salt marshes was physically controlled in the first instance (Odum 1971, cited in Gedan et al. 2009). Today's salt marsh research recognises that they are largely consumer controlled (Bertness and Silliman 2008; Gedan et al. 2009). Changes in consumer control can be induced by overexploitation of coastal fish and crab populations. Current events of marsh die-off in Northern American marshes (250,000 ha were affected in the U.S. alone) were explained by fast growing populations of invertebrates feeding on salt marsh plants, such as the native crab *Sesarma reticulatum* (Holdredge et al. 2009) or the marsh snail *Littoraria irrorata* (Silliman and Bertness 2002).

Sea-level rise is one of the major future threats to low lying areas (IPCC 2007) along the coasts and therefore to salt marshes. Opposed to some salt marshes in North America, which are critically threatened by this development (Reed 1989; Boesch et al. 1994), Wadden Sea salt marshes are less threatened. Rates of surface elevation change of 11-16 mm yr⁻¹ in the Netherlands, 6-26 mm yr⁻¹ in Schleswig-Holstein and 10 mm yr⁻¹ in Denmark (Dittmann and Wilhelmssen 2004, citing several authors) are expected to compensate for sea-level rise at least in the forthcoming decades. Of course, vertical marsh growth is subject to strong local variability, but salt marshes are not considered to be endangered as long as enough sediment is supplied by the North Sea and as long as sea-level rise stays below a critical level of 8.5 mm yr⁻¹ (Oost et al. 2005). The critical limit was defined as a threshold up to which salt marshes are expected to be able to keep pace with sea-level rise (Oost et al. 2005).

In the recent past, the largest loss of salt-marsh area did not occur on the sea side but at the mainland side of the marshes. When people started to build sea walls as a measure of coastal defence and for land reclamation, the total area of salt marshes was considerably reduced in Europe (Esselink et al. 1998). Even today, the existing sea walls endanger salt marshes by acting as the landward barrier for lateral marsh growth. Against the background of a rising sea level, this ‘coastal squeezing’ can lead to a loss of salt-marsh area and endangers especially the high marsh zone (Gedan et al. 2009).

Another consequence of climate change is an elevated average temperature in many regions in the world. This could alter the geographical distribution of salt marshes, which now span between 30° and 80° latitude. Salt marshes exhibit azonal vegetation (Ellenberg 1996), which is more driven by local site conditions such as high salinities and frequent inundations rather than by climatic conditions such as temperature and precipitation. It is therefore likely that salt marshes are less sensitive to temperature induced changes in species composition than ecosystems with predominant zonal vegetation. However, changes in atmospheric CO₂ concentrations are suspected to favour C3 plants over C4 plants, possibly leading to a shift in species composition in the long term (Rozema et al. 1991).

High inundations are generally less of a threat to the salt marsh system as a whole, but can have devastating effects on the salt marsh’s fauna. Normally, damage is normally only local and of short duration (e.g. loss of breeding-bird nests or drowned mammals; Valiela et al. 1998). In the recent years, however, an unusual number of summer floods have been observed, destroying breeding-bird nests in several years in a row (C. Erb, personal communication). If this development continues, this might indeed have deteriorating effects on population sizes of bird species such as the oystercatcher (*Haematopus longirostris*) or the arctic tern (*Sterna paradisaea*; Koffijberg et al. 2006; van de Pol et al. 2010).

1.2 The Wadden Sea coast

1.2.1 Geology

The Wadden Sea is a shallow coastal system, stretching from Denmark to the Netherlands (Fig. 1.5), which includes the largest area of coherent tidal flats of the temperate zone (4,700 km²). In geological terms, the system is comparably young, since it only developed during and after the last two ice ages (Ahrendt 2006). When the Weichselian ice age reached its maximal glaciation (ca. 25,000-18,000 before present), the sea level was approximately 110-130 m lower and the coast line was situated 600 km further North, exposing the entire area of today’s North Sea (Streif 1990). With the beginning of the Holocene, 10,000 years ago, glaciers melted, and large amounts of sediment were deposited at the shallow coastlines of the North Sea. Around that time, the sea level was still 65 m below its today’s level, and phases of transgression and regression of the sea alternated (Streif 1990).



Fig. 1.5: Map of the Wadden Sea coast (modified from Marencic et al. 2009).

The emergence of tidal marshes is directly connected to transgression phases of the North Sea. Sand, silt and clay were deposited at the coastline and formed the basis for early marsh genesis. Approximately 90% of the Holocene deposits in the Wadden Sea are imported from the North Sea basin and another 10% originate from erosion processes within the Wadden Sea area (Ahrendt 2006). In Nord Friesland (Schleswig-Holstein, Germany), such marine sediments can be up to 24 m thick (“nordfriesische Rinne”), getting shallower towards the Geest (i.e. Pleistocene sand deposits of the Saale ice age on the mainland; Ahrendt 2006). During regression phases, low-lying coastal areas became desalinated and extended fens and swamp forests emerged (Fig. 1.6). Their development was supported by a natural levee, parallel to the coast, which resulted from repeated inundations during spring and storm tides and which was up to 2 m higher than the land behind it (Pott 1995).

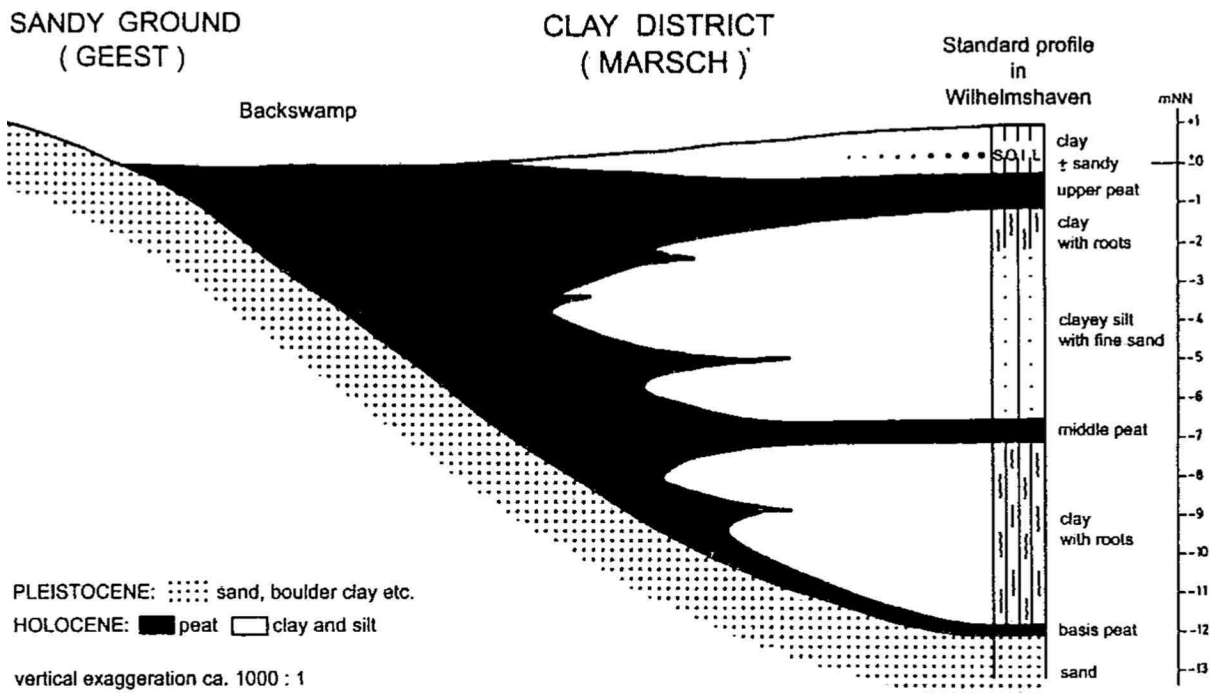


Fig. 1.6: A typical profile through marsh sediments. The white pattern symbolises clay and silt deposition during transgression phases. The black pattern symbolises peat formation during regression phases (from Behre 2002).

1.2.2 Human alterations of the coast line

Humans had used the coastal landscape for hunting and gathering since the end of the Weichselian ice age, but it was not until the early Iron Age (8th to 5th century BC) that settlement started in the salt marshes of the Wadden Sea region. In that period, sea-level rise decelerated and people began to build the first small dwelling mounds in the region of Friesland and Groningen (Bazelmans et al. 2012). Due to the large storage capacity in the extended coastal wetlands, devastating floods occurred relatively seldom and the population density in this fertile landscape was up to five to ten times higher than in the hinterland (Bazelmans et al. 2012).

Colonisation of the salt marshes varied not only with transgression and regression of the North Sea, but also political and social reasons led to repeated decolonisation of the landscape. During the Migration Period (5th to 6th century AD) for instance, settlement of salt marshes came nearly to an end and almost no archaeological finds of that period exist (Segschneider 2000). Resettlement of the German Wadden Sea coast after the Migration Period was especially driven by Frisians, which were also the first to construct sea walls to protect their homes and their belongings (Bazelmans et al. 2012). In the 11th century AD, people started building small ring sea walls around single settlements giving protection against minor storm floods in summer. Later, they joined their forces to erect higher winter sea walls around whole villages (Erchinger 2005). In the 13th century people also began to construct brushwood embankments to stimulate sedimentation in front of already embanked areas with the

purpose of land reclamation (Krämer 1984, cited in Bazelmans et al. 2012). Protected by sea walls, the settlement of the marshland and adjacent peat land continued.

The resulting land use pressure was not without consequences for the coastal population. Especially the cutting of peat for salt production and the drainage of agricultural land led to a quick decrease in surface elevation of the hinterland. These activities coincided with a further rise in sea level, and since the shortened coastline has led to a decreased storage capacity of the coastal landscape, storm surges became an increasing threat to the coastal population (Bantelmann 1960). The coastal population suffered from many storm surges that caused breaches in the sea walls and caused large damage in the hinterland. At least for the Schleswig-Holstein Wadden Sea coast, the most devastating storm surges were the Marcellus storm surge in 1362 (“Grote Mandränke”) and the Burchardy storm surge in 1634 (“Zweite Grote Mandränke”). These two storm surges led to a loss of about 1,300 km² marsh land in North Friesland and completely reshaped the coast line (Fig. 1.7; Behre 2002).

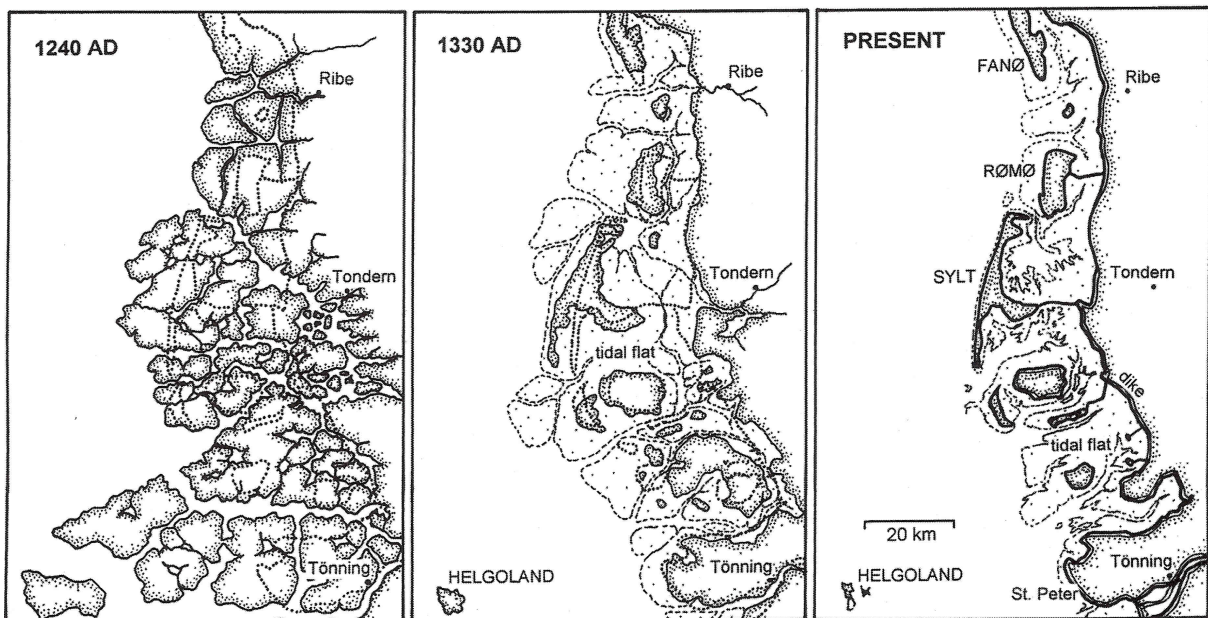


Fig. 1.7: Historic and recent map of North Friesland (Germany), displaying the development of the coastline after several devastating storm surges in the Middle Ages (Flemming 2002).

After these two major and several smaller storm surges, the western edge of the Geest became the new coastline. From here, people started to reclaim the land (Behre 2002). Especially between the 15th and 18th century, numerous hydraulic improvements were applied which allowed to reclaim new land and to efficiently drain existing land (Bazelmans et al. 2012). When base elevations were sufficiently high, sea walls were erected around an area to prevent it from further flooding. To stimulate vertical growth of tidal flats, sedimentation fields were constructed in front of the sea wall. Sedimentation fields are regularly shaped, artificial low-energy environments, surrounded by groynes, which are made from brushwood or stones (Fig. 1.8; Hofstede 2003). These measures were generally accompanied by the dredging of furrows, which

had the purpose to drain the sediments and consequently promote colonisation by pioneer salt marsh species (Hofstede 2003). Once a salt marsh had developed, a new sea wall was constructed. After some years of desalination, the area, which was called ‘Koog’ if the former seawall was not deconstructed, could be used as fertile farm land. Centuries of experience in land reclamation led to elaborated and diverse techniques in the Wadden Sea area, which are today only applied to sustain the current salt marsh area for both coastal protection and nature conservation purposes (Goeldner 1999).

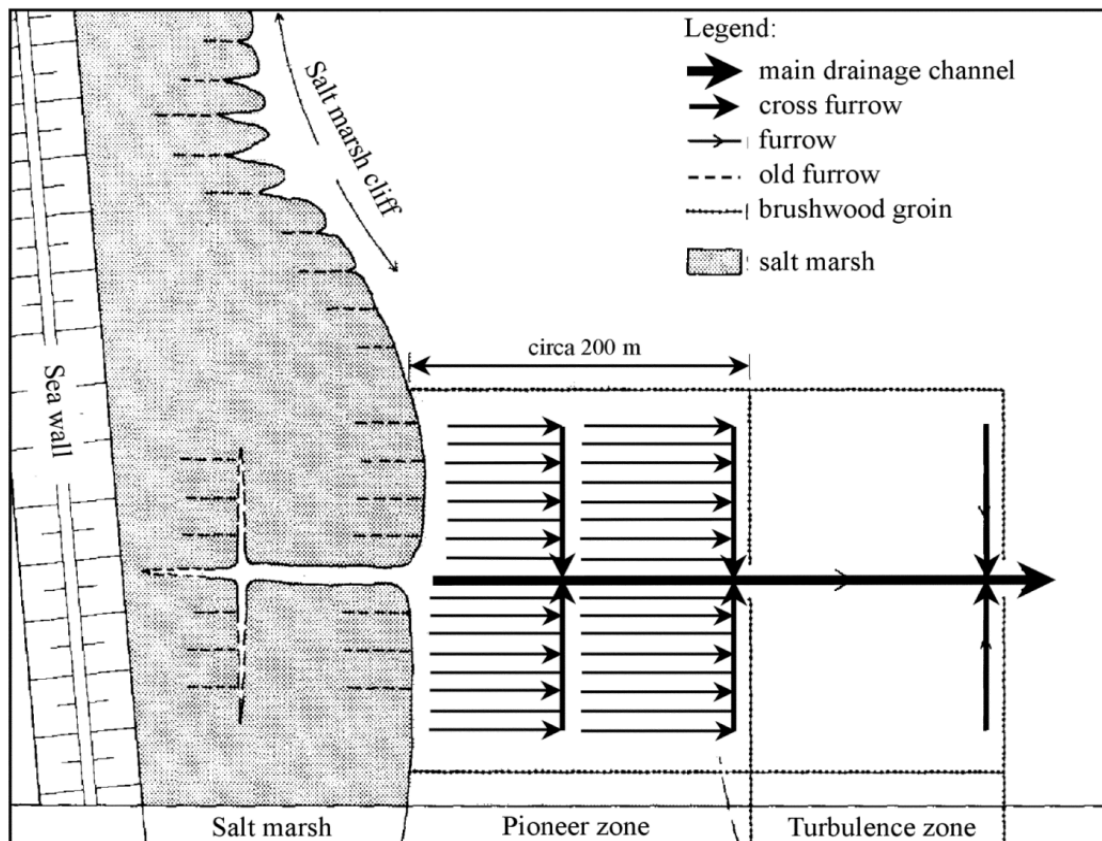


Fig. 1.8: The ‘Schleswig-Holstein echelon system’ for the creation of salt marshes in front of the sea wall (from Hofstede 2003).

1.2.3 Schleswig-Holstein Wadden Sea National Park

The geomorphological diversity combined with the rich history of the Wadden Sea coast entailed a diverse landscape, which is the living environment for a variety of plant and animal species. Already in the late 19th century, the local population in Schleswig-Holstein was aware of the uniqueness of their surrounding, and the first nature conservation ideas arose in today’s North Friesland (Riedel 2000). Bird hunting and the collecting of eggs were frowned upon, and in 1907 one of Germany’s first nature conservation associations was founded (“Verein zur Begründung von Vogel-freistätten an den deutschen Küsten – Jordsand”). In the following decades, a number of nature protection areas were designated in Schleswig-Holstein, many of them at the Wadden Sea coast.

Although nature conservation has a long history in Schleswig-Holstein, it was not until 1985 that the federal government decided to establish the Schleswig-Holstein Wadden Sea National Park. On 22 July 1985, the national park law „Gesetz zum Schutze des schleswig-holsteinischen Wattenmeeres (GVOBl. Schl.-H.)” came into force. Its aim was the protection and development of the Wadden Sea area in Schleswig-Holstein and the preservation of its special nature, beauty and originality. Where possible, natural processes should be allowed and stimulated.

With a total area of 4,415 km², the Schleswig-Holstein Wadden Sea National Park is the largest national park in Germany. Together with the high-altitude mountain area it represents the last predominantly natural region in Europe (Riedel 2000). Depending on ecological criteria, the national park is divided in two protection zones. In zone 2 (2,840 km²), access and even agricultural use are allowed under certain conditions; in zone 1 (1,570 km²), access is strongly restricted. Approximately two thirds of the area of the National Park is permanently under water (sublittoral), 30% consists of mud flats (eulittoral) and 2% are terrestrial (Stock et al. 2005). The tidal flats in the Wadden Sea area, which are partly situated in Schleswig-Holstein constitute a highly productive ecosystem (Reise 2010). Accordingly, the whole area is considered to be Europe’s most important resting habitat for migratory birds on their way to their breeding habitats or wintering grounds (Blew et al. 2004). In total 2,500 marine and 2,300 semi-terrestrial species were recorded in the Schleswig-Holstein Wadden Sea National Park (Heydemann 1998).

In Germany, the major purpose of a national park is to protect natural processes. At the same time, however, it is also aiming to avoid unacceptable restrictions for humans. Nordfriesland and Dithmarschen, the two districts bordering the Wadden Sea coast in Schleswig-Holstein, have in total 300,000 inhabitants. Additionally, 14 million tourists visit the German Wadden Sea coast every year (Kalisch 2011). Consequently, tourism contributes to 37% of the people’s income (Gätje 2007). Since wild life and people often have conflicting interests, opposition against the national park was strong in the 1980s. Since that time, however, the acceptance increased and in 2005 nearly 80% of the local population had a positive opinion about the existence of the Schleswig-Holstein Wadden Sea National Park (Gätje 2007).

Even within nature conservation, conflicting protection aims exist. While the national park allows for a natural development with as little human interference as possible, other legislations require active conservation measures. In the Habitat Directive for instance, all EU member states have agreed on protecting especially endangered natural habitats and species. Some rare breeding birds, like the avocet (*Recurvirostra avosetta*) or the arctic tern (*Sterna paradisaea*), for instance, cannot cope with the high and dense canopy of ungrazed salt marshes and avoid these sites (Koffijberg et al. 2006). Keeping the populations of these species in a favourable conservation status makes it necessary to provide salt marshes with a short canopy. Additional legislations, which apply to the national park are:

- the Water Framework Directive;

- the Conservation of Wild Birds Directive;
- the protection as a Particularly Sensitive Sea Area (PSSA);
- the Convention on Wetlands of International Importance especially as Waterfowl Habitat (RAMSAR);
- the UNESCO Man and the Biosphere program; and
- the nomination as UNESCO World Heritage Site.

The Schleswig-Holstein Wadden Sea National Park is part of a larger network of coastal protection areas. In 1986 and 1990, Lower-Saxony and Hamburg established their Wadden Sea national parks, respectively. The Dutch part of the Wadden Sea is protected as a nature conservation area, but, with the exception of two smaller sites, not as a national park. The Danish Wadden Sea national park was established in 2010. The three countries have already been cooperating since 1978 in the “Trilateral Cooperation on the Protection of the Wadden Sea”. In 1987 “The Common Wadden Sea Secretariat” was established to support, initiate, facilitate and coordinate the activities of the collaboration (CCWS 2010). Ten years later, the member states agreed on the Wadden Sea plan (The Stade-Declaration), containing long-term targets for the ecological development of the Wadden Sea region. The plan was updated in 2010. In order to assess whether the targets are met, a comprehensive monitoring scheme was set up. In the framework of the Trilateral Monitoring and Assessment Program (TMAP), the status and development of the Wadden Sea ecosystem is regularly assessed on the basis of a common package of monitoring parameters. Every six years, detailed reports are published on abiotic conditions of the Wadden Sea and on the status of habitats including the flora and fauna living in the area. Overall, the gathered data make up a unique database, containing also valuable long-term data on salt marshes in the Wadden Sea.

1.2.4 Salt marshes in the national park

The majority of the terrestrial systems within the Schleswig-Holstein Wadden Sea National Park consist of salt marshes (in total 122 km², Fig. 1.9). Of this total area, 78 km² are situated on the mainland, 22 km² on the Halligen (e.g. remnants of former mainland) and 14 km² on the islands (Esselink et al. 2009). In 1988, shortly after the designation of the national park, only 2% of the salt marshes were ungrazed and 3% were moderately grazed (Kempf et al. 1987, cited in Bakker et al. 2005). The remaining area was used for intensive sheep grazing. These proportions shifted gradually until 2006, when the percentage of ungrazed salt marsh area increased to 44% and moderately grazed sites made up 7% (Esselink et al. 2009). As described above, the abandonment resulted in a shift in species composition and in some areas of the national park, plant species diversity was reduced (Esselink et al. 2000).

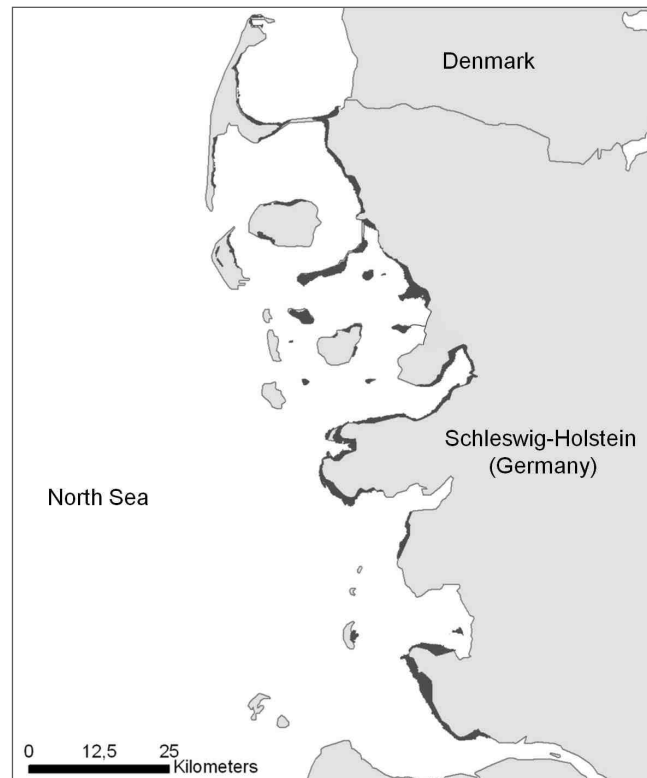


Fig. 1.9: Distribution of salt marshes in the Schleswig-Holstein Wadden Sea National Park, Germany. Dark grey areas represent salt marshes.

1.2.5 Research project BASSIA

Maintaining biodiversity and ecosystem functions of salt marshes in the Wadden Sea area requires sustainable management strategies. To base these strategies on sound scientific knowledge, the Junior Research Group BASSIA (Biodiversity, management and ecosystem functions of salt marshes in the Wadden Sea National Park of Schleswig-Holstein) was established. Its objective was to analyse effects of conservation management on plant species diversity, breeding bird communities and on abiotic ecosystem functions. TMAP vegetation maps of the last 20 years were analysed to quantify changes in structural and species diversity on different spatial scales and to better understand factors responsible for the different pathways of succession. Structure and composition of the vegetation can determine which birds use the salt marsh as a breeding habitat. In BASSIA, the diversity of vegetation types was therefore related to the number and diversity of breeding bird pairs at the mainland coast and at the Halligen. A further focus of the project was the abiotic ecosystem functions of salt marshes. Here, sedimentation processes and silica cycling in salt marshes were analysed. The results regarding these processes are presented in this thesis. Based on the investigated effects of salt marsh management on vegetation succession and diversity, breeding bird communities and ecosystem functions, BASSIA developed recommendations for an optimised and sustainable salt marsh management (Wanner et al. 2012).

1.3 Silica cycling

1.3.1 Global silica cycling

Silicon (Si) is the second most abundant element on earth (Wedepohl 1995). Several organisms depend on it, since Si is an essential nutrient for radiolarians, sponges, diatoms and many higher plants. It further plays a role in carbon fixation and in acid buffering of soils (Derry et al. 2005). Naturally, Si does not appear in its elementary form, but as a derivate of Si dioxide or ‘silica’ (SiO_2). In this thesis, the term ‘Si’ will therefore be used as an equivalent for silica which is common practice in literature on Si cycling. During chemical weathering, when CO_2 reacts with silicates to hydrogen-carbonates (HCO_3^-), Si is released to the biosphere as silicic acid (H_4SiO_2). In this dissolved form (DSi), it can be transported to the ocean by ground water and rivers. On its way to the ocean and in the ocean itself, Si is recycled by sponges, radiolarians, diatoms or higher plants. Diatoms for instance use Si to construct their frustules. Yearly, about 2% of all Si in diatoms settles down to the bottom of the ocean, where it eventually re-enters the geological cycle (Treguer et al. 1995).

In the early years of Si research, it was assumed that the Si cycling was only geologically driven (e.g. Garrels 1967, cited in Derry et al. 2005; White and Blum 1995). Only recently, the buffering role of terrestrial ecosystems in Si cycling was fully recognised (Lucas 2001; Derry et al. 2005). A large fraction of Si is recycled within ecosystems, when after plant decomposition, DSi is directly taken up by the plants again. Especially in systems with highly productive plants, large reservoirs of biogenic silica (BSi) can accumulate (Clarke 2003). Plants are not only storing Si, they can also influence weathering rates by changing equilibrium concentrations of Si (Exley 1998). When plants take up DSi, they lower DSi concentrations in the pore water of the soil and enhance weathering rates of silicates. Furthermore, respiration of plants can lead to soil CO_2 concentrations up to five times higher compared to the atmosphere (‘biological pumping’, Lucas 2001), which again increases weathering rates (Raven 2003).

1.3.2 Silica as a nutrient

Plants take up Si as silicic acid (H_4SiO_4) and store it in their cell walls (Samuels et al. 1991). Most plants take up Si passively, and increased transpiration rates or simply the plants’ progressing age will therefore lead to enhanced Si content in its leaves (Jones and Handreck 1967). Some plants, most of them monocotyledons, are able to actively take up Si. The highest concentration ever measured was attained by the bamboo *Sasa veitchii* (41% SiO_2 of dry weight; Motomura et al. 2002), but also rice, soybean, sugar cane and oat are known for high Si contents (Cornelis et al. 2011). In rice plants, two genes (LSI1=low silicon 1, LSI2 =low silicon 2) were identified to code for proteins that actively transport Si from soil solution to the plant cells (Jaenicke 2008; Ma and Yamaji 2008). The immobile agglomerations of amorphous Si ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) in the plants’ leaves are called phytoliths (Piperno and Pearsall 1998). In

general, plants can be divided in high-, intermediate- or non-accumulators of Si (Takahashi et al. 1990), depending on their mechanism to take up or to exclude Si.

Although not being essential for most plants, a sufficient Si supply to plants generally enhances their resilience to various stressors (Liang et al. 2007; Currie and Perry 2007; Cooke and Leishman 2010). The presence of phytoliths can, for instance, improve the rigidity and hardness of the plant and thus the resistance to wind and currents and against feeding damage (Schoelynck et al. 2010; Massey et al. 2009). As a physical barrier they prevent penetration of fungi and bacteria into the organism (Wiese et al. 2005). Si also plays a role in the chemical defence of plants. It affects the release of plant hormones and gene expression in the case of pathogenic attack (e.g. Samuels et al. 1991; Fauteux et al. 2006). The negative influence of heavy metals on plant growth can be reduced if Si forms complexes with toxic metal ions such as aluminium, manganese or cadmium in the soil or in the plant itself (e.g. Neumann and zur Nieden 2001; Liang et al. 2007; Vatehová et al. 2012). Si can further improve the plant's resistance against increased salinity (e.g. Matoh et al. 1986; Tahir et al. 2011), heat (e.g. Wang et al. 2005), drought stress (e.g. Hattori et al. 2005; Eneji et al. 2008) and UV-B radiation (e.g. Wen-Bin et al. 2004). Consequently, Si is contained in many agricultural fertilisers to improve plant growth and resistance to stressors (e.g. Datnoff et al. 2001). Only a few taxonomic groups of plants absolutely require Si for growth, e.g. diatoms or Equisitaceae (horsetail family; Cornelis et al. 2011). Nevertheless, Si is at least beneficial for the majority of plants. For this reason, Epstein (1999) introduced the term 'quasi-essential' element.

1.3.3 Diatoms and silica limitation

Diatoms depend on the availability of Si to synthesise their frustules (Epstein 1999). The Si content of a diatom is largely related to their life form: benthic diatoms need to be armed against physical forces and contain about five times more Si (Si:Chlorophyll *a* ratio: 14.3:1) than planktonic diatoms (Si:Chlorophyll *a* ratio: 2.8:1; Hackney et al. 2000). Taxonomically, diatoms are classified in Coscinodiscophyceae (centric diatoms), Fragilariophyceae (araphid pennates) and Bacillariophyceae (raphid pennates), but due to recent developments in phylogenetic taxonomy, it can be expected that diatom classification will change considerably in future (Round et al. 1990). At least 20,000 diatom species are known, but presumably more than a million exist (Round et al. 1990).

Almost all habitats that are sufficiently moist can be colonised by diatoms (Round et al. 1990). They are also present in creeks and the upper soil layers of salt marshes (Fig. 1.10; Pinckney and Zingmark 1993; Whitcraft et al. 2007). The golden-brown colour on the sediment surface, indicating the presence of diatoms, is caused by fucoxanthin, a photosynthetic pigment contained in diatoms (Sullivan and Currin 2000).

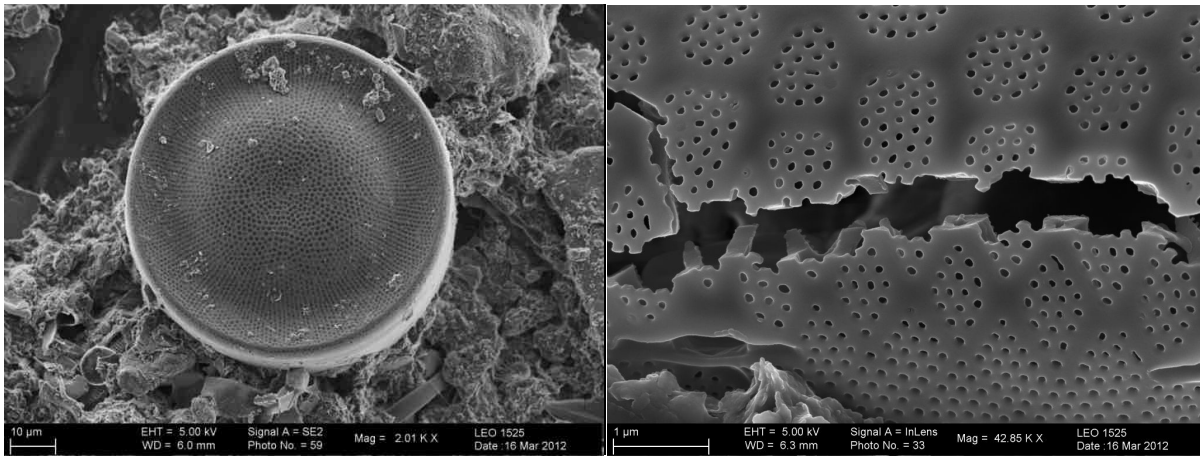


Fig. 1.10: Raster electron microscope images of diatom shells from creeks in the salt marsh Dieksanderkoog.

Diatoms fulfil a number of important functions in estuarine and marine ecosystems. As the basis of the aquatic food web, they play a key role in the productivity of the coastal zone (Admiraal 1977; Sullivan and Moncreiff 1990). Diatoms make up the major part of benthic microalgae in estuaries (Pinckney and Zingmark 1993) and are therefore the main food source for many invertebrates, which again serve as nutrition for birds, fish and mammals. Stable isotope analyses proved that the high productivity of estuaries is not directly linked to marsh plants, as it was previously thought, but to diatoms (Haines 1976; Kang et al. 2003). Benthic diatoms further act as ‘ecosystem engineers’, when they stabilise loose sediments in tidal flats or the pioneer zone of a marsh (Paterson et al. 1990). Finally, diatoms contribute significantly to biological carbon pumping in the oceans. Although only 3% of all dead diatoms sinking to the ground actually reach the sea floor (the other 97% is decomposed in the water column; van Cappellen 2003), they account for 50% of all organic carbon buried in marine sediments (Rabosky and Sorhannus 2009). Diatoms hence cause a yearly CO_2 fixation of 240 Tmol yr^{-1} (Conley 2002). In highly productive zones such as estuaries or continental shelves, Si is often a limiting factor for diatom growth (Schelske et al. 1983).

1.3.4 Silica supply from tidal freshwater marshes

In contrast to N and P, the Si concentration in rivers and oceans is not anthropogenically increased (Anderson et al. 2002; Ittekkot et al. 2006). On the contrary, the ‘artificial lake effect’, thus the enhanced sedimentation of BSi due to embankments and the construction of dams and barrages, caused a reduction of Si reaching the ocean (Humborg et al. 1997; Dürr et al. 2011). This shift in nutrient relations is stimulating the growth of algae species that are not Si-limited (Anderson et al. 2002). Especially in spring and summer, these species are able to reach high abundances in the coastal zone and sometimes even form toxic algal blooms (e.g. *Chrysochromulina* sp. or *Phaeocystis* sp.; Conley et al. 1993; Struyf et al. 2006).

Tidal freshwater marshes in estuaries are considered to be very efficient in recycling Si (Struyf et al. 2006), and adjacent ecosystems benefit from this trait. DSi and BSi reach the marsh surface with the inundation water, resulting in high DSi concentrations in the soil pore water. With a continuous stream of seepage water, DSi drains from the marsh soil into the river. Especially in times of Si limitation, this process constitutes an important additional source of DSi for diatoms in the estuary and therefore stabilises the estuary's food web. Salt marshes might contribute even more to the supply of DSi to coastal waters than tidal freshwater marshes. Due to their large extent, higher salinity and relatively strong tidal influence, salt marshes are suspected to export considerable fluxes of DSi (Struyf et al. 2006). A so far poorly regarded aspect is the influence of different management approaches on Si cycling in tidal marshes. The investigation of Si concentration, pools and fluxes in grazed and ungrazed salt marshes of the Wadden Sea coast is therefore a matter of particular interest.

1.4 Sedimentation processes

1.4.1 Sedimentation in salt marshes

Sedimentation is a geomorphological process that determines the shape of most estuarine and coastal landscapes. In the shallow Wadden Sea for instance, where ocean and tidal currents slow down, suspended sediments settle on tidal flats, beaches or salt marshes. Where currents hit an obstacle, flow velocities decrease and transported sediments can settle. Sand particles ($>63\ \mu\text{m}$) are heaviest and settle first; silt ($2-63\ \mu\text{m}$) and clay ($<2\ \mu\text{m}$) particles are lighter and are transported as suspended matter further towards the mainland. These physical characteristics determine the formation of barrier islands and sandbanks and the distribution of mudflats and salt marshes in the Wadden Sea. The deposited sand mainly originates from the bottom of the North Sea and partly from erosion of beaches and sandbanks (Wilhelmsen and Dittmann 2004). Sources of the suspended sediments are the North Sea, the Channel and rivers discharging to the Southern bight (Eisma and Kalf 1979).

For the development of salt marshes, sedimentation during tidal flooding is a crucial process. If flow conditions allow for sediment settling, mudflats can increase in elevation and the daily inundation time decreases. Biological processes contribute to a positive feedback loop in marsh formation; they play a critical role in this early stage of marsh development by increasing the accumulation of organic material and by increasing sediment stability (ten Brinke et al. 1995; Bayerl et al. 1998). Once a threshold elevation is reached, the mudflat can be colonised by pioneer salt marsh species, further enhancing sediment trapping. If colonisation continues, the salt marsh system develops a typical zonation, as outlined above. Since resuspension of sediments from a vegetated marsh surface is marginal (Braskerud 2001), the marsh surface continues to rise. Accordingly, the frequency of inundations in ageing marshes declines and so does the rate of sediment deposition. This negative feedback loop largely determines the elevation of salt marshes (French 1993).

1.4.2 Terminology

The terminology of sedimentation processes in salt marshes is complex (Fig. 1.11). In this thesis, ‘sediment deposition’ (or simply ‘sedimentation’) points to the weight of sediment settling on the marsh surface, generally expressed as a rate in $\text{kg m}^{-2} \text{yr}^{-1}$. The rate can be divided into its mineral and organic components (see chapter 7 for details). The term ‘accretion’ describes the vertical rise of the marsh’s surface (Redfield 1972). Furthermore, it is important to distinguish between accretion and ‘surface elevation change’. Both terms are usually expressed as a rate (mm yr^{-1}), but they differ in the way they are measured. Surface elevation change is determined relative to a fixed (often subsurface) datum (Cahoon et al. 1995; Nolte et al., under review). Accretion is measured in relation to a subsurface datum which is not fixed (e.g. a marker horizon; Cahoon et al. 1995). This difference is important because salt marsh soils can be subject to compaction processes and to deep subsidence. The subsurface datum used for accretion measurements often lies in between compacting soil layers; an overestimation of vertical marsh growth is therefore likely (Cahoon et al. 1995). The measurement of surface elevation change, on the contrary, is not affected by compaction processes and allows the determination of net changes. Unfortunately, the terminology of sedimentation processes is not always well-defined in the literature (Nolte et al. under review).

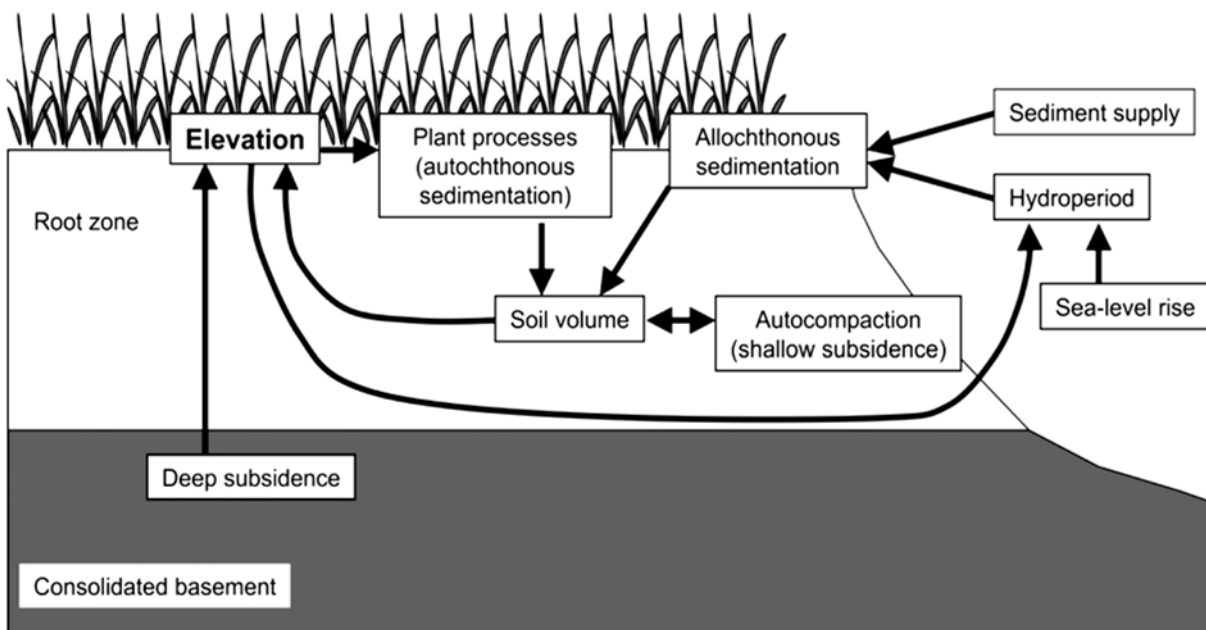


Fig. 1.11: Conceptual model of factors driving surface elevation change in a salt marsh (from French 2006, modified from USGS 1997).

In Wadden Sea salt marshes, no large differences between surface elevation change and accretion rates are expected. These marshes are situated at meso- and macrotidal coasts and are therefore primarily of allochthonous origin. In allochthonous marshes, accretion is generally driven by sediment inputs rather than by *in situ* primary productivity (Dijkema 1987). Low organic matter content in these ‘mineralogenic’

marshes increases dry bulk densities of the soil (Kolker et al. 2009). This again leads to high compaction rates already in upper soil layers and minimises compaction processes in deeper soil layers. At microtidal coasts, sediment deposition is limited, and accretion is mainly driven by high rates of plant productivity (Dijkema 1987; French 2006). Such ‘organogenic’ marshes (Kolker et al. 2009) can especially be found along North American coast lines. In a coastal marsh in Texas, for instance, the average relation between surface elevation change and accretion rate was 1:2.5 (Williams 2003). If the data we present in chapter 0 was analysed according to Williams (2003), the relation between accretion and surface elevation change is only 1:1.1 for four salt marshes at the Wadden Sea coast. This low value implies that measurements on accretion rates and on surface elevation change in Wadden Sea salt marshes can be compared with each other without causing a large bias.

1.4.3 Influencing factors

Next to the frequency of inundations, a number of further abiotic factors can influence the surface elevation change of a salt marsh. Most of these factors primarily affect the process of sediment deposition, and many of them are interrelated. Examples are: inundation duration (e.g. Donnelly and Bertness 2001); inundation height (e.g. Temmerman et al. 2005); surface elevation (e.g. van Wijnen and Bakker 2001); tidal range (e.g. Friedrichs and Perry 2001); distance to a sediment source (e.g. Temmerman et al. 2003); suspended sediment concentration in the inundation water (e.g. Childers and Day 1990); temperature (e.g. Watson 2008); flow velocities (e.g. Kozerski and Leuschner 1999); creek systems (e.g. Reed 1999); wind-wave-activity (e.g. Reed 1998); and generally the occurrence of storm surges (e.g. McKee and Cherry 2009). Factors influencing surface elevation change without directly affecting sediment deposition are for instance auto-compaction (e.g. Williams 2003), deep subsidence (e.g. Callaway et al. 1996) and soil characteristics such as organic matter content, grain size distribution or dry bulk density (e.g. Kolker et al. 2009).

Biological factors can also affect surface elevation change (Pasternack and Brush 1998). These are for instance: vegetation structure (e.g. Leonard and Croft 2006); aboveground biomass production (e.g. Morris et al. 2001, Culbertson et al. 2004); root biomass production (e.g. Callaway et al. 1996); decomposition rates (e.g. Callaway et al. 1996); and grazing by domestic or wild life animals (e.g. Andresen et al. 1990). Most of these factors are directly or indirectly influenced by salt marsh management. Even though surface elevation change is certainly driven by the abovementioned abiotic factors in the first instance, biotic factors might be especially relevant in explaining local or short term differences in surface elevation change. So far, the relevance of salt marsh management to sedimentation processes was assessed in only a limited number of studies. Most authors found significantly higher rates of accretion or surface elevation change in ungrazed compared to intensively grazed marshes (Andresen et al. 1990; Neuhaus et al. 1999; Stock et al. 2011; Suchrow et al. 2012), but the results were not always consistent along the coast (Suchrow et al. 2012). Furthermore,

it was not clarified which mechanisms explain the differences between grazed and ungrazed salt marshes.

1.4.4 Measurement of sedimentation processes

Various methods exist to analyse sedimentation processes in salt marshes. These differ not only in their target parameters (sediment deposition, accretion or surface elevation change), but also in spatial and temporal resolution. Extensive overviews of methods were given by Steiger et al. (2003), Thomas and Ridd (2004) and recently by Nolte et al. (under review). In the following, the most frequently applied approaches are presented.

Sediment deposition is generally measured by trapping sediments on rather short term scales, ranging from one single tide to several months (Nolte et al., under review). Suitable for the measurement are for instance plate-like sedimentation traps (e.g. Kozerski and Leuschner 1999; Temmerman et al. 2003). These devices consist of a plate, which can be attached to the ground, and a floatable lid, avoiding washout by rain (Fig. 1.12 A). Pasternak and Brush (1998) fixed ceramic tiles to the soil on which sediments could settle (Fig. 1.12 B). With this method, however, sediments are not protected from washout. Another approach is to place pre-weighed filters in petri-dishes on the marsh surface (e.g. Reed 1998; 1999; Fig. 1.12 C). Filters are particularly suitable to measure one or a few tides in high precision. A further method is to apply artificial turf mats on the marsh (e.g. Steiger et al. 2003; Schwartz et al. 1997). Mats have the advantage that their surface is not flat as it is the case for the above listed devices, but instead simulates some kind of vegetation structure (Fig. 1.12 D). The spatial resolution of all these methods is medium to high, depending on the number of replicates. Generally, smaller devices (e.g. filters) are easier to handle in the field and will therefore allow for a higher spatial resolution than for instance large and heavy turf mats.

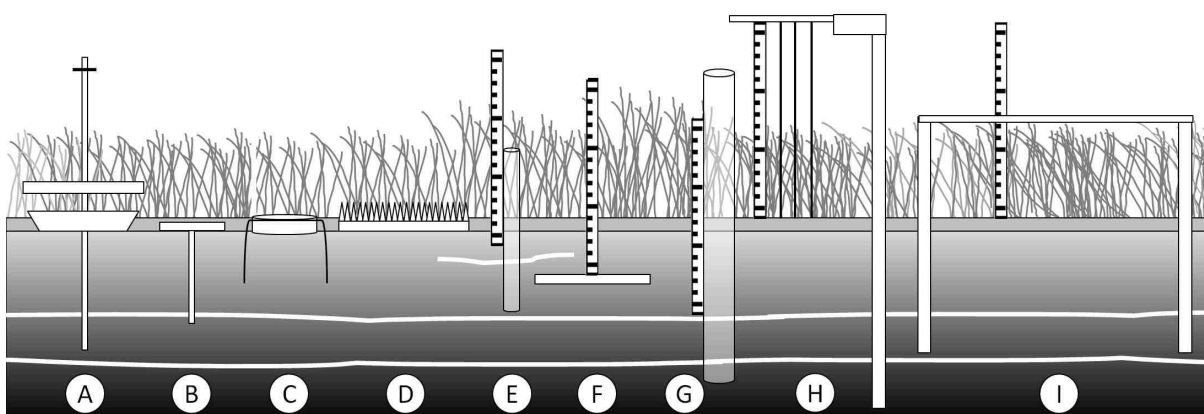


Fig. 1.12: Measurement devices for the determination of sediment deposition, accretion and surface elevation change. A=sedimentation trap; B=ceramic tile; C=filter; D=artificial turf mat; E=marker horizon; F=sediment plate; G=radionuclidic measurement; H=sedimentation-elevation table; I=sedimentation erosion bar.

Accretion rates are usually determined on medium to long term scales. One approach is, for instance, to apply an artificial marker on the soil surface (French and Spencer 1993; Harter and Mitsch 2003; Fig. 1.12 E). In subsequent years, small soil cores can be retrieved with a hand corer to detect the marker horizon in the soil. This method, however, is destructive and only a finite number of measurements can be conducted. Similarly, stable ‘marker plates’ (French and Burningham 2003) or ‘sedimentation plates’ (Nolte et al., under review; Fig. 1.12 F), made from plastics or metal, can be buried in the soil. Their disadvantage is that the soil is heavily disturbed during their fixation in the field. However, after some time of soil settlement, an unlimited number of measurements can be carried out with a thin pin.

Core sampling and dating is another approach to determine accretion rates in salt marshes (Fig. 1.12 G). This can be done by detecting the activity of radionuclides lead-210 (^{210}Pb) or caesium-137 (^{137}Cs) in the soil (DeLaune et al. 1978). Unsupported ^{210}Pb is a naturally occurring radionuclide, which is atmospherically deposited on soil surfaces everywhere in the world (McCaffrey and Thomson 1980; Kolker et al. 2009). Once deposited in a salt marsh, ^{210}Pb becomes buried under an ever increasing cover of sediments. The decay of ^{210}Pb is exponential, and if the shape of the activity curve is determined in the soil core, the age of each sampled soil depth can be calculated. This works slightly differently for ^{137}Cs dating. Nuclear emissions from bomb tests in the 1960s and incidents like Chernobyl in 1986 caused periods of high ^{137}Cs loads in the atmosphere. In sedimentary systems, such as salt marshes, surface layers from these periods can be identified because they show a peak in ^{137}Cs activity (Callaway et al. 1996). An average accretion rate can be calculated by dividing the thickness of the soil above this peak by the number of years that have past. Further detail on the ^{137}Cs dating is given in chapter 0.

As outlined above, compaction can be significant in salt marshes and should be considered when drawing conclusions from accretion rates. Especially, if a marker horizon is located close to the soil surface, it can be expected that (short to medium-term) accretion rates overestimate (long-term) vertical marsh growth as it was shown by Bartholdy et al. (2010).

Surface elevation change in itself is generally measured on medium to long term scales. An often applied method is the sedimentation erosion table (Schoot and de Jong 1982, cited in Boumans and Day 1993), which is today more widely known as surface elevation table (SET; Cahoon et al. 2000; Nolte et al., under review). With a SET, the distance from a measurement table, attached to a pole, down to the soil surface is determined with 9 metal pins (Fig. 1.12 H). A decreasing distance indicates accretion, whereas increasing values point to erosion processes. The necessity of adjusting each single pin makes it comparably time consuming to take a reading from SETs. An alternative construction is the sedimentation erosion bar (SEB; Fig. 1.12 I; van Duin et al. 1997, cited in van Wijnen and Bakker 2001) or the ‘Bridge Method’ as it was called by Perillo et al. (2003). Here, instead of a table, a bar can be at-

tached to two poles, which were driven into the soil. From this bar, a defined number of measurements are taken.

In the Schleswig-Holstein Wadden Sea National Park, for instance, 18 transects of SEBs have been installed in different salt marshes. Each SEB has 17 holes, in which a metre rule can be positioned (Stock 2011). On the contrary, the Bridge Method-SEB after Perillo et al. (2003) allows for only one measurement per pair of poles. To ensure that surface elevation change is measured and not accretion, the SET- and SEB-poles need to reach the base sand-layer or at least the depth of maximal soil compaction. A further method, often applied for long term or large scale monitoring, is levelling (Oloff et al. 1997; De Groot et al. 2011). Levelling can be carried out with a receiver and a theodolite station with known elevation sending out a laser signal (Lavine et al. 2003). A simpler, though less accurate method is differential GPS (DGPS), which uses satellite information and for which no theodolite station is needed.

1.4.5 Storm surges and sea-level rise

Especially during storm surges, large amounts of sediments are imported to salt marshes (van Wijnen and Bakker 2001). Alongside sediments, vast amounts of organic matter and elements such as Si can be imported to tidal marshes during major floods (Struyf et al. 2007). In Europe, storm induced sediment and organic matter imports are generally lower as it was frequently reported for hurricane events in North America (during hurricane Katrina in August 2005, for instance, 3 to 8 cm of sediments were deposited on a coastal marsh; McKee and Cherry 2009). Nevertheless, imports during storm surges in the Wadden Sea can contribute significantly to surface elevation change. Most studies on sedimentation processes in tidal marshes reported highest rates of sediment inputs in autumn and winter months (e.g. Reed 1989; Erchinger et al. 1996; Temmerman et al. 2003). This can be related to a higher suspended sediment concentration in the water column and to a higher wind activity (Allen 2000; Callaghan et al. 2010). However, depending on local conditions, sediment deposition can also be higher in summer than in winter as it was reported by Pastermack and Brush (1998). Bartholdy and Aagaard (2001) further point out that regularly occurring strong winds which mobilise sediments, can be more important for the yearly sediment budget of a salt marsh than single storm events.

Independently from when and how sediments are deposited, salt marsh accretion is an essential process for marshes to keep pace with sea-level rise. In the period between 1961 and 2003, global sea-level rise was on average 1.8 mm yr^{-1} (ranging from 1.3 to 2.3 mm yr^{-1}). In the period between 1993 and 2003, it accelerated to 3.1 mm yr^{-1} (ranging from 2.4 to 3.8 mm yr^{-1} ; IPCC 2007). For the Wadden Sea, an average sea-level rise for the last 50 to 100 years of $1\text{-}2 \text{ mm yr}^{-1}$ was reported (Oost et al. 2009, citing several authors). Considering only the German Bight, Wahl et al. (2011) calculated 3.6 mm yr^{-1} of relative sea-level rise, which takes subsidence into account. However, to assess the consequences of sea-level rise for coastal wetlands, it is pivotal to

also consider differences in MHT. In the last 50 to 100 years, MHT at the Wadden Sea coast increased on average 2-2.5 mm yr⁻¹ (Oost et al. 2009, citing several authors).

In contrast to salt marshes at microtidal coasts, it is believed that sites at macrotidal coasts are less endangered from a rising sea level (Friedrichs and Perry 2001). Allochthonous marshes, as they are found at macrotidal coasts are generally more frequently inundated and receive therefore higher amounts of sediments, usually outpacing sea-level rise. For this process, however, a sufficient concentration of suspended sediments in the inundation water is crucial. Although this might not be a major problem in the near future, for the long term Ahrendt (2006) predicted a declining sediment supply from the North Sea. The relation between eu- and sublittoral zones in the Wadden Sea is expected to shift to the benefit of the submerged areas (Ahrendt 2006). This will most likely have far-reaching consequences also for salt marshes in the region. Monitoring and research is therefore needed to analyse the reaction of salt marsh systems to a rising sea level and to assess whether a specific management better enables salt marshes to keep pace with sea-level rise.

1.5 Objectives of the study

The aim of the thesis was to address open questions concerning the ecosystem functions of Si cycling and sedimentation processes in salt marshes. For some of the research, the scope was extended to tidal freshwater marshes and the river continuum in general. The objectives can be summarised in three groups:

- 1) What is the role of salt marshes in coastal Si cycling? Answering this question required:
 - a. quantifying Si gross export rates from salt marshes (chapter 2);
 - b. assessing the relevance of DSi exports from salt marshes compared to rivers (chapter 4);
 - c. quantifying Si pools and fluxes in salt marshes and calculating a net budget of Si imports and exports (chapter 3); and
 - d. relating the impact of Si on tidal marsh plant communities to Si impacts in other ecosystems along the river continuum (chapter 6).
- 2) How can sedimentation processes in Wadden Sea salt marshes be characterised? Addressing this objective included:
 - e. calculating long term accretion rates (chapter 7);
 - f. measuring short term surface elevation change (box 2); and
 - g. quantifying the impact of storm surge sedimentation on Si supply (chapter 3).
- 3) What is the influence of grazing and restoration management on the Si supply to the coastal zone and on long term sedimentation processes? This question was answered by:
 - h. assessing the built-up of a vegetation Si pool in a restored tidal freshwater marsh (chapter 5);

- i. comparing Si pools, fluxes and budgets in grazed and ungrazed salt marshes (chapters 3, 3 and 5);
- j. comparing sediment deposition rates and soil compaction on grazed and ungrazed salt marshes (chapter 7).

1.6 Outline of the author's contribution

The thesis consists of six manuscripts, presented in chapters 2-7. The author of this thesis contributed to the chapters as follows:

- Writing the manuscripts for chapters 2, 3 and 7. Stefanie Nolte and the author of this thesis contributed equally to writing of chapter 7.
- Sampling, sample processing and data analysis for chapters 2, 3 and 7. Stefanie Nolte and the author of this thesis contributed equally to the sampling, sample processing and data analysis for chapter 7.
- Preparing all maps, figures and tables for chapters 2, 3 and 7. Stefanie Nolte and the author of this thesis contributed equally in creating the artwork for chapter 7.
- Co-authoring in chapters 4, 5 and 6, which included: delivering data on DSi exports from Wadden Sea salt marshes for calculations in chapter 4, gathering literature values for DSi concentrations in tidal marshes, being responsible for all text passages concerning salt marshes and biological cycling of Si and contributing to introduction, discussion and conclusion of the manuscript; rewriting parts of the manuscript for chapter 5; writing the section on “Tidal wetlands” in chapter 6; and contributing to the introduction, discussion and conclusion of the manuscript.

2

Silica export dynamics of salt marshes in the Wadden Sea area

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Estuarine, Coastal Shelf Science, under review

2.1 Abstract

In times of silica (Si) limitation, its supply from tidal marshes is important for the stability of estuarine and coastal food webs. Salt marshes are highly dynamic, grass dominated ecosystems: their large area, high salinity and location adjacent to the sea, imply that they could efficiently contribute to the buffering of Si depletion events in the coastal zone. As grazing management potentially alters vegetation and sedimentation dynamics in salt marshes, it could have an indirect impact on Si cycling in these systems. In two salt marshes of the Wadden Sea coast, concentrations of dissolved and biogenic silica (DSi and BSi) were measured in eight creeks in four seasons under different management conditions. By means of simultaneous discharge measurements, export rates were calculated. Concentrations ranged from 17 to 561 $\mu\text{mol l}^{-1}$ for DSi and from 7 to 259 $\mu\text{mol l}^{-1}$ for BSi. DSi in the seepage water was on average 338 $\mu\text{mol l}^{-1}$ and exceeded all concentrations previously reported for salt and tidal freshwater marshes. Ungrazed sites had significantly higher seepage water DSi concentrations than sites which were grazed by sheep in high densities. BSi concentrations were, in general, lower and more variable. Export rates from ungrazed sites were twice as high as from grazed salt marshes. Although differences between grazing regimes were partly explained by Si-uptake of benthic diatoms in the creeks, differences in hydrology appeared to be a superimposing factor, controlling Si exports from Wadden Sea salt marshes.

2.2 Introduction

As an essential nutrient for diatoms, silica (Si) has a key function in the food web of coastal waters (Sullivan and Moncreiff 1990). In pristine rivers, dissolved Si (DSi) is delivered to the coastal zone in excess over nutrients as N and P (Justic et al. 1995). Under conditions of eutrophication, however, it often becomes a limiting factor for diatom growth. In contrast to N or P, land-ocean Si-fluxes are not anthropogenically enhanced (Anderson et al. 2002; Ittekkot et al. 2006). On the contrary, constructional changes like embanking and damming have led to increased sedimentation of biogenic Si (BSi) incorporated in diatoms, sponges or litter of vascular plants in the river systems (Humborg et al. 2005; Beusen et al. 2009; Dürr et al. 2011). A depletion of DSi in spring and early summer, leading to limited diatom production, can cause a shift in species composition of phytoplankton communities (Heckey and Kilham 1988). As a consequence of this process, harmful algae blooms, anoxic conditions and increased water turbidity can occur. These changes constitute a disturbance of the aquatic food web by constraining the transfer of carbon to higher trophic levels (Conley et al. 1993; Smayda et al. 1997; Anderson et al. 2002).

Estuarine tidal freshwater marshes are known to be recycling surfaces of BSi, exporting relatively high amounts of DSi to the adjacent water body (Struyf et al. 2005a, 2006). BSi is deposited on the marsh surface during inundation events. It is mineralised and taken up by plants and benthic diatoms as DSi. After dieback of the vegetation, dissolution of plant BSi leads to high DSi concentrations in the soil water. DSi not taken up by plants can leach from the marsh soil and, finally, increase the concentrations in the main stream. Even if, on a yearly base, many tidal freshwater marshes trap more Si than they release, it is clear that in times of Si limitation (spring and early summer), they are acting as an additional DSi source for the estuary (Struyf et al. 2005a, 2006).

Salt marshes might contribute even more to the supply of DSi to coastal waters than tidal freshwater marshes. The increasing influence of seawater can be expected to enhance BSi dissolution rates along an estuary (Yamada and D'Elia 1984). According to Loucaides et al. (2008), higher pH and salinity are responsible for a fivefold enhancement of BSi solubility in seawater compared to freshwater conditions. Furthermore, salt marshes are often more exposed to tidal forces during storm tides than tidal freshwater marshes. This enhances the supply of nutrients to the coastal zone in general (Odum 2002) and is, therefore, also likely to increase the supply of Si. Finally, the global area covered by salt marshes is five times larger than that covered by tidal freshwater marshes (Mitsch and Gosselink 2009) and the supply to the Si limited coastal zone is more direct since salt marshes are located at the coast line. Vieillard et al. (2011) have recently shown that significant amounts of DSi can be exported from a North-American salt marsh, corroborating this hypothesis.

As in tidal freshwater marshes, the vegetation in salt marshes is dominated by grasses, which in general contain higher amounts of Si compared to most other plants

(Lanning and Eleuterius 1983; Epstein 1994). Si is taken up as monosilicic acid (H_4SiO_4) and precipitates in cell lumens, cell walls, and intercellular spaces as amorphous silicon dioxide ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), also known as opal-A or phytoliths (Jones and Handreck 1965). The solubility of this form of BSi (1.8 mmol l^{-1} at 25°C and pH 8) is up to 17 times higher than the solubility of quartz (Frayssé et al. 2006). The soil of tidal freshwater marshes, salt marshes and grasslands in general is highly enriched with phytoliths, which are the main source of pore water DSi in soils (Farmer et al. 2005). Given the fact these systems cover more than 40% of the terrestrial earth surface (Melzer et al. 2010), grasslands are likely to play an important role in the global Si cycle (Blecker et al. 2006; Borrelli et al. 2008; Melzer et al. 2010, 2011). Most grasslands are exposed to grazing, be it by wildlife or livestock. In addition, the digestion by grazers enhances local nutrient cycling (Kitchell et al. 1979; Olsen et al. 2011). However, so far only one study has identified the impact of grazing on Si cycling on the ecosystem level (Melzer et al. 2010). In temperate, annually burned grasslands, these authors found significantly larger soil BSi pools under grazed than under ungrazed sites. Plant BSi concentrations and plant BSi pools, however, did not differ between management types.

Long term grazing is known to change both biotic and abiotic conditions in salt marshes (Bakker 1985) and can consequently affect nutrient cycling. With intensive grazing, plant species composition shifts towards species less sensitive to soil compaction and to browsing and trampling by herbivores (Andresen et al. 1990; Esselink et al. 2000). During the last decades, grazing was stopped in many salt marshes at the Wadden Sea, allowing for the re-establishment of more natural dynamics in the system. Additionally, at most sites the artificial draining system was no longer maintained (Stock et al. 2005). This led to a shift towards species more typical for high marsh zones, towards taller species, towards more aboveground standing biomass, towards litter accumulation and on some marshes towards reduced species diversity (Bakker 1985; Andresen et al. 1990; Esselink et al. 2000). On many salt marshes, abandonment led to a dominance of the grass *Elymus athericus* (Bockelmann and Neuhaus 1999). Since this species is known to accumulate more Si in its tissue than many other salt marsh plants (16.0 mg g^{-1} dry weight; de Bakker et al. 1999) and at the same time produces large amounts of biomass (Groenendijk 1984), it can be hypothesised that Si cycling is indirectly affected by the changes in salt marsh management. The objective of this study was to evaluate the impact of grazing management on lateral Si exports of salt marshes in the Wadden Sea area. We aimed to answer the following questions:

- 1) Which concentrations of DSi and BSi can be observed in the creek water of salt marshes?
- 2) Which seasonal patterns occur in BSi and DSi concentrations?
- 3) How high are DSi and BSi exports?
- 4) What is the impact of salt marsh management on Si concentrations and on Si exports to the coastal zone?

2.3 Methods

2.3.1 Study sites

The study was conducted in the Schleswig-Holstein Wadden Sea National Park in Germany (Fig. 2.1). The Wadden Sea, stretching from Denmark to the Netherlands, is a tidal-flat and barrier-island system. It includes the largest coherent area of tidal flats in the temperate zone (4,700 km²) and more than 400 km² of salt marshes (Reise et al., 2010). Yearly precipitation in the region amounts to 800 mm, and long-term mean temperature is 8.2 °C (January: 0.3 °C; July: 16.2 °C; DWD, 2011).

To allow for generalisations on the role of salt marshes in silica cycling, the study took place on two distinct salt marshes. A low lying salt marsh with high flooding frequency (Sönke-Nissen-Koog) and a slightly higher elevated salt marsh (Dieksanderkoog) with decreased flooding frequency were chosen. The adjacent coastal zone has a macrotidal regime and experienced a relative sea level rise of approximately 3.6 mm yr⁻¹ from 1971 to 2008 (Wahl et al. 2011). According to a definition of Dijkema (1987) both study sites can be classified as mainland salt marshes. They are man-made landscapes, originally created for land reclamation at the beginning of the 20th century. A rectangular network of main creeks, side creeks, ditches and levees still reveals this artificial formation (see Fig. 2.1). Surface elevation is generally decreasing along a gradient from the seawall to the mudflats. However, both sites show the formation of a natural levee along the marsh edge and a local depression near the seawall. To be able to draw conclusions about the impact of management on the silica cycling, we chose salt marshes in which grazed and ungrazed conditions still coexist.

In 1924, the land-reclamation polder Sönke-Nissen-Koog (SNK) in the North of Schleswig-Holstein was embanked (Kunz and Panten 1997), and, after construction of brushwood groins, the adjacent salt marsh began to build up. The tidal range in front of the marsh is 3.4 m, with a mean high tide at +1.59 m NHN (according to German Ordnance Datum; BSH, 2010). The salt marsh extends 900 m from the seawall to the mudflats, and mean elevation of the area is +2.02 m NHN, ranging from +0.9 to +2.6 m NN. Flooding frequency is relatively high for the largest part of this lowly elevated marsh. One part of the study site is partly intensively grazed (10 sheep ha⁻¹), while another part has been ungrazed since 1988 (Kiehl 1996). The two management categories are adjacent to each other, but separated by a creek. Predominant vegetation is the *Puccinellia maritima*-type for the grazed site and the *Elymus athericus*-type for the ungrazed part of the salt marsh (according to the vegetation typology of the Trilateral Monitoring and Assessment Program: TMAP; Stock et al. 2005).

The polder Dieksanderkoog (DSK) is located in the South of Schleswig-Holstein at the outer mouth of the Elbe Estuary. It was embanked in 1935 (Kohlus 2000), and high sedimentation rates led to a quick growth of the adjacent salt marsh. Even when the maintenance of brushwood groins and ditches was stopped, the marsh continued to grow and finally reached today's area of 1,900 m from the seawall to the mudflats.

With a mean elevation of +2.11 m NHN, ranging from +1.2 to +2.8 m NHN, the marsh is slightly higher elevated than SNK. Due to this elevation difference and due to extended tidal flats in front of the marsh, which attenuate the tidal wave, flooding of the whole marsh occurs less often than in SNK. Even at spring tide, most of the area is not inundated. The tidal range of the area is 3.0 m with a mean high tide at +1.62 m NHN (BSH, 2010). Until 1992, the whole foreland was intensively grazed by sheep (Stock et al. 2005). The research for this study was carried out in an area of the marsh where a large creek divides the foreland in an ungrazed and a grazed part. The latter is dominated by the *Festuca rubra*-type, whereas on the ungrazed part, the *Elymus athericus*-type is dominant.

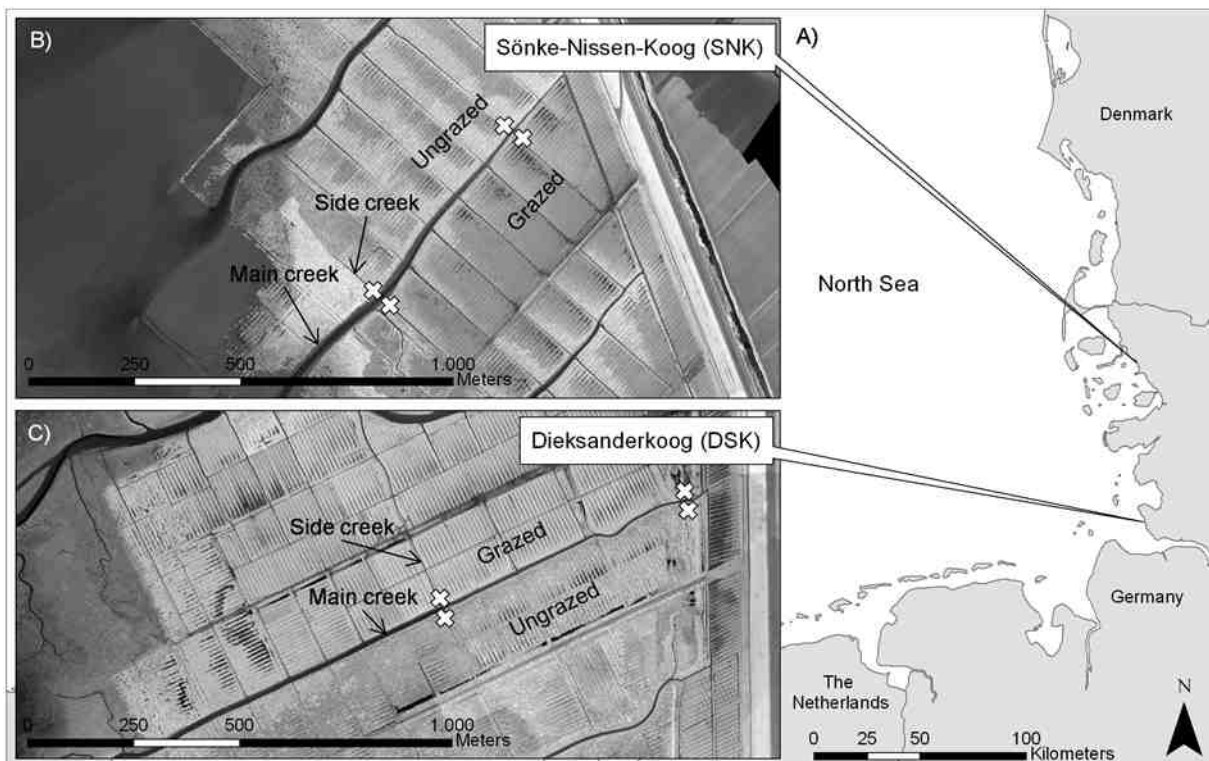


Fig. 2.1: A) Location of study sites in the German Bight. B) and C) Aerial pictures of study sites; white crosses mark the sampling locations. Base maps: Amtliche Geobasisdaten Schleswig-Holstein, © VermKatV-SH.

2.3.2 Field and laboratory methods

Between March 2010 and January 2011, creek water of the two salt marshes was collected in four sampling campaigns covering all seasons. Samples were taken simultaneously at the mouth of four side creeks over a period of ten hours (Fig. 2.1). Two of these side creeks were located in the grazed and two in the ungrazed part of the salt marshes. One grazed and one ungrazed creek were close to the seawall (“landward”), the other two were situated at a distance of approximately 600 m (“seaward”).

The sampling interval was 1 hour in the seepage water phase, when no flood water was in the creeks. Seepage water is water that leaches out of the marsh soil by gravitational force, and contributes the major part of DS_i export from tidal marshes

(Struyf et al. 2006). During bulk tide, the main inflow and outflow stage, samples were taken every half an hour at SNK. A small number of samples that could not clearly be classified as seepage water or bulk tide (intermediate samples) were excluded from analysis. At DSK, flooding frequency is low, and major inundations are rare. Here we sampled only seepage water as no bulk tide was observed during the campaigns. No heavy rainfalls or exceptional floodings of the sites had been recorded within seven days prior to the sampling campaigns.

Discharge of the seepage water was measured in summer, autumn and winter with portable weirs, buckets and stopwatches. Four measurements were carried out every half an hour. For practical reasons, no measurements were carried out in spring. Furthermore, measurements could not be carried out at the landward site in DSK during the autumn campaign (discharge too low to measure) and at the seaward, grazed site in SNK during the winter campaign (broken weir). In both cases, discharge values were estimated based on the relative differences observed in the other creeks where discharge measurements were performed during all sampling campaigns.

To estimate creek surface area, width and length of the creeks were measured. Soil bulk density samples were taken at four locations and in three depths for each marsh with steel cylinders with a volume of 100 ml. Furthermore, depth to ground water table and thickness of litter layer were noted.

Water samples were transported to the lab at 4 °C and filtered over 0.45 µm nitrocellulose filters within 24 hours of sampling. Filters were weighed before and after filtering to determine the concentration of suspended particulate matter (SPM) in the samples. Conductivity and pH were determined with standard electrodes, and DSi analysis was carried out photometrically (Hansen and Koroleff 1999). For BSi analysis, filters were dried in the oven at 50 °C and digested in 30 ml of 0.1 M Na₂CO₃ in a shaking water bath at 80 °C (Struyf et al. 2006). After 1, 2 and 3 hours subsamples were taken and analysed with an ICP-OES (iCAP 6300 Duo, © Thermo Scientific). To correct for the amount of Si resulting from mineral dissolution, the Si 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 content (DeMaster 1981). Soil bulk density was determined by weighing soil samples after drying to constant weight at 105 °C.

2.3.3 Calculation of export rates

To allow for conclusions on Si exports, discharge and Si concentrations were related to the catchment area of each creek. By using contour lines as a proxy for isopiestic lines, creek catchments were determined. The catchments were not verified by additional groundwater level measurements but are assumed to be reliable thanks to a very level surface and a regular arrangement of drainage creeks and ditches. 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 duration of the bulk tidal phase was therefore not subtracted when daily export

rates were calculated. Average discharge value per sampled seepage water phase was calculated, multiplied by DSi and BSi concentrations and divided by catchment area.

To test for differences between management categories (grazed/ungrazed), sampling location (seaward/landward) and site (SNK/DSK) the ‘two sampled t-test for homogeneous variances’ and the ‘two sampled t-test for heterogeneous variances’ were used. If necessary, data was transformed before applying the test. If no normal distribution could be reached, a Mann-Whitney-U-Test was performed instead. To detect differences between vegetation types (see tab. 1), a one-way analysis of variance (ANOVA) was performed. For the subsequent pairwise comparison, a Tamhane-Test for heterogeneous variances was used. The relation of DSi and BSi concentrations to conductivity, pH and suspended matter concentration of the water samples were described with Pearson’s correlation coefficient r_p and with Spearman’s correlation coefficient r_s . To describe the relation between the creek surface area and DSi and BSi concentrations, a linear regression was applied. All statistical analyses were carried out in PASW 18 (IBM SPSS inc. 2010). The symbol “ \pm ” indicates standard deviation.

Tab. 2.1: Key parameters of sampled creek catchments.

Catchment	Dominant vegetation type	Mean elevation	Area	Mean discharge	Creek surface	Mean depth to water table (Jan. 2011)	Mean litter layer (Aug. 2009)	Mean bulk density
		+m NN	m ²	ml day ⁻¹ m ⁻²	m ²	cm	cm	g cm ⁻³
Dieksanderkoog (DSK)								
grazed						33	0.6	1.17
landwards	<i>Festuca rubra</i>	1.95	32,156	14	255			
seawards	<i>Festuca rubra</i>	2.02	31,537	121	168			
ungrazed						18	4.8	1.16
landwards	<i>Elymus athericus</i>	2.05	17,829	471	198			
seawards	<i>Elymus athericus</i>	2.07	30,928	454	283			
Sönke-Nissen-Koog (SNK)								
grazed						11	2.3	0.94
landwards	<i>Puccinellia maritima</i>	1.91	25,132	410	1225			
seawards	<i>Atriplex portulacoides</i>	1.96	23,046	780	981			
ungrazed						20	3.2	0.98
landwards	<i>Elymus athericus</i>	2.06	8,505	704	166			
seawards	<i>Elymus athericus</i>	2.10	9,929	746	195			

2.4 Results

2.4.1 DSi and BSi concentrations

DSi concentrations ranged from 17 to 561 $\mu\text{mol l}^{-1}$ with large differences between bulk tide and seepage water (Fig. 2.2 and Fig. 2.3). In seepage water, DSi concentrations averaged at $338 \pm 112 \mu\text{mol l}^{-1}$. During bulk tide, DSi concentrations were significantly lower: on average $99 \pm 75 \mu\text{mol l}^{-1}$ ($T=20.9$; $p<0.001$; $N=311$). Mean DSi concentrations in the seepage water were significantly lower seaward than landward ($Z=-2.66$; $p<0.01$; $N=260$), and they were nearly equal for SNK and DSK.

For BSi concentrations, no difference between the tidal phases was observed (Fig. 2.2). Concentrations were on average $50 \pm 43 \mu\text{mol l}^{-1}$ in the seepage water and

$55 \pm 32 \mu\text{mol l}^{-1}$ in the bulk tide. In general, BSi values were more variable than DSi concentrations and peak values were found in both seepage water and bulk tide samples (Fig. 2.3, Fig. 2.4). Mean BSi concentrations in the seepage water were nearly equal for seaward and landward sites and were significantly lower for DSK than for SNK ($Z=-2.44$; $p<0.01$; $N=182$).

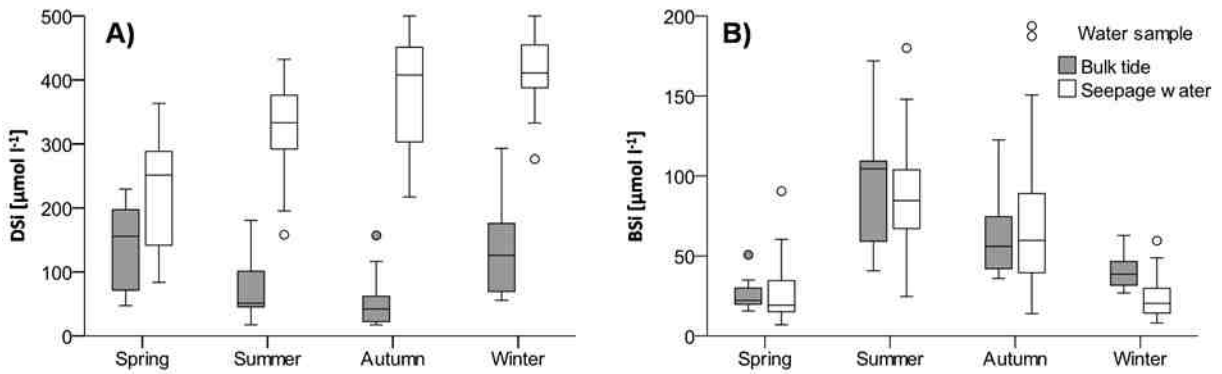


Fig. 2.2: Concentrations of DSi (A) and BSi (B) in bulk tide and seepage water phase per season on both salt marshes. For sampling dates see Fig. 2.3. Error bars: standard deviation, box: 25, 50 and 75%-quantiles, circle: outliers (if distance from box > 1.5fold box height).

Dissolved silica (DSi) concentration

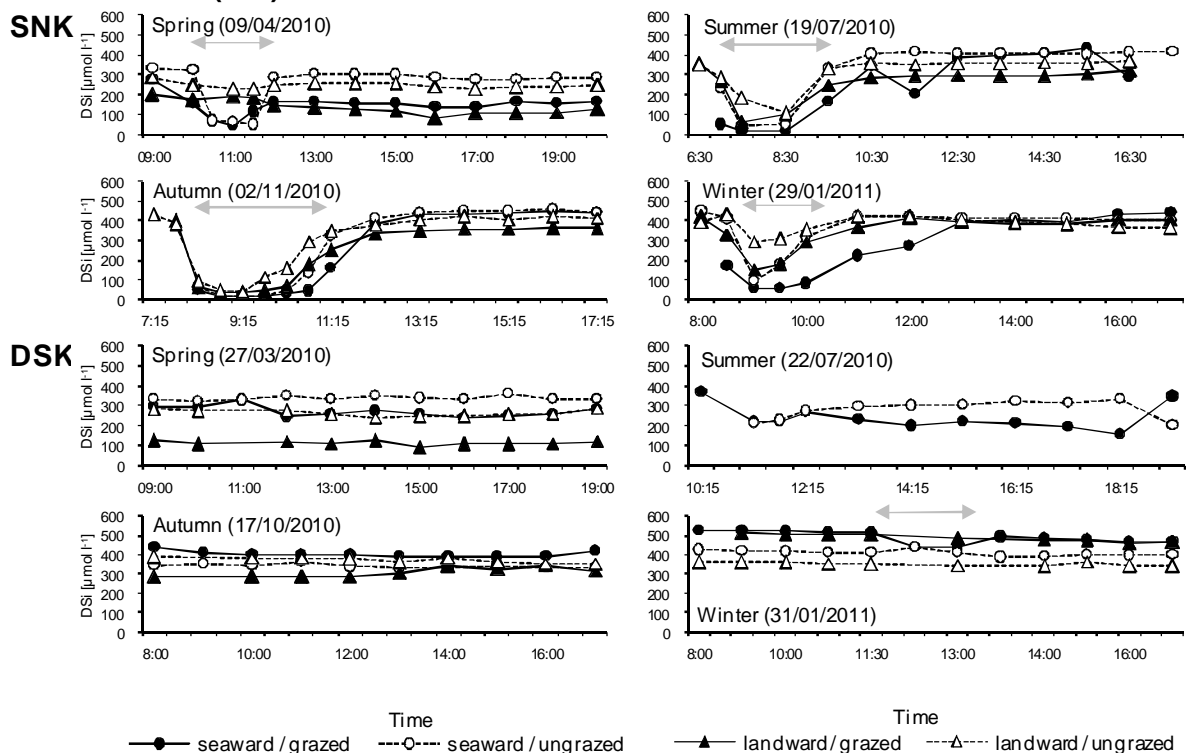


Fig. 2.3: Seasonal semidiurnal cycles of DSi concentrations at Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK). Grey arrows indicate duration of the bulk phase (i.e. the time period when flood water is present in the creek). An overview of mean DSi and BSi concentrations and exports, conductivity and pH can be seen in Appendix 2.1.

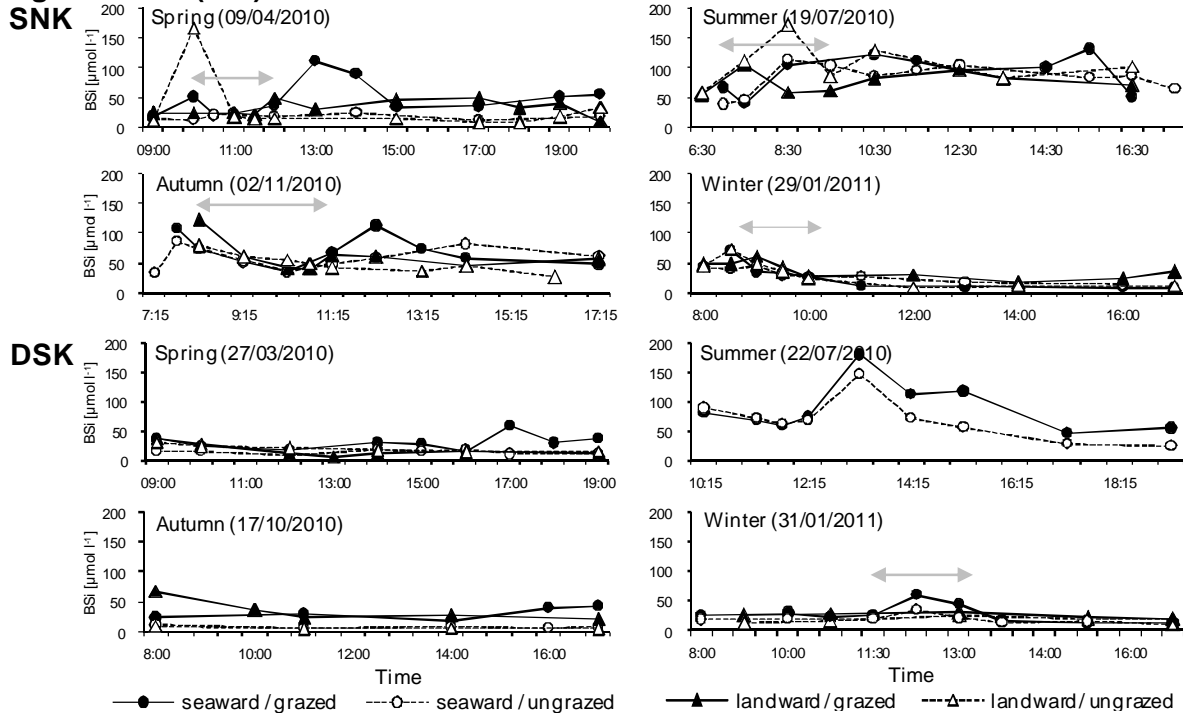
Biogenic silica (BSi) concentration

Fig. 2.4: Seasonal semidiurnal cycles of BSi concentrations at Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK). Grey arrows indicate duration of the bulk phase (i.e. the time period when flood water is present in the creek). An overview of mean DSi and BSi concentrations and exports, conductivity and pH can be seen in Appendix 2.1.

2.4.2 Seasonality of concentrations

The seasonal patterns of both DSi and BSi concentrations were similar on the two marshes (Fig. 2.3, Fig. 2.4). DSi concentrations during the seepage water phase increased in the course of the year from lowest mean values in spring ($228 \mu\text{mol l}^{-1}$) to highest in winter ($418 \mu\text{mol l}^{-1}$). This pattern was nearly reversed for the bulk tide. Here, lowest mean values were found for autumn ($50 \mu\text{mol l}^{-1}$) and highest values for spring ($139 \mu\text{mol l}^{-1}$). As mentioned above, bulk tide was only sampled at SNK.

BSi showed nearly the same seasonal pattern in both seepage water and bulk tide: Both marshes had low average BSi concentrations in spring (seepage water: $27 \mu\text{mol l}^{-1}$; bulk tide: $26 \mu\text{mol l}^{-1}$) and reached a peak in summer (seepage water: $88 \mu\text{mol l}^{-1}$; bulk tide: $91 \mu\text{mol l}^{-1}$).

2.4.3 Impact of management on concentrations

Salt marsh management had an effect on DSi concentrations in the seepage water (Fig. 2.5). Taking all sampling campaigns on both marshes into account, concentrations were significantly lower in seepage water from grazed compared to ungrazed sites (on average 303 ± 81 and $371 \pm 128 \mu\text{mol l}^{-1}$, respectively; $T=-5.19$; $p<0.001$; $N=260$). For BSi concentrations, differences between grazed and ungrazed sites were not significant (on average 55 ± 48 and $43 \pm 33 \mu\text{mol l}^{-1}$, respectively). Differences between the two marshes were more complex if patterns were discerned seasonally.

At SNK, the difference between the grazing regimes was strongest in spring, when DSi values on ungrazed sites were almost twice as high as values on grazed sites ($T=-11.22$; $p<0.001$; $N=39$). In winter, concentration differences between the grazing regimes levelled off and were not significant. For BSi, a significant difference between grazed and ungrazed sites occurred in spring as well (higher concentrations on grazed site; $T=4.44$; $p<0.001$; $N=27$). In all other seasons, only a tendency of higher values for the grazed sites was found for BSi at SNK.

At DSK, differences in DSi concentrations between grazed and ungrazed sites were even more evident than for SNK and significant in all seasons (spring: $Z=-3.94$; $p<0.001$; $N=40$; summer: $T=-2.43$; $p<0.05$; $N=16$; autumn: $Z=-4.42$; $p<0.001$; $N=27$; winter: $T=11.86$; $p<0.001$; $N=43$). The largest difference occurred in autumn, when concentrations on the ungrazed site were, on average, twice as high as on the grazed one ($539 \mu\text{mol l}^{-1}$ and $246 \mu\text{mol l}^{-1}$ respectively). Different from SNK, the pattern switched in winter and concentrations were higher on grazed sites. Again, for BSi the pattern was less obvious, but a tendency of higher values on the grazed area was observed.

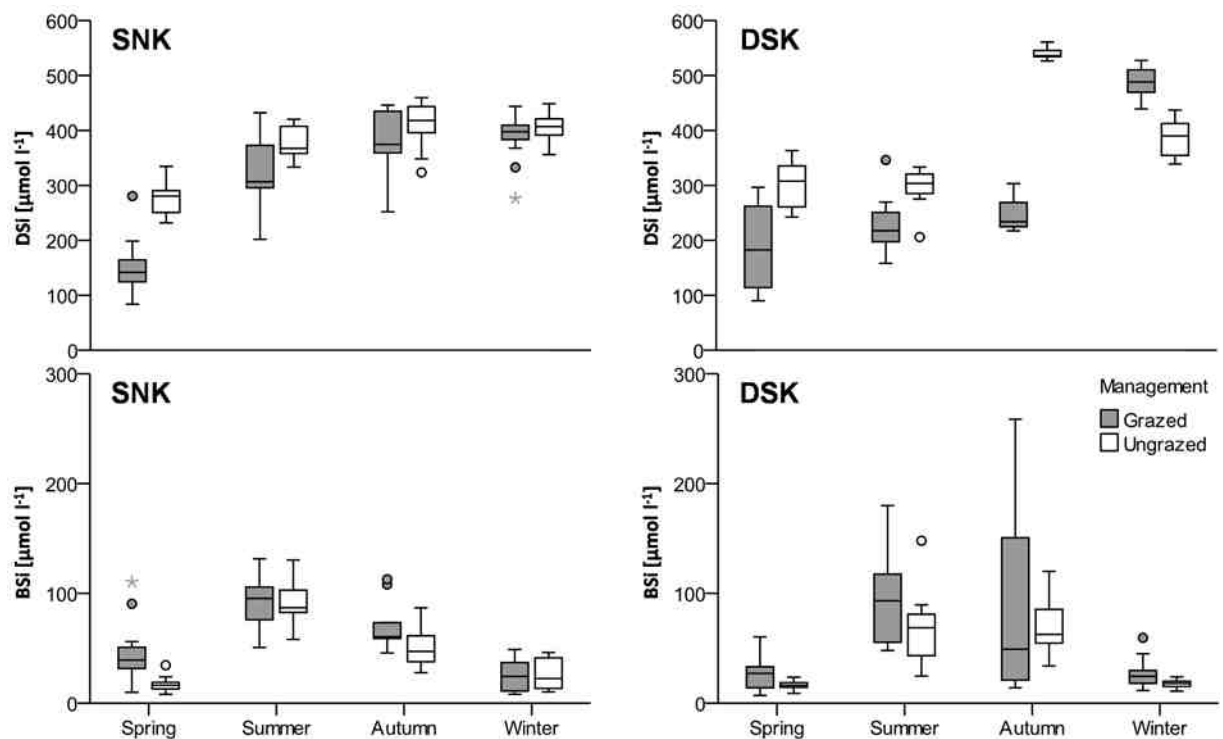


Fig. 2.5: DSi and BSi concentrations in the seepage water of Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK). Error bars: standard deviation, box: 25, 50 and 75%-quantiles, circle: outliers (if distance from box > 1.5 fold box height); stars: extreme values (if distance from box > 3 fold box height). For sampling dates see Fig. 2.3.

DSi concentrations in the seepage water were negatively correlated with conductivity ($r_s=-0.24$; $p<0.001$; $N=240$), which was, in summer, lower on ungrazed sites ($Z=-2.95$; $p<0.01$; $N=49$). Furthermore, in spring DSi concentrations showed a negative correlation with creek surface area ($r_s=-0.36$; $p<0.01$; $N=79$). BSi concentrations

in the seepage water were positively correlated with conductivity ($r_s=0.39$; $p<0.001$; $N=170$) and with SPM ($r_s=0.89$; $p<0.001$; $N=239$).

DSi concentration in catchments dominated by the *Elymus athericus*-vegetation type were significantly higher than in catchments dominated by the *Puccinellia maritima*-type ($F=14.59$; $p<0.001$; $N=221$). For BSi no differences between the dominant vegetation types was discovered.

2.4.4 DSi and BSi exports

The average discharge of all ungrazed sites ($605 \pm 421 \text{ ml m}^{-2} \text{ day}^{-1}$) exceeded the average of all grazed sites ($360 \pm 389 \text{ ml m}^{-2} \text{ day}^{-1}$). However, the difference was not significant. Differences between the two marshes were significant: On SNK, discharge was twice as high ($660 \pm 348 \text{ ml m}^{-2} \text{ day}^{-1}$) as on DSK ($269 \pm 401 \text{ ml m}^{-2} \text{ day}^{-1}$; $Z=-2.18$; $p<0.05$; $N=22$). However, variation in the data was very high in both cases.

DSi and BSi export rates were significantly higher for SNK than for DSK in all seasons (Fig. 2.6): DSi exports from SNK were on average $255 \pm 143 \mu\text{mol m}^{-2} \text{ day}^{-1}$ and from DSK $136 \pm 160 \mu\text{mol m}^{-2} \text{ day}^{-1}$ ($Z=-5.30$; $p<0.001$; $N=181$). BSi exports from SNK were on average $37 \pm 27 \mu\text{mol m}^{-2} \text{ day}^{-1}$ and from DSK $8 \pm 8 \mu\text{mol m}^{-2} \text{ day}^{-1}$ ($Z=-7.09$; $p<0.001$; $N=125$).

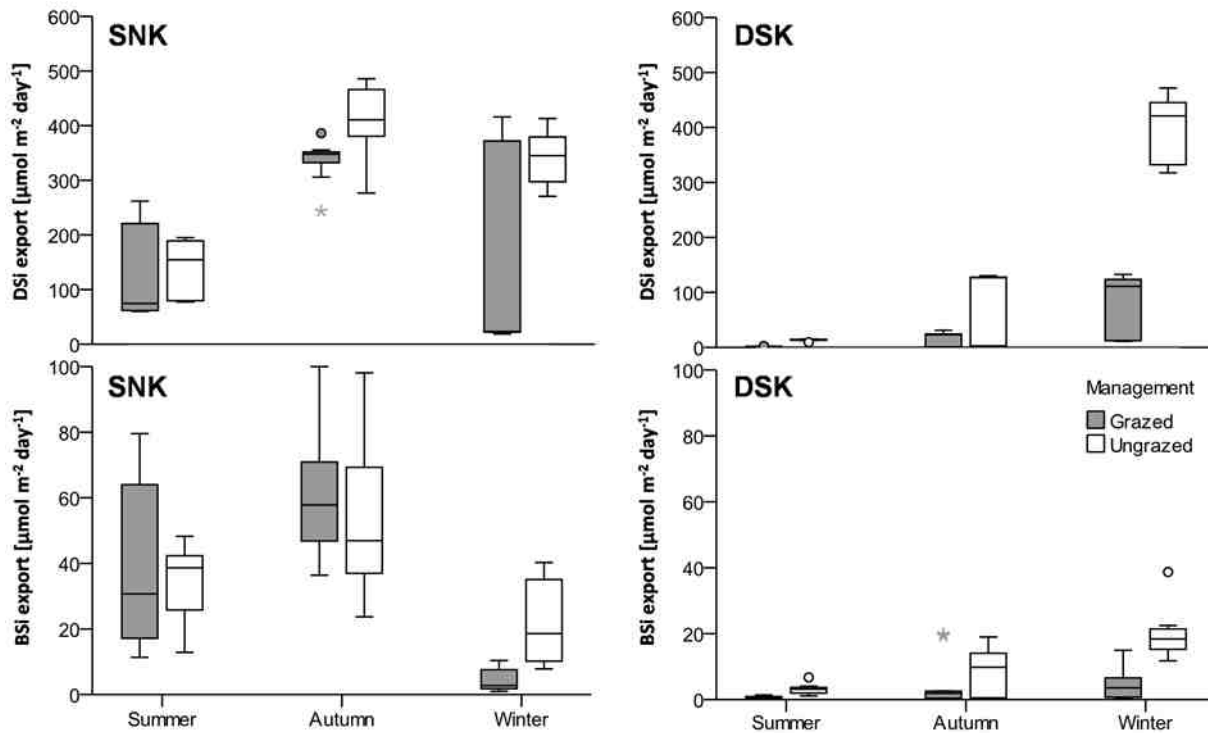


Fig. 2.6: DSi and BSi exports (concentrations in seepage water related to discharge, catchment area and time). Error bars: standard deviation, box: 25, 50 and 75%-quantiles, circle: outliers (if distance from box > 1.5fold box height); stars: extreme values (if distance from box > threefold box height). For sampling dates see Fig. 2.3.

2.4.5 Seasonality of exports

The seasonal patterns of the exports did not follow the patterns observed for the concentrations. Instead of a steady increase throughout the year, average DSi exports at SNK were low in summer ($135 \pm 69 \mu\text{mol m}^{-2} \text{day}^{-1}$), intermediate in winter ($258 \pm 153 \mu\text{mol m}^{-2} \text{day}^{-1}$) and highest in autumn ($379 \pm 60 \mu\text{mol m}^{-2} \text{day}^{-1}$). A similar pattern was observed for BSi, with low values for summer and winter (37 ± 21 and $13 \pm 13 \mu\text{mol m}^{-2} \text{day}^{-1}$, respectively; Fig. 2.6) and maximum exports in autumn ($60 \pm 26 \mu\text{mol m}^{-2} \text{day}^{-1}$). At DSK, the average DSi export showed the same gradual increase throughout the year as was seen in the concentrations. They were lowest in summer ($8 \pm 6 \mu\text{mol m}^{-2} \text{day}^{-1}$) and highest in winter ($237 \pm 169 \mu\text{mol m}^{-2} \text{day}^{-1}$). BSi exports followed the same pattern, being low in summer ($2 \pm 2 \mu\text{mol m}^{-2} \text{day}^{-1}$) and reaching a maximum in winter ($12 \pm 9 \mu\text{mol m}^{-2} \text{day}^{-1}$).

2.4.6 Impact of management on exports

For exports, the differences between the management regimes become even more pronounced than for concentrations. On SNK, DSi exports from ungrazed sites exceeded those from grazed sites by 42% ($Z=-3.34$; $p<0.01$; $N=95$); BSi exports however, were nearly equal for both management regimes (Fig. 2.6). At DSK, DSi exports from ungrazed sites were 440% higher than from grazed sites ($Z=-5.04$; $p<0.001$; $N=86$) and BSi exports were 220% higher ($Z=-3.85$; $p<0.001$; $N=65$).

2.5 Discussion

2.5.1 DSi and BSi concentrations

During the whole year, the investigated Wadden Sea salt marshes exported DSi to the coastal zone. The DSi concentrations in the seepage water (annual average $325 \pm 70 \mu\text{mol l}^{-1}$) were four times higher than the mean DSi content in European rivers ($93 \mu\text{mol l}^{-1}$; Dürr et al. 2011). To our knowledge, these concentrations exceed all values reported for salt marshes hitherto reported; average concentrations in the seepage water of salt marshes in North America ($253 \mu\text{mol l}^{-1}$ in Gardner, 1975; $55 \mu\text{mol l}^{-1}$ in Vieillard et al. 2011) and Belgium ($219 \pm 39 \mu\text{mol l}^{-1}$; Appendix 2.2) and in the outflow of a recently restored salt marsh in France ($70\text{-}140 \mu\text{mol l}^{-1}$; Struyf et al. 2006) were all lower. Concentrations in discharge water from other grass-dominated systems with comparable mean annual temperature and precipitation, like a tidal freshwater marsh ($250\text{-}310 \mu\text{mol l}^{-1}$; Struyf et al. 2005a) or a mixed grass steppe ($303 \pm 12 \mu\text{mol l}^{-1}$; Blecker et al., 2006) were slightly lower as well. Also, the average BSi content in the seepage water ($50 \pm 43 \mu\text{mol l}^{-1}$) surpasses values presented for other salt and tidal freshwater marshes ($9 \mu\text{mol l}^{-1}$ in Vieillard et al. 2011; $14\text{-}32 \mu\text{mol l}^{-1}$ in Struyf et al. 2006).

On a yearly base, our two study sites had nearly the same Si concentrations in the seepage water. However, we found spatial differences within each marsh: values were always higher at the seaward sites than at the landward sites (Fig. 2.1). This is prob-

ably due to higher import rates of DSi and BSi, caused by more frequent and longer-lasting inundations near the sea. Struyf et al. (2009) ascribed increasing Si concentrations in the soil towards a river to increased BSi input with suspended matter in inundation water.

2.5.2 Seasonality of concentrations

Silica concentrations in coastal waters follow a strong seasonal pattern. In spring and summer, DSi values in coastal waters can drop below the detection limit, mainly due to diatom uptake (Egge and Asknes 1992). Consequently, the seasonal behaviour of possible Si sources is of high relevance. In all seasons, DSi and BSi concentrations in outgoing seepage water were higher than in incoming bulk tide (average ratio of seepage water to bulk tide concentration: 5:1). In tidal freshwater marshes, such concentration differences only occurred in a few months in spring and summer; in the rest of the year, concentrations were similar in both ingoing and outgoing waters (Struyf et al. 2006). This implies that the investigated salt marshes probably exceed tidal freshwater marshes in their capacity as BSi recyclers.

Biological activity is low in winter, and DSi uptake by diatoms can be assumed to be negligible (Colijn and Dijkema 1981). Seepage water DSi and BSi concentrations measured in winter can, therefore, be regarded as ‘baseline value’, reflecting the export potential of the sites. For SNK, this implies that the potential to export DSi and BSi is equal for both grazed and ungrazed sites (Fig. 2.6). For DSK, this only holds true for BSi. The winter DSi concentrations were unexpectedly lower on the ungrazed site than on the grazed site. We do not have a coherent explanation for this difference. For the rest of the year, the pattern was reversed and, especially, in autumn, concentrations on the ungrazed sites by far exceeded those on the grazed site. Hypothetically, this could be explained by quick mineralisation of plant material under well aerated conditions (Dahl 2000), owed to the higher sand content and thicker litter layers of *Elymus athericus* at DSK compared to SNK.

2.5.3 DSi uptake by benthic diatoms

Fulweiler and Nixon (2005) suggested the uptake by terrestrial vegetation as the driving force behind the spring decrease of stream DSi in a forested catchment. Diatoms are known for their ability to regulate nutrient fluxes across the sediment water interface as well (Sigmon and Cahoon 1997; Bartoli et al. 2003) and might have an impact on DSi concentrations in salt marsh creeks. Benthic diatoms can occur in high densities in intertidal areas (Colijn and Dijkema 1981).

During a supplementary measurement in March 2011, we observed a decrease of seepage water DSi concentrations in the main creek from sunrise to midday. During the first four hours, DSi concentrations decreased linearly by $20 \mu\text{mol l}^{-1} \text{h}^{-1}$ ($R^2 = 0.99$) from 349 to 287 $\mu\text{mol l}^{-1}$ (Weiss et al. 2012) and stayed at this low level until sunset, when concentrations started to increase again. Dissolved oxygen was negatively correlated to DSi concentrations during the day ($r_s=0.95$; $p<0.001$; $N=12$). This

observation suggests that the microphytobenthos which populates the creek surface is able to regulate DSi concentrations during the seepage phase. The negative correlation between DSi concentrations in seepage water and the creek surface supports the hypothesis of DSi uptake by diatoms in maintained, broad creeks.

The creeks on the ungrazed sites are not only narrow and steep, they are also shaded by a dense *Elymus athericus* cover growing at their edges. Shade has a negative influence on the density and the growth of benthic diatoms: Despite the fact that DSi uptake and photosynthesis are uncoupled in diatoms (Brzezinski 1992; Claquin et al. 2002), light availability seems to affect their DSi uptake (Bartoli et al. 2003; Leynaert et al. 2011). The creeks on the grazed sites are broader, resulting in better light conditions and a higher surface area which can be populated by diatom mats. The fact that the seepage water has already covered a distance up to 260 m in the creek channel before it was sampled at the mouth of the side creeks ensures a sufficiently long reaction time between diatoms and seepage water to alter the DSi concentrations.

2.5.4 Impact of management on concentrations

By altering species composition and vegetation structure, management can have an indirect impact on the silica cycling of an ecosystem. Different plant species contain different amounts of silica, with highest contents generally reported for grasses (1-50 mg g⁻¹ dry weight), which contain more Si than most dicotyledons (0-1 mg g⁻¹ dry weight; Epstein, 1994). The soil under grass-dominated ecosystems is often highly enriched with phytoliths, which control the DSi content in the soil pore water (Miretzky et al. 2001; Farmer et al. 2005; Borrelli et al. 2010). In our study, the influence of phytoliths is supported by the fact that mean seepage water DSi concentration (338 $\mu\text{mol l}^{-1}$) corresponds very closely to equilibrium concentrations typical for grass phytoliths (approx. 360 $\mu\text{mol l}^{-1}$; Bartoli and Wilding 1980).

If soil water concentrations are driven by equilibria, this implies that DSi uptake by plants will enhance Si mobilisation from the soil (Exley 1998). *Elymus athericus* is known for its high Si content – in our study site it had the highest content (12.1 mg g⁻¹ dry weight) out of five analysed typical salt marsh species (Appendix 2.3). The plant is, furthermore, highly productive compared to other salt marsh plant species (Valéry et al. 2004) and is, therefore, likely enhancing BSi dissolution by taking up a considerable amount of DSi from the soil pore water.

Higher bulk densities caused by trampling can lead to a smaller coefficient of permeability and, consequently, longer retention times of pore and ground water (Tate et al. 2004). In contrast to our expectations, we did not observe significant differences in mean soil bulk density between the grazed and the ungrazed sites. We assume that the time of abandonment was not long enough to induce such differences in the soil structure. By enhancing evaporation, grazing can further lead to increased soil water salinities (Srivastava and Jefferies 1996; Yu and Chmura 2010) and pH-value (Binkley 2003). These factors are known to increase the solubility of silica (Frayse et al. 2006; Loucaides et al. 2008). In summer, conductivity as a proxy for salinity was in-

deed higher in the seepage water of grazed sites. However, it is not clear if these higher salinities led to increased dissolution of Si from the soil. On the contrary, DSi concentrations in the seepage water were negatively correlated with conductivity. This can be explained by the above mentioned effect of benthic diatoms on DSi concentration in creeks of the grazed sites. Seepage water pH did not differ between grazed and ungrazed sites. However, it was approximately one pH unit higher than in soil water in tidal freshwater marshes at the river Elbe (median pH 7.9 in near surface groundwater near Wedel; IFB, 2006), which can generally increase the solubility of phytoliths by approximately 5% (Fraysse et al. 2006).

Not only the effects of grazing, but also the grazing animal itself might play a role in silica cycling. Bidle and Azam (1999) found that the removal of organic coatings from diatom frustules accelerates their mineralisation. A similar mechanism is conceivable if plant tissue around phytoliths is removed during gut passage, although the phytolith itself will stay almost unaffected by the digestion process (Jones and Handreck, 1965).

2.5.5 Silica exports

Although it is essential to consider Si concentrations, as they reflect the export potential of a site, total Si exports are at least equally important when evaluating the role of salt marshes in coastal Si cycling. For this purpose, hydrology has to be accounted for. Hydrology has an important influence on Si cycling in ecosystems (Struyf and Conley 2009). Congruently, discharge per area appeared as a superimposing factor in the present study: exports generally increased with increasing discharge. The higher discharge rates consequently lead to higher DSi and BSi exports on SNK compared to DSK, even though annual average concentrations were nearly the same at both sites.

The variation in the discharge data set was relatively large; probably because it was measured in three different seasons with different discharge characteristics. Still, it was obvious that there was a clear difference between differently managed sites: With only two exceptions, discharge rates on ungrazed sites exceeded those on grazed sites in all sampling campaigns. The question may arise, how it is possible that the discharge of two adjacent sites can differ if the meteorological and abiotic conditions, such as soil structure, grain size and relief, are similar. The main differences between the sites are vegetation cover and creek structure. Thick litter layers on grasslands are known to increase the residence time of rain and inundation water considerably (Naeth et al. 1991; Facelli and Pickett 1991). The intensively grazed part of the marsh did not have any litter layer at all, whereas on the ungrazed sites litter accumulated to up to 10 cm. Due to this litter layer, discharge is likely to be retarded on ungrazed sites. Furthermore, already at the beginning of the 1990s, the maintenance of the drainage system was ceased on the ungrazed sites, leading to an additional retention effect. Five days after a storm surge in November 2010 (2 m above average high tide), the discharge from the ungrazed site at DSK was still remarkably high, whereas

the inundation water on the grazed site had already drained completely (F. Müller, personal observation). This litter-induced ‘sponge-effect’ on the ungrazed site allows more inundation and rain water to percolate into the soil and to become enriched with DSi in the soil. Runoff water from grazed sites, on the other hand, is not retained by vegetation and litter, and is more exported in pulses.

This might explain both the higher concentrations and export fluxes of DSi from the ungrazed sites compared to grazed sites. Longer residence time could increase mobilisation of DSi into the soil water eventually seeping out, adding to the effect of decreasing DSi concentrations in grazed creeks due to diatom mats. For BSi, the superimposing effect of hydrology actually switches the observations; in contrast to concentrations, the export fluxes are higher from ungrazed sites (at DSK) or equal for both management regimes (at SNK). However, we should emphasise that, by not measuring export pulses (for example after storm tides), we might underestimate DSi and BSi exports from grazed sites.

Besides enhancing DSi exports, the thick litter layer of *Elymus athericus* might also constitute a sink for BSi. Valéry et al. (2004) described decreased carbon fluxes from the marsh due to higher trapping and burial rates related to a dominance of *Elymus athericus*. An analogous pattern is conceivable for silica. This would imply that, at their current development state, the investigated ungrazed salt marshes top the grazed marshes in both being a sink for BSi and in being a source for DSi. However, the burial function cannot be generalised. It largely depends on sedimentation conditions, like frequency and duration of flooding events and the amount of sediment in the water column.

Our study underlines the importance of considering not only DSi but also BSi in Si export studies. Blecker et al. (2006) considered BSi exports from North American grasslands as negligible and did not measure it. However, in agreement with Grady (2007), we oppose this opinion since BSi exports made up 11% of the total Si exports and were probably even higher since pulse events, during which diatoms may be flushed from the marsh surface (Colijn and Dijkema 1981), were not covered. On a North American salt marsh, BSi exports at ebb tide made up 20% of the total Si exports (Vieillard et al. 2011) and in European first-order river basins as much as 40% (Smis et al. 2011). BSi should, therefore, not be neglected in future budget studies.

Although the DSi and BSi concentrations in the seepage water of SNK and DSK differed in some of the investigated seasons, the annual average was not significantly different between the two sites. This indicates that the observed concentrations are not attributed to special features of one of the marshes, but are probably valid for many salt marshes with a comparable history of development. The determining factor for Si exports is the hydrological status of a marsh, which can be influenced by inundation patterns, connectivity to groundwater reservoirs and vegetation structure.

2.6 Conclusion

Grazing management had a strong influence on concentrations of DSi and BSi in the seepage water of the two salt marshes and an even stronger influence on export rates. DSi concentrations, for instance, were 23% higher on ungrazed sites compared to grazed sites; export of DSi in the seepage water of ungrazed sites was 110% higher. BSi exports, which were almost one magnitude lower than DSi exports, did not differ significantly between the management types. In figure 2.7 we present a conceptual model of the observed and assumed relationships between compartments and processes that influenced Si export rates on grazed and ungrazed sites of the investigated salt marshes.

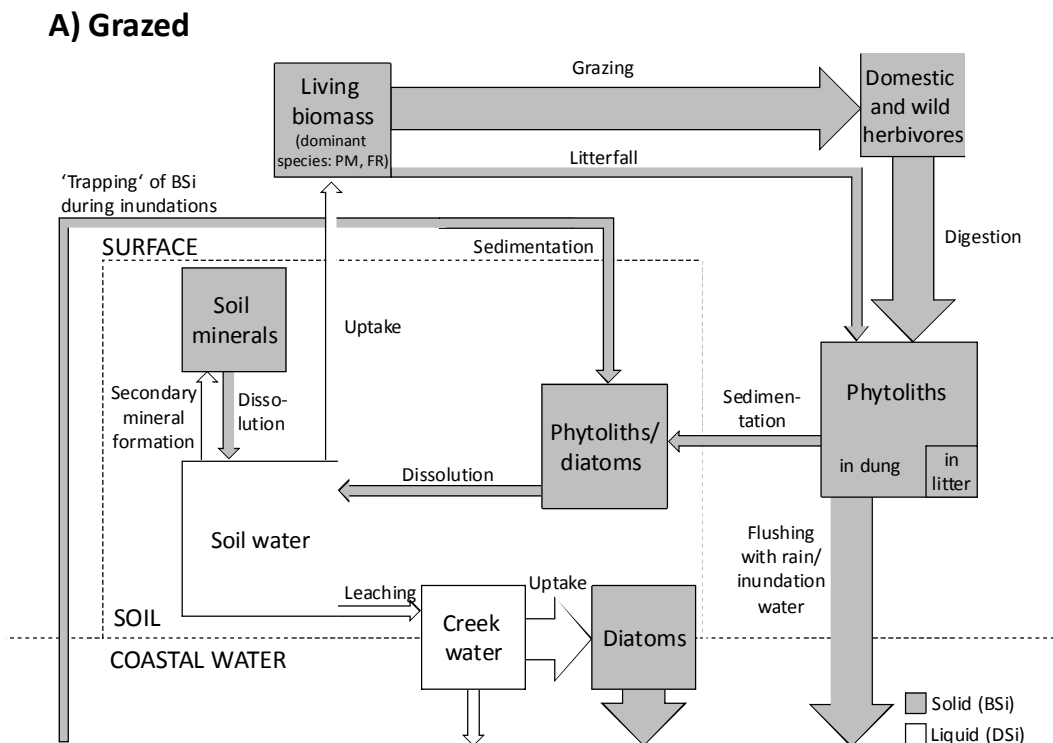


Fig. 2.7. A: Conceptual model of processes and factors that control Si exports from salt marshes under grazed conditions. Size of the arrows does not represent real numbers but indicates the importance of pathways under the respective management regime (thin: less important; thick: more important). Abbreviations: PM=*Puccinellia maritima*, FR=*Festuca rubra*, EA=*Elymus athericus*.

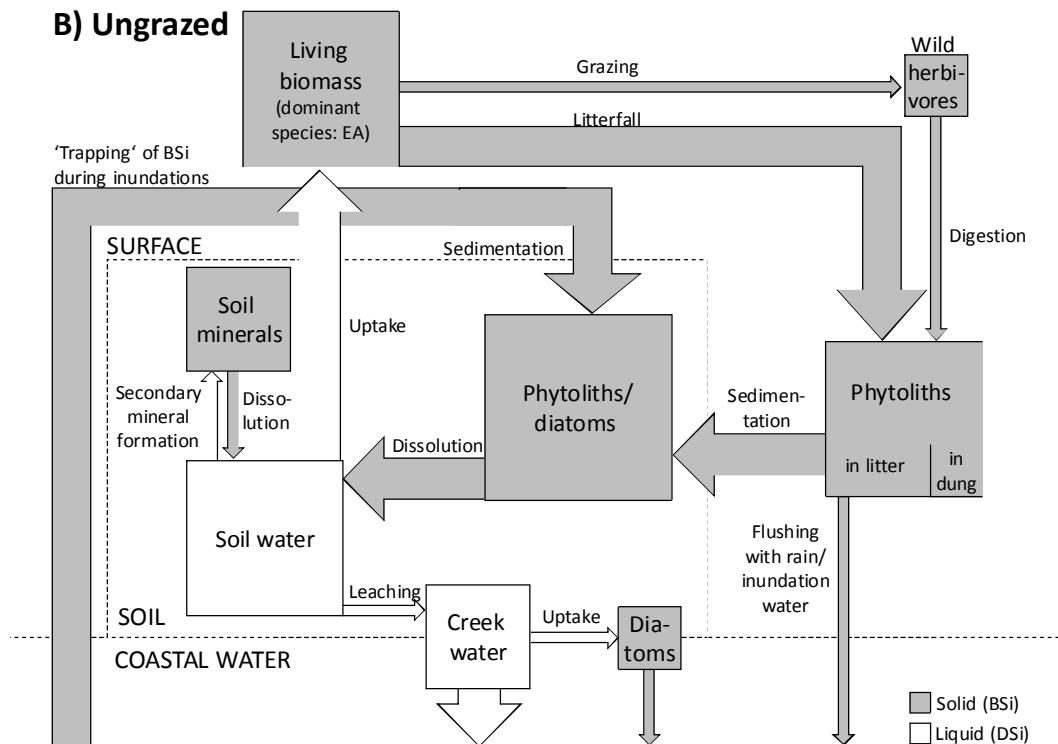


Fig. 2.7 B: Conceptual model of processes and factors that control Si exports from salt marshes under ungrazed conditions. Size of the arrows does not represent real numbers but indicates the importance of pathways under the respective management regime (thin: less important; thick: more important). Abbreviations: PM=*Puccinellia maritima*, FR=*Festuca rubra*, EA=*Elymus athericus*.

On grazed sites (Fig. 2.7 A), domestic herbivores are assumed to accelerate BSi dissolution because the biomass around the phytoliths is removed during digestion. During pulse events like floodings or heavy rain fall, phytoliths in dung may be flushed into the sea easier than on ungrazed sites since no vegetation will hold it back. We hypothesize that regular dredging of creeks leads to good growing conditions for benthic diatoms, which take up DSi at the sediment water interface and reduce DSi concentrations in the seepage water.

We hypothesize that on ungrazed sites (Fig. 2.7 B), less benthic diatoms were present and, especially in spring, DSi concentrations were higher on these sites. Even if present in lower numbers, also wild animals like geese and hares might contribute to silica cycling in the marsh. However, since these animals generally prefer grazed sites over ungrazed sites (van der Wal et al. 2000), the effect of wild animals can not clearly be separated from the effect of livestock grazing. An overlaying factor is hydrology. Thick litter layers can lead to retention of rain and inundation water, thereby increasing percolation into the soil and subsequently increasing dissolution of soil BSi. This equilibrium driven dissolution can also be enhanced by DSi uptake by plants

like *Elymus athericus*. On the other hand, tall vegetation and thick litter layers can also lead to increased sedimentation rates and, therefore, burial of BSi in the soil.

In order to achieve a comprehensive understanding of Si cycling in salt marshes, DSi uptake rates of benthic diatoms in salt marsh creeks, the influence of herbivore digestion on dissolution of phytoliths and BSi and DSi pools in salt marsh soils still need to be quantified.

2.7 Acknowledgements

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Appendix 2.1: Overview of measured DSi and BSi concentrations and exports, conductivity and pH. SNK=Sönke-Nissen-Koog; DSK=Dieksanderkoog; SD=Standard deviation; N=number of samples. For sampling dates see Fig. 2.4.

Season	DSi concentration			BSi concentration			Discharge	DSi export			BSi export			Conductivity			pH				
Sample	mean	SD	N	mean	SD	N		mean	SD	N	mean	SD	N	mean	SD	N	mean	SD	N		
Catchment	$\mu\text{mol l}^{-1}$			$\mu\text{mol l}^{-1}$			$\text{ml day}^{-1} \text{m}^{-2}$	$\mu\text{mol m}^{-2} \text{day}^{-1}$			$\mu\text{mol m}^{-2} \text{day}^{-1}$			mS cm^{-1}							
Spring 2010																					
Bulk tide																					
SNK	landward	grazed	190	8	3	27	7	3													
		ungrazed	218	18	3	23	11	3													
	seaward	grazed	98	48	4	32	17	3													
		ungrazed	62	10	3	21	2	2													
Seepage water																					
DSK	landward	grazed	114	11	10	18	11	7													
		ungrazed	264	17	10	21	6	6													
	seaward	grazed	267	20	10	31	13	9													
		ungrazed	340	12	10	14	4	8													
SNK	landward	grazed	127	30	10	35	14	8													
		ungrazed	251	18	9	16	10	6													
	seaward	grazed	169	40	10	54	31	8													
		ungrazed	295	17	10	18	4	5													
Summer 2010																					
Bulk tide																					
SNK	landward	grazed	83	25	2	82	33	2						45,5	0,0	2	7,9	0,02	2		
		ungrazed	145	51	2	141	44	2						44,8	0,1	2	7,91	0,01	2		
	seaward	grazed	29	19	3	70	32	3						45,3	0,2	3	7,83	0,03	3		
		ungrazed	48	4	2	80	48	2						45,7	0,8	2	7,85	0,08	2		
Seepage water																					
DSK	seaward	grazed	230	57	8	98	50	6	8	2	0	8	1	0	6	31,3	1,1	8	8,22	0,25	8
		ungrazed	295	40	8	70	42	7	46	13	2	8	3	2	7	30,1	1,9	9	8,08	0,23	9
SNK	landward	grazed	308	23	8	77	16	5	207	64	5	8	16	3	5	45,6	0,7	8	7,79	0,32	8
		ungrazed	359	6	8	93	31	4	222	80	1	8	21	7	4	41,1	0,7	8	7,93	0,12	8
	seaward	grazed	350	81	7	102	28	6	605	212	49	7	62	17	6	44,4	0,4	7	8,03	0,07	7
		ungrazed	401	26	9	89	13	7	464	186	12	9	41	6	7	39,5	0,7	9	8,04	0,05	9
Autumn 2010																					
Bulk tide																					
SNK	landward	grazed	50	14	5	54	19	3						39,8	1,3	5	7,7	0,13	5		
		ungrazed	90	49	5	55	19	3						40,0	1,5	5	7,70	0,05	5		
	seaward	grazed	29	14	6	67	38	4						40,3	0,3	6	7,72	0,08	6		
		ungrazed	34	20	5	66	13	3						38,9	4,4	5	7,84	0,05	5		
Seepage water																					
DSK	landward	grazed	245	20	5	153	67	5	3	1	0	5	0	0	5	25,8	0,8	5	8,22	0,20	5
		ungrazed	546	11	4	92	25	4	5	3	0	4	0	0	4	23,0	0,1	4	7,75	0,28	4
	seaward	grazed	246	33	9	59	75	9	103	25	3	9	6	8	9	24,1	0,3	9	8,42	0,21	9
		ungrazed	536	7	9	56	15	7	238	128	2	9	13	4	7	24,4	0,2	9	7,81	0,09	9
SNK	landward	grazed	347	43	8	78	26	6	968	336	41	8	76	25	6	34,6	0,8	8	7,92	0,08	8
		ungrazed	401	26	9	62	20	6	1130	453	29	9	70	22	6	34,5	1,1	9	7,83	0,12	9
	seaward	grazed	429	23	6	55	8	3	797	342	18	6	44	6	3	37,0	0,3	6	7,87	0,10	6
		ungrazed	426	47	7	39	8	4	855	364	40	7	33	7	4	33,7	0,8	7	7,83	0,08	7
Winter 2010/11																					
Bulk tide																					
SNK	landward	grazed	164	14	2	52	15	2						40,9	0,3	2	7,7	0,01	2		
		ungrazed	293		1	48		1						40,3		1	7,71		1		
	seaward	grazed	65	15	3	32	5	3						40,8	0,2	3	7,76	0,06	3		
		ungrazed	138	57	2	38	11	2						40,6	0,2	2	7,65	0,02	2		
Seepage water																					
DSK	landward	grazed	487	19	9	25	5	5	24	12	0	9	1	0	5	18,3	1,3	10	7,68	0,03	10
		ungrazed	352	9	10	18	4	5	937	330	9	10	17	4	5	14,9	0,1	10	7,92	0,02	10
	seaward	grazed	489	31	12	27	16	9	251	123	8	12	7	4	9	20,3	0,9	12	7,76	0,10	12
		ungrazed	409	14	12	19	8	8	1079	442	15	12	21	8	8	19,7	0,6	12	7,80	0,02	12
SNK	landward	grazed	390	27	9	35	13	6	56	22	2	9	2	1	6	39,4	2,2	9	7,65	0,07	9
		ungrazed	389	23	9	22	15	5	760	295	18	9	16	11	5	35,9	2,5	9	7,72	0,10	9
	seaward	grazed	392	60	6	10	2	3	937	367	56	6	9	1	3	40,5	1,4	6	7,61	0,02	6
		ungrazed	417	14	9	29	13	5	920	384	13	9	27	12	5	33,8	2,2	9	7,61	0,04	9

Appendix 2.2: Results of a supplemental 10hour-sampling campaign in an ungrazed Belgian salt marsh (“Het Zwin” near Knokke-Heist) on 9 August 2011. Sampling locations A and B were located at two different creeks in a distance of about 400 m to each other. Sampling was carried out as described in this study. No bulk tide could be measured, since high water level was too low on the sampling day. SD=Standard deviation; N=number of samples.

Site	Concentration						Conductivity			pH		
	DSi			BSi			mean			mean		
	mean	SD	N	mean	SD	N	mean	SD	N	mean	SD	N
	$\mu\text{mol l}^{-1}$			$\mu\text{mol l}^{-1}$			mS cm^{-1}					
Het Zwin - A	195	34	9	7,5	3,3	9	43,7	0,9	9	7,88	0,09	9
Het Zwin - B	236	30	10	12,3	5,8	10	43,4	0,3	10	7,82	0,07	10

Appendix 2.3: BSi content of five salt marsh plant species typical for grazed and ungrazed conditions and for the pioneer zone (ungrazed). Biomass was harvested in both Dieksanderkoog and Sönke-Nissen-Koog in 400cm²-plots and species were separated from each other. BSi content was analysed photometrically by Andrea Bauer (25 mg biomass digested with 10 ml 0.2 M NaOH for 2 h at 85 °C); SD=Standard deviation; N=number of sampled plots.

Management	Plant species	BSi content		
		mean	SD	N
		mg g^{-1} dry weight		
grazed	<i>Festuca rubra</i>	11,76	2,28	10
	<i>Puccinellia maritima</i>	5,25	0,61	10
ungrazed	<i>Elymus athericus</i>	12,06	3,87	10
	<i>Atriplex portulacoides</i>	1,46	0,39	10
Pioneer zone	<i>Spartina anglica</i>	4,70	1,30	10

3

A comprehensive study of silica pools and fluxes in Wadden Sea salt marshes

Frauke Müller, Eric Struyf, Jens Hartmann, Antonia Wanner and Kai Jensen

Estuaries and Coasts, under review

3.1 Abstract

As an essential nutrient for diatoms, silica (Si) plays a key role in the estuarine and coastal food web. High concentrations of dissolved Si (DSi) were found in the seepage water of tidal freshwater marshes, which were therefore assumed to contribute to the Si supply to estuarine waters in times of Si limitation. A comprehensive budget calculation for European salt marshes is presented in this study. Earlier, salt marshes were considered to have even higher Si recycling rates than tidal freshwater marshes. Between 2009 and 2011, concentrations, pools and fluxes of Si 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 Si cycling. Our results show that the two salt marshes were sinks for Si. The average BSi imports with freshly deposited sediments ($979 \text{ kmol km}^{-2} \text{ yr}^{-1}$) largely exceeded the DSi and BSi exports with seepage water ($80 \text{ kmol km}^{-2} \text{ yr}^{-1}$). Grazing management can affect Si 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 Si budget of tidal marshes. This aspect has been widely neglected in earlier studies, what might have led to an underestimation of Si import rates to tidal marshes hitherto.

3.2 Introduction

Silica (Si) 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 Si (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 a reduced resolution of Si and to an enhanced Si 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 Si (BSi), which partly gets buried in the marsh sediments and partly re-dissolves. In its dissolved form, Si is either taken up by plants or it 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 Si 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 and Gosselink 2009) and the location of salt marshes at the shore line favours a direct supply of Si 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 Si cycling in salt marshes, such as Si in vegetation (Lanning and Eleuterius 1983; De Bakker 1999; Hou et al. 2010; Querné et al. 2011), soil (Hou et al. 2008; 2010), pore water (Scudlark and Church 1989; Wang et al. 2010) or on Si 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 Si cycling, it is important to not solely measure concentrations, but also to estimate pools of Si, imports and exports of Si and to finally calculate a budget from these fluxes.

A factor potentially affecting Si 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% were 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 (Andresen et al. 1990; 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 Si 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 Si cycling as well. To our knowledge, only one study identified the impact of grazing management on Si 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, Si 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 i.) quantify concentrations and the size of BSi and DSi pools in two European salt marshes, ii.) link these pools to Si imports and exports and iii.) identify whether or not grazing has an influence on Si pools and budgets.

3.3 Methods

3.3.1 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. 3.1). The Wadden Sea includes the largest coherent tidal flat area of the temperate zone (4,700 km²) and more than 400 km² 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 per year (DWD 2011). The region experienced a mean sea level rise of approximately 3.6 mm yr⁻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 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 20th 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, 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 Si 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.

In 1924, the land reclamation polder Sönke-Nissen-Koog (SNK) was embanked, and after construction of sedimentation fields the adjacent salt marsh began to develop ($54^{\circ}38'N$, $8^{\circ}50'E$). 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 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 *Elymus 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, unpublished data).

The land reclamation polder Dieksanderkoog (DSK) is located north of the Elbe Estuary ($53^{\circ}58'N$, $8^{\circ}53'E$). 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 *Elymus 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, unpublished data).

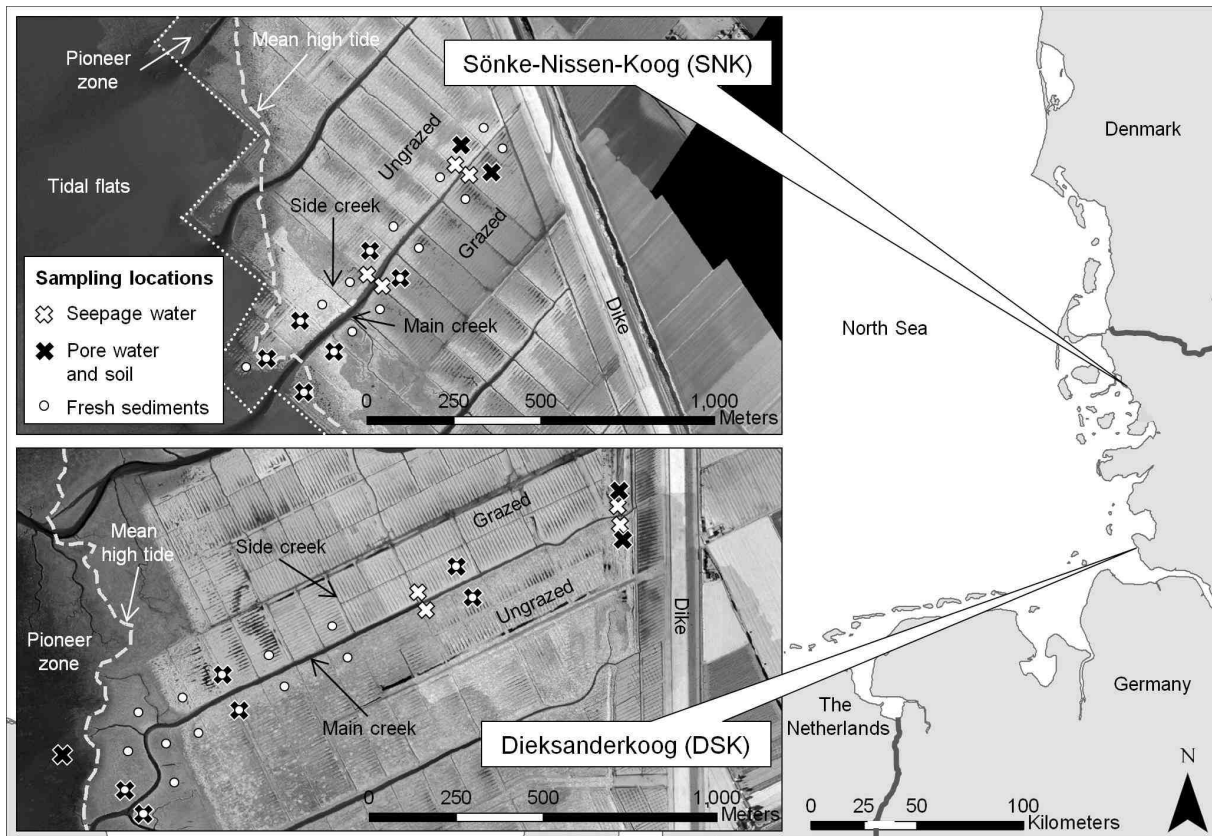


Fig. 3.1: Location of study sites in the German Bight. Aerial pictures of study sites with sampling locations. Base maps: Amtliche Geobasisdaten Schleswig-Holstein, © VermKatV-SH.

3.3.2 Field and laboratory methods

In January 2011, samples from seven different soil depths (3, 7, 10, 15, 20, 40, 60 cm) were taken with a soil corer (\varnothing 3 cm). To ensure a representative sample, four cores were taken at each sampling location (Fig. 3.1) within a radius of 2 m. Soil was subsequently pooled per depth. Soil bulk density samples were taken at all soil sampling locations with 100ml-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 (*Festuca rubra*, *Puccinellia maritima*) and ungrazed conditions (*Elymus 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 cm² 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: 4/2010, summer: 7/2010, autumn: 11/2010, winter: 1/2011). It was sampled from five different depths (3, 10, 20, 40, 60 cm) with porous 'rhizons' (© Eijkelkamp; Shotbolt 2010) connected to a 12ml-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. 3.1). Traps were built of plastic plates (\varnothing 19 cm) and were equipped with a floatable lid, preventing wash out 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 one year (6/2009 – 5/2010). Seepage water and flood water was 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.

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 μ m to remove macroscopic plant material. Fresh sediments and soil samples were dried at 70 °C to constant weight, and 25 mg dry material were weighed into test tubes. Subsequently, the samples were digested in 30 ml of 0.1 M Na₂CO₃ in a shaking water bath at 80 °C (Struyf et al. 2006; Clymans et al. 2011). After 3, 4 and 6 hours, subsamples were taken and analysed on their BSi concentration with an ICP-OES (iCAP 6300 Duo, © Thermo Scientific). To correct for the amount of Si resulting from mineral dissolution, the Si 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 μ m nitrocellulose filters within 24 hours 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 hours. 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 hours 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.

3.3.3 Calculation of pools, fluxes and 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 was 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 2 to 4 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 Si exports with seepage water, discharge and Si 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. Si 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.

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*, *Elymus athericus*, *Festuca rubra*, *Puccinellia 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 “ \pm ” indicates standard deviation.

3.4 Results

3.4.1 Concentrations

BSi concentration in the soil ranged from 40 to 519 $\mu\text{mol g}^{-1}$ and was on average $213 \pm 105 \mu\text{mol g}^{-1}$ (Fig. 3.2). BSi was generally higher at SNK ($249 \pm 104 \mu\text{mol g}^{-1}$) than at DSK ($181 \pm 97 \mu\text{mol g}^{-1}$; $F=5.11$; $N=28$; $p<0.05$; 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 highest values in both 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. 3.2). At DSK, the pattern was opposite and most depths showed a tendency of higher BSi concentrations on ungrazed compared to grazed sites.

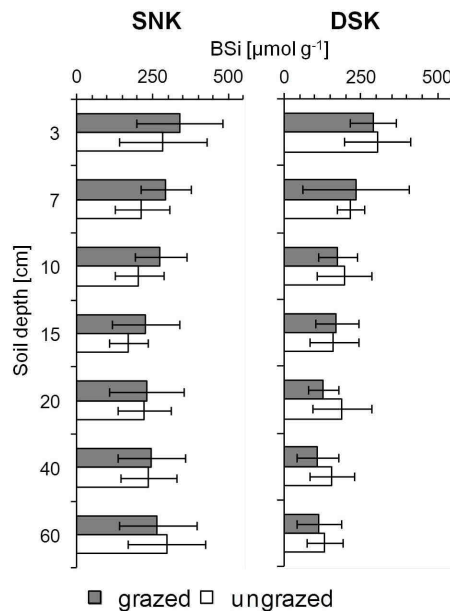


Fig. 3.2: Mean BSi concentration in soil samples of different depths from Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK). Error bars represent 1 standard deviation.

BSi concentration of typical plant species ranged from $52 \pm 14 \mu\text{mol g}^{-1}$ (*Atriplex portulacoides*) to $429 \pm 138 \mu\text{mol g}^{-1}$ (*Elymus athericus*; Fig. 3.3).

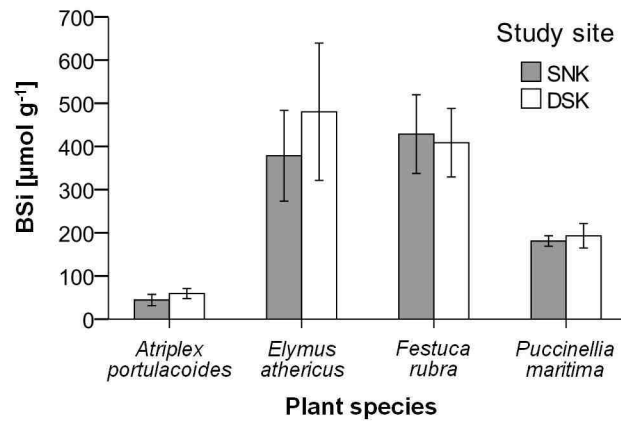


Fig. 3.3: Mean BSi concentration in four typical marsh plants. Error bars represent 1 standard deviation.

DSi concentration in the pore water was on average $408 \pm 128 \mu\text{mol l}^{-1}$ and ranged from 145 to $1,039 \mu\text{mol l}^{-1}$ (Fig. 3.4). It was similar for SNK ($420 \pm 146 \mu\text{mol l}^{-1}$) and DSK ($396 \pm 109 \mu\text{mol l}^{-1}$). 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).

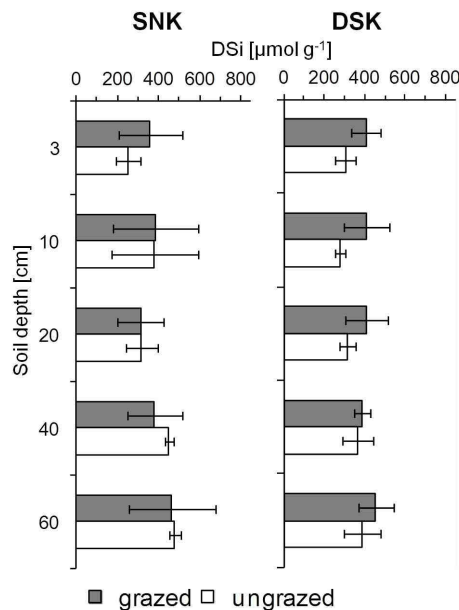


Fig. 3.4: Mean winter DSi concentration in pore water samples from Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK) grouped for sampling depth. Error bars represent 1 standard deviation.

In summer, all pore water samples in 3 and 10 cm depth below *Elymus athericus* had lower DSi concentrations than in the same depth under other dominant plant species (Fig. 3.5). 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. 3.5).

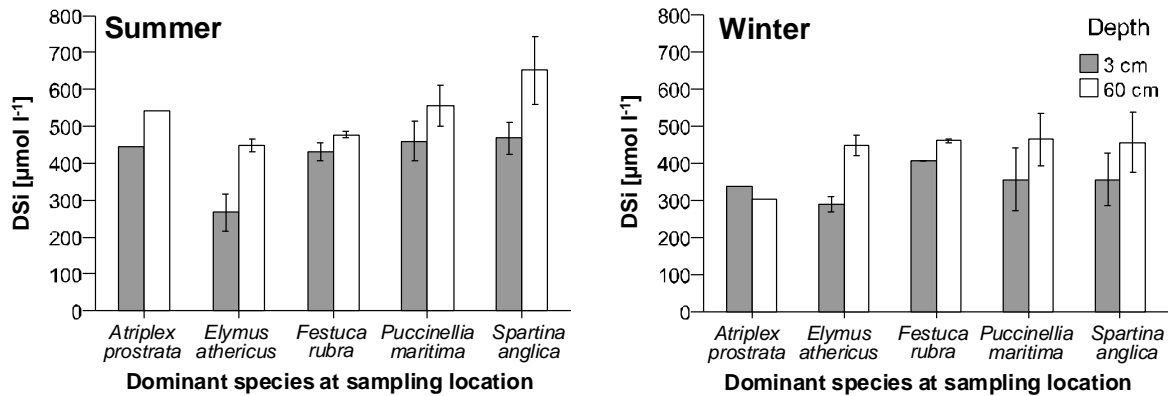


Fig. 3.5: Mean DSi concentration in pore water samples under dominant plant species, averaged for both Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK). Error bars represent 1 standard deviation.

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).

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 ($U=1931$; N=126; $p=0.84$; Mann-Whitney-U-Test) or under different grazing management ($U=1810$; N=126; $p=0.41$; Mann-Whitney-U-Test).

3.4.2 Pools

The spatial distribution of Si pools in the upper 60 cm of soil differed between the two salt marshes (). 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.

Aboveground biomass weighed between 202 ± 91 g m⁻² (DSK, grazed site) and $2,443 \pm 1,103$ g m⁻² (DSK, ungrazed site) and had an average weight of $1,047 \pm 1,084$ g m⁻². Largest Si pools in aboveground biomass were observed on ungrazed sites (Tab. 3.1). The biomass BSi pool made up between 0.04% and 0.58% of the soil BSi pool.

No large variation was observed in the size of the DSi pool in the pore water in the upper 60 cm of soil (Tab. 3.1). It made up between 0.09 to 0.20% of the soil BSi pool.

Tab. 3.1: Pools, fluxes and budgets of Si in Sönke-Nissen-Koog (SNK) and Dieksanderkoog (DSK). The reported standard deviation is calculated according to the law of error propagation from the standard deviations of the input parameters. Si imports via flood water and Si pools in belowground biomass were not determined; see method and discussion sections for further information.

Salt marsh	Sönke-Nissen-Koog (SNK)				Dieksanderkoog (DSK)				
	Grazed		Ungrazed		Grazed		Ungrazed		
	High	Low	High	Low	High	Low	High	Low	
Elevation (high: >2m NN; low: <2m NN)									
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 yr ⁻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 yr ⁻¹]									
Imports - Exports	962 ± 604	4,176 ± 393	475 ± 173	2,477 ± 569	186 ± 61	926 ± 172	55 ± 73		670 ± 382

3.4.3 Fluxes

Yearly sedimentation rates were on average $2.2 \pm 0.5 \text{ kg m}^{-2} \text{ yr}^{-1}$ with maximum values observed for spring and autumn (Fig. 3.6), when storm events caused high inundations. More sediment was deposited at the lower elevated SNK ($3.6 \pm 0.9 \text{ kg m}^{-2} \text{ yr}^{-1}$) than at the higher elevated DSK ($1.0 \pm 0.3 \text{ kg m}^{-2} \text{ yr}^{-1}$). 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 (Tab. 3.1). On average BSi imports were $1,316 \pm 1,019 \text{ kmol Si km}^{-2} \text{ yr}^{-1}$ (Tab. 3.1).

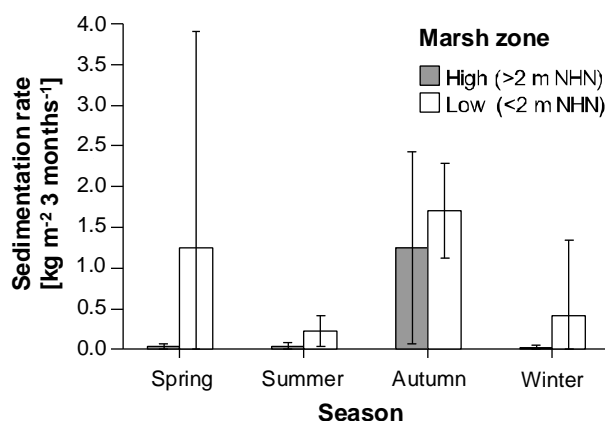


Fig. 3.6: Mean seasonal sedimentation rate between June 2009 and May 2010 per marsh zone, averaged for both study areas. Spring: Mar.–May; summer: Jun.–Aug.; autumn; Sep.–Nov.; winter; Dec.–Feb. Error bars represent standard deviation. Due to a flooding event in spring, the standard deviation is large in this season. If that outlier would be removed, the sum of sediments would be 0.3 instead of 1.3 $\text{kg m}^{-2} \text{ 3 months}^{-1}$. However, since episodic events are part of the dynamic nature of a salt marsh, outliers were not excluded from the data set.

Mean discharge of seepage water was between 28 (DSK, grazed site) and 265 $\text{l m}^{-2} \text{ yr}^{-1}$ (SNK, ungrazed site). DSi and BSi concentrations in the seepage water were on average 338 ± 112 and $49 \pm 42 \text{ } \mu\text{mol l}^{-1}$, respectively (as a comparison: DSi and BSi concentrations in the flood water were on average 90 ± 69 and $54 \pm 34 \text{ } \mu\text{mol l}^{-1}$, respectively). DSi exports via the seepage water were on average $72 \pm 59 \text{ kmol km}^{-2} \text{ yr}^{-1}$ (Tab. 3.1). 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%.

BSi imports with sediments exceeded DSi exports with seepage water by far (Tab. 3.1). The net Si import at both salt marshes was on average $1,334 \pm 736 \text{ kmol km}^{-2} \text{ yr}^{-1}$. 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.

3.5 Discussion

An integrated study about the role of salt marshes in coastal Si 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 Si. Due to the large amount of stored Si, the sites have the potential to become efficient net sources of Si 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 Si cycling appears limited.

3.5.1 Concentrations

BSi concentrations in the soil were in the range of values from other tidal marsh systems, but lower than in many terrestrial soils (Tab. 3.2). 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 $\mu\text{mol g}^{-1}$; Epstein 1994). The measured concentrations of DSi in pore water were relatively high compared to other tidal marshes (Tab. 3.2). Comparably high DSi concentrations were earlier only reported for groundwater and river water in volcanic soils (Miretzki et al. 2001).

Tab. 3.2: BSi concentrations in the soil of tidal marshes and of different grassland ecosystems and DSi concentrations in the pore water of tidal marshes.

Ecosystem	$\mu\text{mol g}^{-1}$		Reference
BSi concentrations in the soil	Range	Mean	
Mesohaline marsh, North Carolina	140-180		Norris and Hackney 1999
Tidal freshwater marshes, Belgium	110-390		Struyf et al. 2005; Struyf et al. 2007
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 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, cit. 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
	$\mu\text{mol l}^{-1}$		
DSi concentrations in the pore water	Range	Mean	
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. 2011
2 salt marshes at the Wadden Sea coast, Germany	150-1,040	408	this thesis
Salt marsh, Het Zwin, Belgium (summer)	80-530	301	this thesis

The ‘u-shaped’ depth distribution of soil BSi at SNK (Fig. 3.2) resembled 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. For our study sites, a combination of both explanations could be considered. On the one hand, plants like *Elymus athericus* and *Festuca rubra* with high Si 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 highly enriched in BSi. Also grain size was discussed as an explanation for BSi distribution in the soil profile. Hou et al. (2008) found a significant positive relationship between BSi and small grain size fractions. At DSK, where BSi concentrations were generally smaller compared to SNK, the percentage of small grain sizes was lower, too.

It has previously been hypothesised that salt marshes might be very active Si recyclers (Hackney et al. 2000; Struyf et al. 2007a), since their high salinities can enhance dissolution rates of BSi (Loucaides et al. 2008). 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 and Si 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).

3.5.2 Pools

Si pools of our study sites appeared to be medium to large compared to comparable ecosystems. 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 Si 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, Si 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 Si 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 differs 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 Si 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 Si 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. (2011). Kiehl et al. (2001) determined belowground biomass at SNK to be on average $2,340 \pm 260$ g m⁻². Using this data, a BSi pool in belowground biomass of 160 ± 150 kmol km⁻² can be estimated. This value lies within the range of the aboveground biomass.

3.5.3 Fluxes

BSi imports to the study sites were one order of magnitude larger than DSi exports, causing an accumulation of Si. As outlined in the method 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 high 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.

Exports of DSi with seepage water were slightly larger than export rates measured for terrestrial grasslands in North America (1-39 kmol Si km⁻² yr⁻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 yr⁻¹. In contrast to our sites, also salt marshes in the Netherlands, Delaware and France were reported to be net exporters of Si (net export rates of 110, 170 and 340 kmol Si km⁻² yr⁻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 Si fluxes via the flood and seepage water were considered by the authors, and no sediment traps were applied on the marsh surface. This methodological difference might have led to an underestimation of Si imports in these studies, since no measurements during heavy storm tides have been conducted. In shrinking salt marshes, also BSi exports with eroding sediments might affect the Si budget. If one aims to determine whether a salt marsh acts as a source or a sink for Si, sedimentation and erosion processes should be considered carefully.

Even though salt marshes are BSi accumulating systems, they still deliver significant amounts of DSi to the adjacent coastal system, which especially in summer could help diatoms to overcome DSi shortage. Very probable, the effect is only local, but

since diatoms play a key role in the productivity of the adjacent tidal flat ecosystem (Admiraal 1977), the additional DSi supply from salt marshes could be important for the 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), Si exports were hypothesised to be the missing link between tidal marshes and productivity in adjacent water bodies (Hackney et al. 2000).

3.5.4 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 autumn average but still higher than yearly average. This single occurrence underlines the importance of rare events like storm tides for the import of BSi.

To assess whether the sedimentation rates reported here are representative, soil bulk density data can be used to calculate accretion rates. The resulting accretion rate of on average $+2 \text{ mm yr}^{-1}$ is below the $+6 \text{ mm yr}^{-1}$ 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 was observed during the study period. Water levels of $1 \text{ m} > \text{MHT}$ were reached 6 times and water levels of $1.5 \text{ m} > \text{MHT}$ 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 can be advised to conduct long term measurements on accretion rates additional to sediment trap measurements to estimate BSi imports.

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 in 5 km distance to Notelaar, Struyf et al. (2005a) measured DSi exports in seepage water of 200 to $13,000 \text{ kmol km}^{-2} \text{ yr}^{-1}$. 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 $15,000 \text{ l m}^{-2} \text{ yr}^{-1}$, equivalent to the 20fold 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.

3.5.5 Marsh maturity

Si budgets in this study differed considerably with elevation. BSi imports were far higher in the low ($<2 \text{ m NHN}$) than in the high ($>2 \text{ m NHN}$) marsh zone, and they were higher at SNK compared to DSK. Modeling 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) were only half of the values measured for SNK (126 ± 115 compared to $260 \pm 68 \mu\text{mol g}^{-1}$). 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 Si at DSK, and pools have 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 3.1). In this marsh, average BSi concentration in 40 and 60 cm depth was only $79 \pm 56 \mu\text{mol g}^{-1}$. Although both DSK and SNK are sinks for Si 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, 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).

3.5.6 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 Si accumulating grass *Elymus 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 Si 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.

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 dif-

ferences 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 *Elymus 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 was 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 Si 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 Si 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.

3.6 Conclusion

Both salt marshes were sinks for Si. 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 Si 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 Si cycling: as seen for other nutrients, mature salt marshes can turn from a sink to a source of Si. However, data on the influence of

maturity on Si fluxes is widely missing. We found different effects of grazing management on the Si budget of the sites. On the one hand, Si 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 Si imports. Little is known about the role of grazing animals in Si 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 Si cycling.

3.7 Acknowledgements

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Appendix 3.1: 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 was carried out as described in this study. N=number of samples; ±=standard deviation.

Soil depth cm	Pore water					Soil		
	DSi concentration		Conductivity		pH	BSi concentration		
	mean	N	mean	N	mean	N	mean	N
3	273 ± 18	4	29 ± 4	4	7.48 ± 0.2	3	350 ± 34	4
7							292 ± 57	4
10	222 ± 12	4	45 ± 6	4	7.37 ± 0.07	3	213 ± 96	4
15							188 ± 36	4
20	286 ± 19	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 ± 10	4	47 ± 3	4	7.32 ± 0.12	4	71 ± 31	4

4

Significance of dissolved silica inputs from salt marshes in European coastal waters at regional scale

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Manuscript

4.1 Abstract

Dissolved silica (DSi) is an important nutrient in coastal marine ecosystems. In salt marshes, biogenic silica (BSi) accumulates and partly redissolves to DSi. It has been hypothesised that the amount of DSi seeping from salt marsh soils contributes significantly to the DSi budgets of coastal waters. In this study, DSi fluxes from salt marshes were extrapolated from literature data of all (five) available local studies and compared to riverine DSi exports to three European sea basins. Salt marshes cover 1,755 km² of the study area. The assumed area specific DSi export from salt marshes is 4.5 and 5.7 times as high as riverine specific DSi fluxes globally and in the study area, respectively. Despite that high specific flux, the total annual DSi flux from salt marshes equals only 0.5% (2.1% during summer) of the riverine export in the study area. Irrespective of the large uncertainties of these values, the regional scale DSi flux from salt marshes seems of minor importance compared to riverine DSi exports in the study area. Locally, salt marshes may of course contribute substantially to the supply of DSi to coastal waters. The construction of coastal levees and canalising of estuaries has reduced salt marsh areas, and thus might have strongly reduced the DSi availability in coastal waters. To identify the major controls of DSi exports from salt marshes based on additional field studies would allow estimating its local significance

which may be higher than the first estimations of its regional significance presented here.

4.2 Introduction

Dissolved silica (DSi) is an important nutrient for diatom primary production, commonly one main column of aquatic ecosystems (Officer and Ryther 1980; Schelske and Stoermer 1971; Treguer et al. 1995). A limitation of this nutrient may lead to harmful blooms of non-diatom algae (Smayda 1990), with potential negative effects on the ecosystem. DSi is mainly supplied to the coastal zone by rivers (Dürr et al. 2011; Laruelle et al. 2009; Treguer et al. 1995). In addition, amorphous silica recycling in coastal salt marshes was reported to account for significant local DSi fluxes to coastal waters (e.g. Daly and Mathieson 1981; Dankers et al. 1984; Gardner 1975; Hackney et al. 2000; Struyf et al. 2006; Vieillard et al. 2011).

The riverine DSi flux is accompanied by significant amounts of biogenic silica (BSi; Admiraal et al. 1990; Conley 1997). In tidal marshes large amounts of that BSi accumulate in the soil (Norris and Hackney 1999), stemming from e.g. diatoms or plant litter (cf. Anderson 1986; Norris and Hackney 1999; Struyf et al. 2007; Struyf et al. 2005b). Some of that silica, which is far more reactive than silicate minerals (Frayse et al. 2009), redissolves and then provides DSi to coastal waters (e.g. Struyf et al. 2006). This process was reported to be age dependent: young freshwater tidal marshes import more BSi than they export DSi (and thus are net Si sinks), while older marshes export more DSi than they import BSi (Struyf et al. 2006). Particularly during the main growing season, when river DSi exports decline because of algae growth (e.g. for the Rhine: Hartmann et al. 2011), tidal marshes may be important for local coastal DSi supply (e.g. Struyf et al. 2005a).

In salt marshes, the seawater influence increases pH and salinity, shown to enhance the dissolution of BSi (Loucaides et al. 2008), and the proximity of the sea allows for a direct supply of DSi to the potentially Si-limited coastal waters. However, continental to global scale studies on terrestrial DSi mobilisation (Hartmann et al. 2010; Jansen et al. 2010; Moosdorf et al. 2011) or its input into coastal waters (Beusen et al. 2009; Dürr et al. 2011) do not account for the effect of DSi fluxes from tidal marshes. In this study, we aim to clarify the significance of DSi fluxes from salt marshes for the regional coastal dissolved-silica budget.

4.3 Data and methods

Only five local studies reporting usable specific DSi export from salt marshes are known to the authors that provide a basis to estimate the DSi export from salt marshes (Tab. 4.1). The mean specific DSi flux of these studies is $0.15 \text{ Mmol km}^{-2} \text{ yr}^{-1}$, which is here rounded to $0.2 \text{ Mmol km}^{-2} \text{ yr}^{-1}$. Two more studies were identified which reported DSi exports from salt marshes which were fed by freshwater creeks (Daly and Mathieson 1981; Poulin et al. 2009). The freshwater input renders a division of the fluxes by the marsh area invalid to obtain specific DSi

fluxes for the salt marshes. These excluded fluxes would have been very small ($0.01 \text{ Mmol km}^{-2} \text{ yr}^{-1}$ for the Pointe-aux-Epinettes salt marsh, Poulin et al. 2009, and $0.03 \text{ Mmol km}^{-2} \text{ yr}^{-1}$ for the Crommet creek marsh, Daly and Mathieson 1981). Another study reported DSi fluxes from a salt marsh on Duplin River, Georgia (Imberger et al. 1983). However, the originally reported total fluxes of $3.5 \cdot 10^9 \mu\text{g Si}$ per day result in a very small specific flux of $0.004 \text{ Mmol Si km}^{-2} \text{ yr}^{-1}$. This small flux could be explained by the influence of dilute groundwater on the marsh water chemistry, which is mentioned by Imberger et al. (1983). This leads to that the named marsh area was not representative for the reported DSi flux. Thus, this study was also disregarded for the used specific Si flux from salt marshes.

Tab. 4.1: Literature values of dissolved silica fluxes from salt marshes.

Reference	Location	Flux Mmol [$\text{km}^{-2} \text{ yr}^{-1}$]	Description	Dominant vegetation
Dankers et al. 1984	Ems-Dollard Estuary, The Netherlands	0.11	low marsh, on average slightly above high tide level	<i>Puccinellia maritima</i>
Scudlark and Church 1989	Delaware estuary, U.S.A.	0.17	High marsh, flooded only during spring tides and storm surges	<i>Spartina alterniflora</i>
Struyf et al. 2006	Carmel Polder, France	0.33	young marsh, macrotidal waters	<i>Salicornia alopaepae</i> , <i>Spergularia marina</i> , <i>P. maritima</i>
Vieillard et al. 2011	Rowley, Massachu- setts, U.S.A.	0.04	fully established, large mature marsh; data only from July	<i>S. alterniflora</i> , <i>Spartina patens</i>
Müller et al. under review	Sönke-Nissen Koog, Germany	0.09	low salt marsh (0.9 - 2.6 m NHN), high flooding frequency	<i>P. maritima</i> , <i>Elymus athericus</i>
Müller et al. under review	Dieksanderkoog, Germany	0.05	higher elevated salt marsh (1.2 - 2.8 m NHN)	<i>Festuca rubra</i> , <i>E. athericus</i>
mean		0.15	(rounded to 0.2 for extrapolation)	

The specific DSi flux was extrapolated to the salt marsh areas of the North Sea, the Atlantic Hutton-Rockall Basin, and Iberian-Biscay Plains (regions defined after Meybeck et al. 2006; Fig. 4.1). The salt marsh areas were taken from EEA CORINE land cover 2006 data (permanent URL: www.eea.europa.eu/data-and-maps/data/ds_resolveuid/f7d1b28c05ce9810df31852becd1c645). However, these data do not cover Great Britain, which was added from originally gridded 2005 data from CORINE (CLC2000 100x100 m version 8/2005). The area of intertidal flats, later used for comparison, was also derived from the latter dataset. No data on salt marshes are available for Norway. However, due to the small contribution of Norway to the total considered coast area, and due to the steep rocky shoreline (Lundberg 1996), which should prevent extensive salt marsh formation, the resulting underestimation of salt-marsh derived DSi is expected to be small.

The calculated DSi fluxes were related to data of riverine DSi input from tributary areas of individual sea basins (Dürr et al. 2011). Therefore, CORINE salt marsh data and coastal segment data (Meybeck et al. 2006) were connected using the software ArcGIS 10 (ESRI®). However, due to the coarse representation of continental geometry in the coastal segments, some salt marshes were situated seawards of the as-

sessed coastal segments while obviously belonging to them. These salt marshes were manually assigned the corresponding coastal segment information.

To quantify the proportion of salt marsh DSi fluxes for the growing season, a detailed analysis of monthly river DSi outputs with data from the GLORICH database (containing data from: Deutsche Kommission zur Reinhaltung des Rheins (DK Rhein) 2008; the DEFRA Harmonized Monitoring Scheme; Krinitz 2000) was performed. In total, 40,076 individual samples from 161 rivers were included in the seasonality analyses (159 British rivers, the Elbe and Rhine rivers). Only sampling locations close to the river mouths were included. On average, the sampling data cover a time span of 22 years per station, which can include gaps without data.

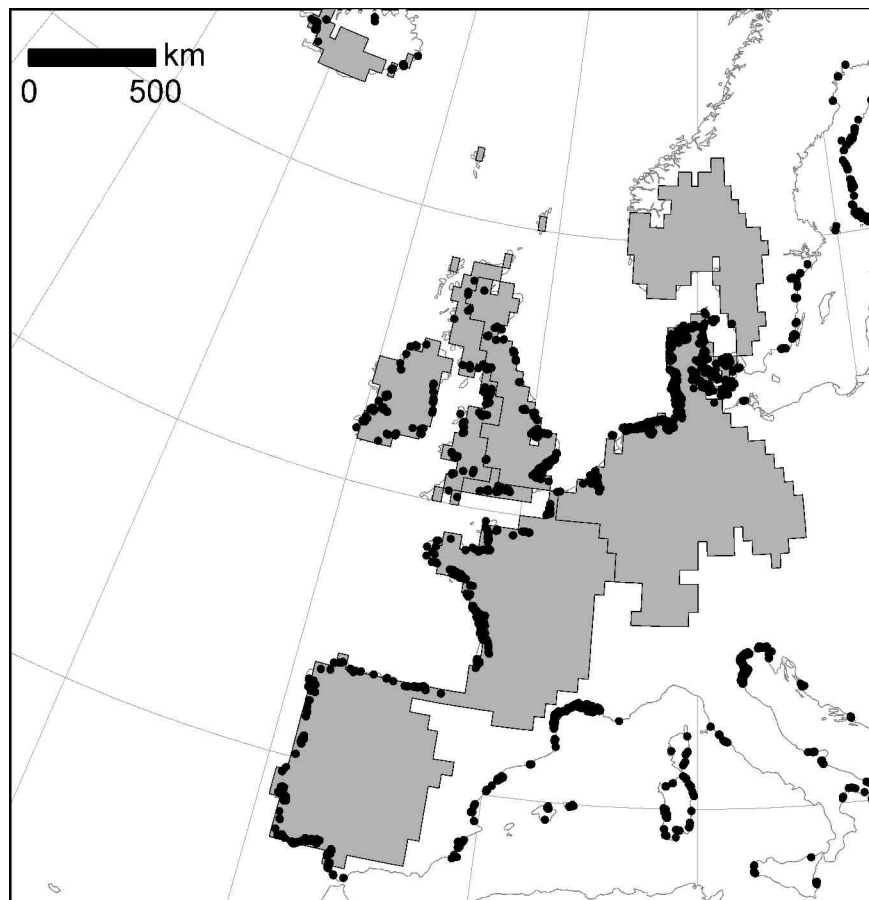


Fig. 4.1: Location of salt marshes in Europe after CORINE data (highlighted in black). The figure exaggerates the area of small salt marshes for visibility reasons. The tributary area of the sea basins (after Meybeck et al. 2006) used for the extrapolation (“study area”) is highlighted in grey.

4.4 Results and discussion

4.4.1 General results

The specific DSi flux from salt marshes was assumed to be $0.2 \text{ Mmol DSi km}^{-2} \text{ yr}^{-1}$ ($=12 \text{ t SiO}_2 \text{ km}^{-2} \text{ yr}^{-1}$). Extrapolating the assumed specific DSi flux to the salt marshes in the study area results in a total DSi flux of 351 Mmol yr^{-1} (Tab. 4.2). This

equals 0.4% of the riverine DSi inputs to the sea basins (after Dürr et al. 2011). The proportion of DSi export from salt marshes is higher in the Iberian-Bascay Basin (0.6%) and the North Sea (0.5%), than in the Hutton-Rockall Basin (0.1%). These results suggest that the DSi exports from salt marshes are in general of minor importance in annual coastal nutrient budgets on the regional scale.

Tab. 4.2: Area and DSi export of whole sea basin tributary regions^A and their salt marshes as well as the proportion of salt marsh export on DSi flux from rivers annually and in summer.

Sea basin name ^A	Area [km ²]		SiO ₂ flux [Mmol yr ⁻¹] from		Salt marsh DSi proportion	
	Basin	Salt marsh	rivers ^B	salt marshes	annual	summer
Iberian-Biscay Plains	820,684	776	25,975	155	0.60%	2.40%
Hutton-Rockall Basin	231,871	215	29,475	43	0.10%	0.60%
North Sea	872,787	764	28,930	153	0.50%	2.10%
Sum /mean	1,925,342	1755	84,380	351	0.40%	1.70%

A) after Meybeck et al. (2006)

B) after Dürr et al. (2011)

The aim of the presented study is to develop a general idea of the importance of the silica buffering of salt marshes by comparing their DSi exports to those of rivers on the regional scale. The exact values given here are subject to a number of uncertainties. Minor uncertainties could result from possible misinterpretation of the salt marsh extent in the CORINE data, or limited data of the riverine export of DSi (cf. Dürr et al. 2011). However, the main uncertainty is the value of DSi flux from salt marshes used here, which is based only on few locations and may insufficiently represent the extrapolation area.

According to the CORINE data set, salt marshes cover 1,755 km² of the study area. However, this value might underestimate the actual salt marsh area, as for the Wadden Sea, CORINE data represent only 75% of the 400 km² salt marsh area reported by Reise et al. (2010). Dijkema (1987) estimated the area of European salt marshes to be at least 2,310 km². Uncertainty in the DSi budgets of rivers is introduced by possible yet unquantified water column DSi removal in estuaries (Garnier et al. 2010; Laruelle et al. 2009; Wollast and Debroeu 1971), because DSi export data for rivers was calculated from water samples usually taken upstream of the estuary.

4.4.2 Local significance

The presented low importance of salt marsh DSi supply at regional scales should not be interpreted as an irrelevance of salt marshes to local coastal nutrient supply, although that potential local importance is not visible at the regional scale – a result in general supported by an analytical model of silica dynamics in the Scheldt estuary (Arndt and Regnier 2007). At local scale, salt marshes may still contribute significantly to the silica supply of the adjacent coastal waters (cf. Struyf et al. 2006). This might especially be true for systems with long water residence times and limited exchange with the open ocean, e.g. the Wadden Sea (e.g. Helder and Ruardij 1982;

Zimmerman 1976). Diatoms are considered the key species in the food web of the productive Wadden Sea (cf. Admiraal 1977). These organisms possibly benefit from their spatial proximity to the salt marshes, which are abundant around the Wadden Sea (Fig. 4.1). In addition, intertidal flats could be relevant for the regional silica cycle, as their extent in the study area exceeds that of salt marshes by a factor of six, where BSi could also be accumulated and processed to DSi. However, only few studies known to the authors address DSi export from intertidal flats and their results hint at a net-DSi release from those areas (Asmus et al. 2000; Leynaert et al. 2011; Postma 1981; Rutgers van der Loeff et al. 1981).

4.4.3 Seasonal significance

In addition to spatial patterns, the seasonal variability of DSi supply to coastal waters should be considered (cf. Fulweiler and Nixon 2005; Jacobs et al. 2008). The DSi fluxes during time of silica scarcity, which is usually spring to summer, are of particular importance to Si-consuming organisms (e.g. diatoms). In summer, regional scale riverine DSi exports are reduced to about half of the annual average (Fig. 4.2). The behaviour of DSi fluxes from salt marshes in summer is less clear. While they were reported to remain constant in two salt marshes in the lower St. Lawrence estuary (Poulin et al. 2009), doubling of DSi fluxes from tidal marshes during summer months was also reported (cf. Scudlark and Church 1989; Struyf et al. 2006). To favour the impact of salt marshes, the latter was assumed for the seasonality analyses presented here. Adding both effects implies that the summer proportion of DSi exports from salt marshes in coastal DSi budgets would rise to four times the annual average. Still, the proportion of DSi from salt marshes remains below 2.5% of the riverine exports of any of the three assessed sea basins during summer (Tab. 4.2). In addition, the summer decrease of riverine DSi is accompanied by an increase of exported BSi (Conley 1997; Roubex et al. 2008), of which a substantial proportion can be redissolved in the coastal zone (Anderson 1986; Yamada and D'elia 1984). This effect reduces the relative proportion of DSi exports from salt marshes. Nevertheless, the assumed four times higher relative DSi contribution from salt marshes might be exceeded locally if summer DSi exports from individual rivers fall below 50% of the annual average. For example, the DSi flux from the Elbe River decreases to below 20% of the annual average flux in summer (Fig. 4.2).

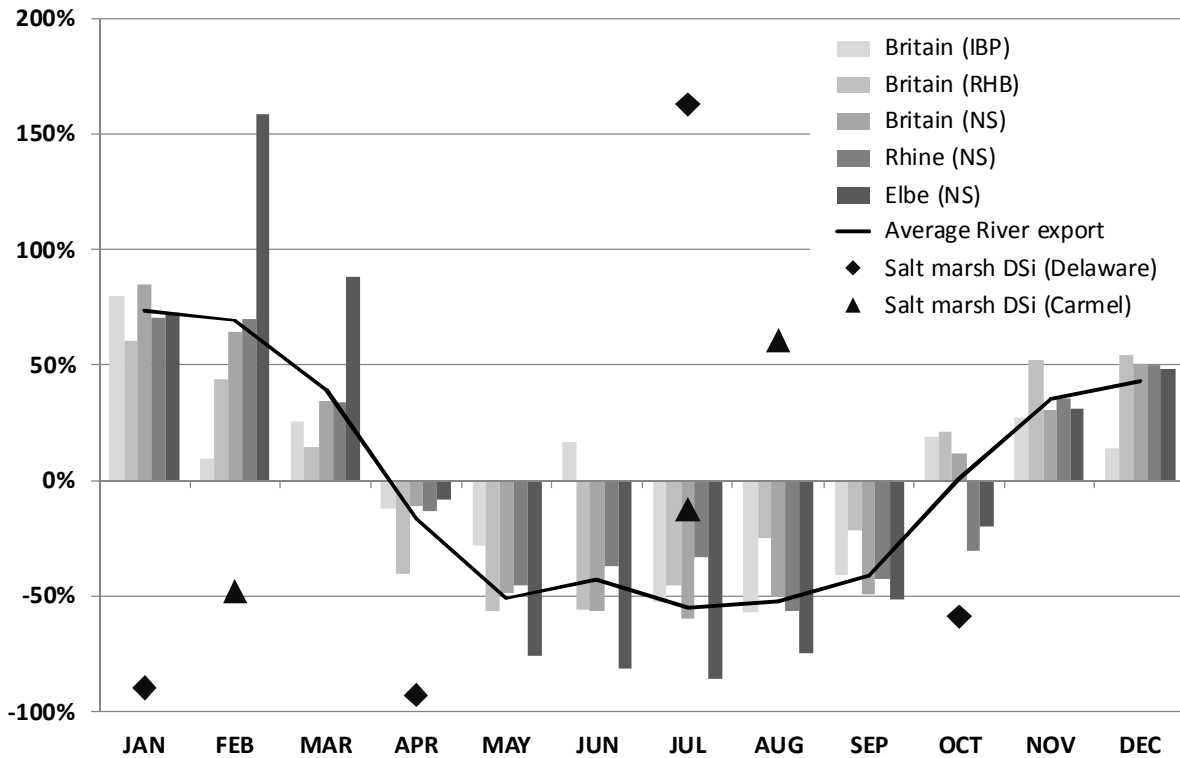


Fig. 4.2: Deviation of monthly average DSi flux from annual average DSi flux for river (bars) and salt marsh (point markers) DSi exports. In Brackets, short codes for the sea basins are given to which the rivers contribute: IBP: Iberian-Biscay Plains, HRB: Hutton-Rockall Basin, NS: North Sea as well as the salt marshes from which the DSi is exported: Delaware (Scudlark and Church 1989) and Carmel Polder (Struyf et al. 2006). For the salt marshes, all available months were taken as annual average, despite not representing a complete annual cycle.

4.4.4 Factors controlling DSi exports

Marshes have been characterised as reactors processing imported and autochthonous BSi to DSi, which is then exported to the water column (Hackney et al. 2000; Struyf et al. 2006; Struyf et al. 2005a). The amount of actually exported DSi is thus controlled by the amount and reactivity of the available BSi and the effectiveness of the reactor, which is affected by the biotic and abiotic environment of the marshes.

Biotically, DSi fluxes are controlled by the vascular and non-vascular plant communities. The importance of vascular plants for salt marsh silica budgets was highlighted by several studies (e.g. Norris and Hackney 1999; Struyf and Conley 2009; Struyf et al. 2007). Additional indirect effects can be expected from the impact of plants on soil hydrology. The importance of the non-vascular ecology was reported by studies e.g. showing that benthic diatoms can reduce the DSi flux to the coastal zone substantially (Leynaert et al. 2011; MacIntyre et al. 1996; Ni Longphuirt et al. 2009; Weiss et al. 2012).

Abiotic control is generally related to hydrology, water and soil properties. Most obviously, the tidal amplitudes influence the water exchange volume (e.g. recently detailed by Wilson and Morris 2012) in the marsh and thus the associated DSi fluxes.

In addition, e.g. salinity and pH were shown to impact silica solubility (e.g. Loucaides et al. 2008) as well as soil temperature (shown for other soil types by Gerard et al. 2002; Richards and Kump 2003). Soil properties obviously affecting the silica mobilisation in salt marshes are their height and permeability. The former controls the marsh area flooded at a usual tidal cycle while the latter controls the amount of water seeping through the marsh soil. In addition, the reactivity of the soil particulate silica is relevant for DSi fluxes (cf. references in Sommer et al. 2006).

Many of these properties depend on the maturity of a marsh, which usually integrates marsh age and elevation (cf. Childers et al. 2000). By determining the degree of flooding during tidal cycles, marsh elevation above mean high tide probably affects silica mobilisation in salt marshes (shown for organic carbon by Taylor and Allanson 1995).

Unfortunately, the listed abiotic and biotic factors cannot be included in the extrapolation presented here, as no empirical data exist that quantify their influence on marsh DSi exports in the field. There is a strong need for more field data on the variability of DSi fluxes from salt marshes in relation to individual influence factors to allow a more detailed extrapolation to larger scales.

The intensity to which DSi fluxes are controlled by marsh properties is highlighted by reported DSi exports from a freshwater tidal marsh (Struyf et al. 2005a) which are tenfold higher than those used for this extrapolation. It seems that the environment in this type of marsh is more favourable to DSi exports than in salt water marshes. However, as it is difficult to constrain freshwater tidal marshes in the CORINE land cover data, and no dataset better representing freshwater tidal marsh area is known to the authors at this scale, this study is confined to salt marshes. Even if a DSi export of 2 Mmol km⁻² yr⁻¹ (tenfold higher than suggested by the used salt marsh data) was used for extrapolation, the proportion of annual DSi fluxes from salt marshes would stay below 5% of that from rivers.

4.4.5 Specific DSi fluxes

Although the total DSi export from salt marshes is small compared to the riverine export at regional scale, the specific fluxes, regarding the area, are high. In the study area, the average specific DSi flux from rivers is 0.04 Mmol DSi km⁻² yr⁻¹; the assumed specific DSi flux from salt marshes is 5 times higher. For comparison, the assumed specific DSi flux from salt marshes equals 3.6 times the global average specific DSi fluxes from the continents (Dürr et al. 2011). It is 5.3 times above the average specific DSi mobilisation into rivers by chemical weathering in North America (Moosdorf et al. 2011), but less than the specific DSi mobilisation on the highly active Japanese Archipelago (Hartmann et al. 2010). The high specific DSi fluxes from salt marshes imply that the reduction of salt marsh areas by levee construction along the coast of the North Sea and the canalisation of European estuaries heavily impacted the DSi supply of coastal waters. The historic salt marsh area, before embankment of tidal areas started, was reported as about tenfold larger than today along the coast

of the Wadden Sea (Reise 2005). If the specific DSi export from these salt marshes followed the same patterns as today, the embankment substantially decreased annual DSi supply to the coastal waters.

4.5 Conclusions

This study compared extrapolated DSi fluxes from salt marshes to the riverine DSi exports to three sea basins in Europe. Despite the high uncertainties, four general conclusions can be drawn:

- 4) Although local studies indicate a high importance of DSi export from salt marshes for the DSi budget of coastal waters, at the regional scale the relevance of salt marshes compared to the annual DSi export from rivers to coastal waters is minor (here estimated at 0.4% of river DSi export).
- 5) Even in summer, when river DSi exports may decrease and those from salt marshes may increase, the proportion of salt marsh derived DSi increases only to 1.7%, and thus still remains small at the regional scale. However, in regions with extensive salt marshes, these fluxes may be substantial even at regional scale.
- 6) Because the area specific DSi flux from salt marshes is 3.6 and 5 times higher than riverine specific DSi fluxes globally and in the study area respectively, it is likely that the reduction of salt marsh area by coastal levee construction and estuary canalisation significantly reduced the DSi supply to coastal waters, particularly in the summer season.
- 7) An accurate representation of local DSi fluxes from salt marshes at regional scale requires increased knowledge of the controlling processes at regional scale as well as more data from salt marshes in varying environmental settings.

4.6 Acknowledgements

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5

The vegetation silica pool in a developing tidal freshwater marsh

Sander Jacobs, Frauke Müller, Johannes Teuchies, Lotte Oosterlee, Eric Struyf and Patrick Meire

Silicon

5.1 Abstract

Tidal marshes play an important role in the estuarine Si cycle. Dissolved silicon (DSi) is taken up by marsh diatom communities and by tidal marsh vegetation. Delivery of DSi back to the estuary after biogenic silica dissolution potentially increases the resilience of the estuary against harmful effects of DSi depletion events. Tidal freshwater marsh vegetation, often dominated by reed (*Phragmites australis*) has previously been hypothesized to contribute to the Si buffering function of tidal marshes, by dissolution of reed biogenic Si (BSi) into the soil pore water and consequent seepage of DSi to the estuary.

In this study the Si pool in the vegetation of a restored tidal freshwater marsh was quantified using species-based cover-biomass relationships and Si analyses. The Si pool in the aboveground biomass increased from 1.2 to 6.5 t km⁻² during the first 6 years of colonization by tidal freshwater marsh species. Our results indicate that young tidal freshwater marshes have a high potential to build up a large vegetation Si pool quickly, mostly due to colonization by species that have both high Si concentrations and high biomass production (e. g. *P. australis*). This Si pool in vegetation could act both as a long-term sink for Si along estuaries (should Si remain buried in the sediments) or as a short-term source for DSi (should Si be dissolved to DSi).

5.2 Introduction

As an essential nutrient for diatoms, silicon (Si) is an important element in estuarine and oceanic biogeochemistry. In nature Si does not appear in its elementary form, but in the form of Si dioxide derivatives, or ‘silica’ (SiO₂). Depletion of the dissolved form of Si (DSi), which is silicic acid or H₄SiO₄⁻, can cause shifts in algal communities in estuaries and coastal zones towards a dominance of non-diatom species (Kilham 1971; Conley et al. 1993). This can have harmful effects on estuarine and coastal food web structure and energy dissipation to higher trophic levels (Ragueneau et al. 2006). Such events are usually characterized by decreased DSi concentrations compared to the Redfield ratio (C:Si:N:P = 106:15:16:1; Redfield 1934). Si cycling in estuarine tidal marshes has been highlighted as a potentially important factor in increasing the resilience of estuaries and coastal zones to DSi depletion as large amounts of DSi are exported from marsh sediments during times of estuarine Si depletion (Struyf et al. 2005a).

The deposition of diatoms, plant debris and sediments during incoming tide results in an import of amorphous Si (ASi) to tidal marshes (Struyf et al. 2007a). Especially young marshes that frequently inundate and still increase in elevation, act as a sink for ASi (Dame and Allen 1996). ASi includes both diatom and plant bound, biogenic Si (BSi) and products of various binding processes such as formation of allophanes together with soluble aluminum (Harsh et al. 2002), precipitation on mineral surfaces (Drees et al. 1989), chemical adsorption on surfaces of carbonates, aluminum hydroxides and iron hydroxides (Beckwith and Reeve 1963) or the formation of polysilicic acid on Fe oxidate surfaces (Dietzel 2002). Part of the ASi is dissolved again to DSi and becomes available for plants and diatoms via the soil pore water (Struyf et al. 2005a; 2005b; 2006). It can be taken up by marsh plants and precipitate in their cell walls and intracellular spaces. Most of it gets released as DSi after the plant decomposes (Jones and Handreck 1967; Raven 1983). If it is not taken up by the vegetation, DSi can percolate through the soil and either re-precipitate or seep out of the marsh during ebb tides. In this way, tidal marshes potentially buffer estuarine Si depletion events, which often occur in spring and summer (Struyf et al. 2006) when diatom communities have taken up all DSi available in the water column.

The size of Si pools in ecosystems is receiving increasing attention. An overview has been given in Conley et al. (2006) and Struyf and Conley (Struyf and Conley 2012). Large stocks are often found in ecosystems with high productivity, and highest pools are observed in vegetation consisting of Si-accumulators like rice (Lucas et al. 1993), sugar cane (Berthelsen et al. 2001), bamboo (Lanning and Eleuterius 1983) or reed (Struyf et al. 2005b). In general, grasses contain higher concentrations of Si compared to most other plant families (Lanning and Eleuterius 1983; Epstein 1994; Berthelsen et al. 2001). Grassland soils are therefore often enriched with Si, and soil pore water as well as surface water from streams in grass dominated catchments show high DSi concentrations (Blecker et al. 2006; Borrelli et al. 2010; Borrelli et al. 2011b; Melzer et al. 2011). Since the vegetation of tidal (freshwater) marshes is often dominated by

grasses with a high productivity, a large Si pool can be expected as it was shown for *P. australis* (Struyf et al. 2005b) and *Spartina anglica* dominated systems (Norris and Hackney 1999; Querné et al. in press). The consequent large dissolution of Si into the pore water during litter dieback could contribute significantly to the DSi export from tidal marshes to the estuary, which has now been observed in both European and North-American marshes (Struyf et al. 2007b; Vieillard et al. in press).

The restoration of tidal freshwater marshes is expected to contribute to an improvement of estuarine water quality (Van den Bergh et al. 2005), partly through the buffering of Si depletion events by a larger area of tidal freshwater marsh in an estuary (Jacobs et al. 2008). However, no study has hitherto evaluated the evolution of marsh vegetation Si pools after tidal marsh restoration, and it is currently unknown whether Si pools and fluxes of a restored marsh are similar to those of a natural marsh. Therefore this study aimed at I) developing an efficient method to quantify the Si pool in the vegetation of a tidal freshwater marsh, II) assessing the buildup rate of this pool in a recently restored tidal marsh and III) comparing it to the pool of tidal freshwater marshes.

5.3 Methods

5.3.1 Study site

The Scheldt estuary is a highly eutrophic, macrotidal estuary, which has been extensively described in earlier studies (Wollast 1988, Meire et al. 2005, Soetaert et al. 2006). Its 21,863 km² drainage basin, situated in France, Belgium and the Netherlands (Fig. 5.1), is inhabited by over 10 million individuals. The study site Lippenbroek is a former embanked area (“polder”), now restored to a tidal freshwater marsh. It is situated near Hamme, Belgium (51°05′10″N; 4°10′20″E), and has a surface area of approximately 0.08 km². The site is situated in the tidal freshwater zone of the estuary, with an average specific conductivity ranging from 1,000 (winter) to 1,500 $\mu\text{S cm}^{-1}$ (summer). The tidal range in the Scheldt at this location is about 6 m. Daily tidal inundation was restored by implementing a controlled reduced tide (CRT) in March 2006 (Maris et al. 2007; Beauchard et al. 2011). The CRT technique allows the restoration of typical tidal freshwater habitats on former agricultural land by exposing the area to equivalent tidal variations as the adjacent marshes (Jacobs et al. 2008; Jacobs et al. 2009).

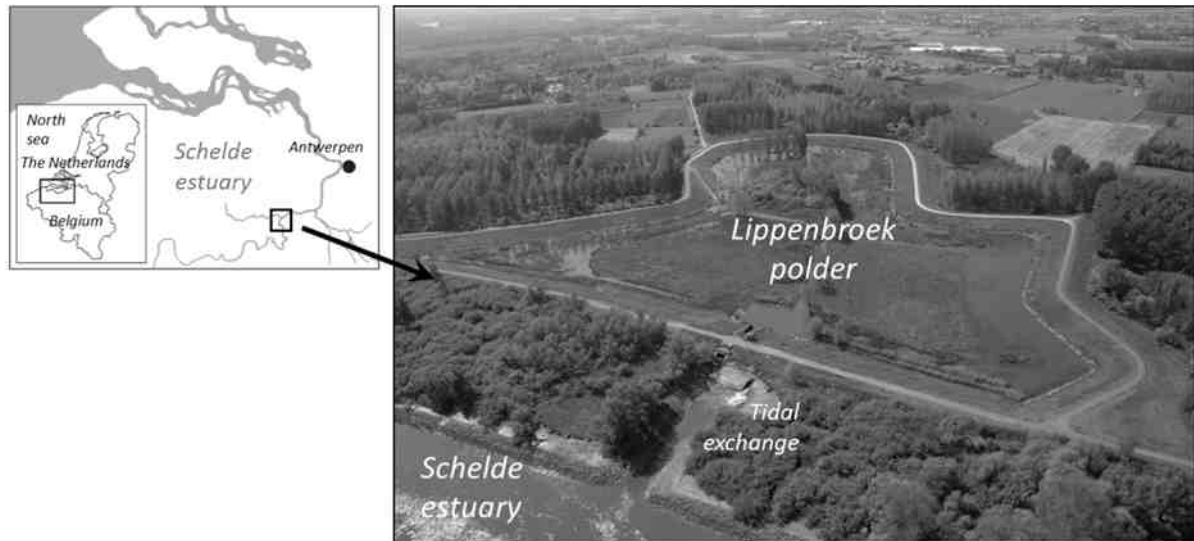


Fig. 5.1: Location of the study area. The restored site is connected to the estuary by in- and outlet culverts and is exposed to the equivalent tidal variations as the nearby estuarine marshes.

5.3.2 Cover-biomass conversion: the CBC-method

A method was developed to obtain repeatable, non-destructive biomass estimates of the dense and variable vegetation of the whole study area. The method links field estimates of total leaf area (TLA) to measured biomass of individual species through linear modeling. 95% confidence intervals of individual species' models and species TLA estimates within vegetation patches were used to obtain minimum and maximum estimates of total vegetation biomass.

Vegetation mapping was performed in the beginning (April) and at the end of the growing season (October) in 2007 and 2008. In 2009, 2011 and 2012, mapping was carried out in September. The Lippenbroek site was divided into patches or polygons characterized by homogenous vegetation (Fig. 5.2). In each polygon, TLA of all abundant species, defined as species with a TLA of at least 20%, was estimated. TLA estimates included regular double checks with several observers. In traditional vegetation surveys, *projected* leaf area estimates are used, which are truncated at 100%, regardless of a possibly layered structure or a high density of the vegetation. Determining a relationship between cover and biomass is not possible in that case. Using TLA implies that for polygons with layered or dense vegetation, cover estimates can exceed 100%, when TLA exceeds the total surface area of the polygon.

Aboveground biomass measurements were carried out in parallel with the four sampling campaigns in 2007 and 2008. For all abundant species, as obtained from the vegetation mapping, TLA was noted in 0.25 m² plots, and aboveground plant parts were harvested and rinsed. For each species, at least five of such cover-biomass replicates were obtained throughout the marsh in each of the four campaigns. Dry weight of the plants was determined after drying for 48 hours at 70 °C.

To link cover estimates to biomass measurements, we used a linear model to determine the relationship between TLA and dry weight data of the 0.25 m² plots. Mean

conversion factor and 95% confidence intervals were determined. The models always included the origin (0,0) to avoid unrealistic intercepts. Cover-biomass conversion (CBC) thus was possible. Total biomass of a single species (Eq. 1) and of all species (Eq. 2) is then represented by:

$$B_{Sp} = \sum_{i=1}^n [T_{Sp} * f_{Sp} * S_n] \quad (\text{Eq. 1})$$

$$B_{\text{Total}} = \sum_{i=1}^m B_{Sp} \quad (\text{Eq. 2})$$

Here, T_{Sp} is the estimated TLA of a species in a certain polygon, f_{Sp} the conversion factor to estimate biomass per percent cover, S_n the surface area of the corresponding polygon, n the number of polygons where the species was found, and m the number of species. Minimum and maximum estimates for B_{Sp} were obtained using the lower and upper 95% confidence interval of the f_{Sp} -value (Eq. 3).

$$\sum_{i=1}^n [T_{Sp} * f_{Sp(0.05)} * S_n] < B_{Sp} < \sum_{i=1}^n [T_{Sp} * f_{Sp(0.95)} * S_n] \quad (\text{Eq. 3})$$

Si content in above ground parts of individual plants, including shoots, leafs and stems of the mapped plant species was analyzed during the four surveys of 2007 and 2008. Plants were harvested throughout the marsh and covered a wide range of plant sizes. After cutting, the plants were rinsed thoroughly with river water in the field as well as with demineralized water in the laboratory, dried for 48 h at 70 °C, weighed and ground. Si content was determined using elemental Si analysis of extraction solutions by an inductively coupled plasma (ICP) spectrometer, type radial plasma iris/charge injection device (CID) after complete (min. 4 hours) alkaline extraction in 0.1 M Na_2CO_3 at 80 °C (see also Norris and Hackney 1999; Struyf et al. 2005a; 2005b). At least five replicates for each of the 26 abundant species were analyzed for each of the first four campaigns. To estimate the Si pool per plant species in the study area, the average Si concentration of that species was multiplied with the result from equation 1. For minimum and maximum Si pool estimates, lower and upper standard deviations of Si contents ($n=20$) were added in CBC equation 3.

5.4 Results

5.4.1 Vegetation mapping

In total, 112 plant species or taxa were found in this study, but only 26 species were classified as being abundant in at least one of the polygons, hereafter termed ‘abundant species’ (Fig. 5.2). Dominance shifted from plant species (characteristic of terrestrial pioneer vegetations and highly elevated marshes e.g. *Epilobium hirsutum*, *Urtica dioica*) to (semi-)aquatic species (e.g. *Lythrum salicaria*, *Phragmites australis*), although *E. hirsutum* remained important until 2009. Fewer species were dominant with increasing total vegetation cover (Fig. 5.3).

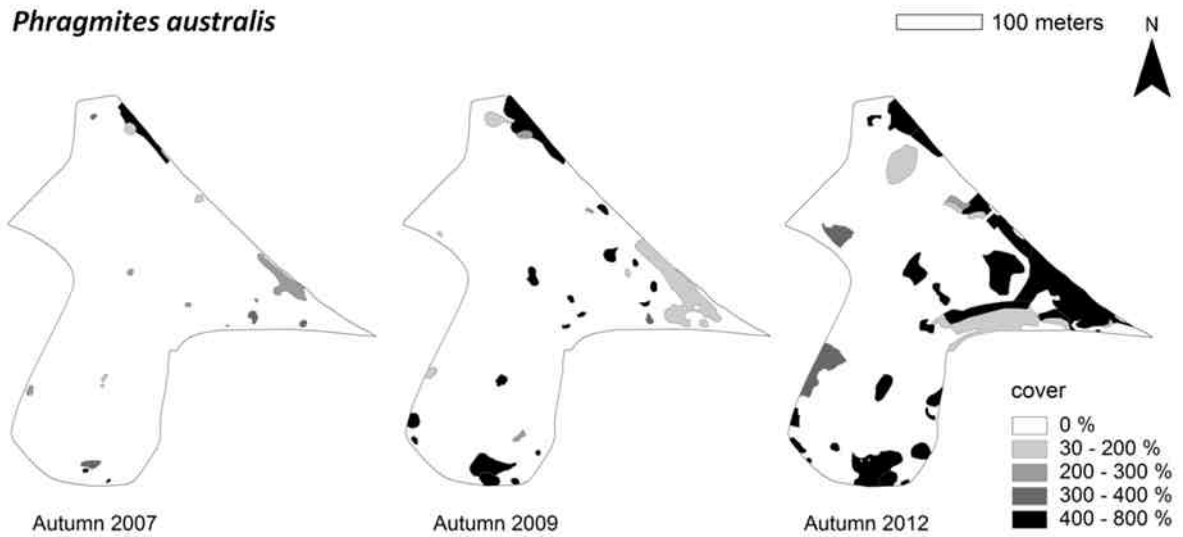


Fig. 5.2: Sample map for the cover estimation in autumn 2007, 2009 and 2012, representing total leaf area (TLA) of *Phragmites australis*.

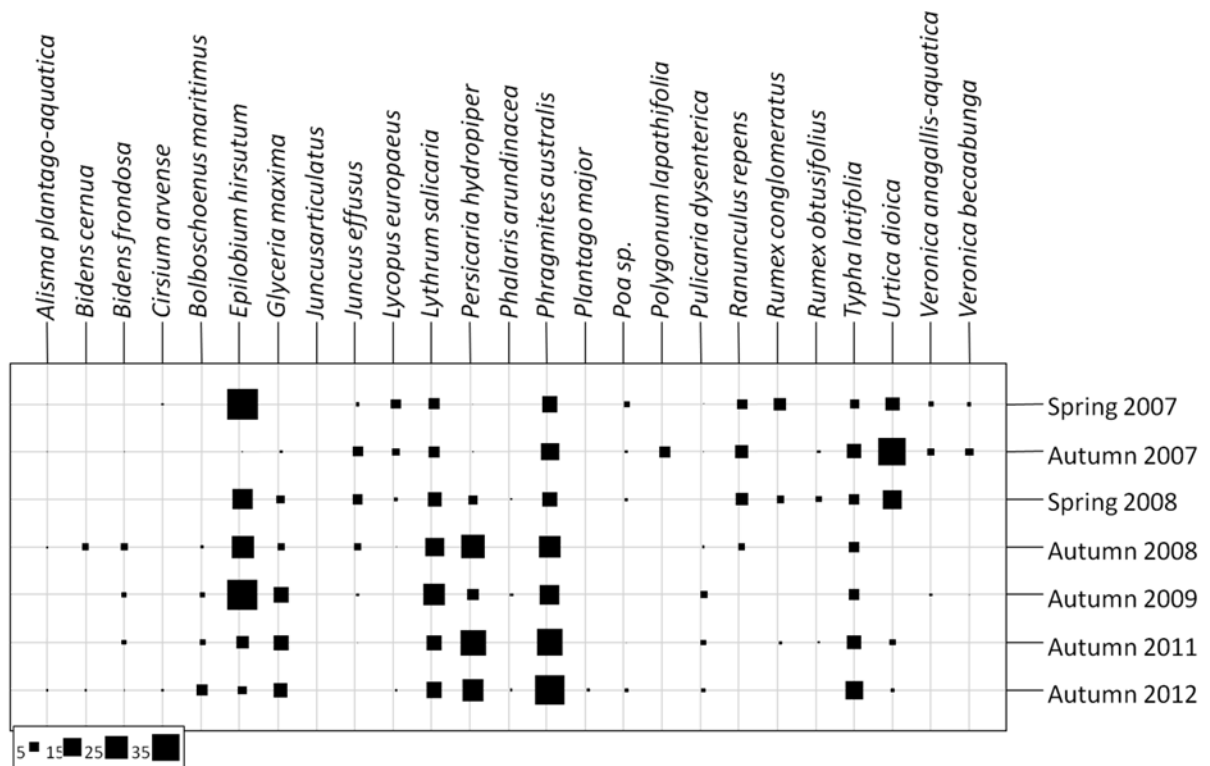


Fig. 5.3: Relative cover of abundant species per measuring campaign. The sum of the products of polygon cover and polygon surface ($\Sigma(CA)$) for each species was divided by the seasonal sum for all species and thus represents the relative contribution (%) of the species to the vegetation cover of the season.

5.4.2 CBC results

Cover-biomass conversion (CBC) models showed a strong relation between TLA and dry weight of each abundant species per 0.25 m² plot. Mean R-squared value of all 26 models was 0.81, ranging from 0.36 to 0.99 (Fig. 5.4). Cover-biomass conversion (CBC) models showed a strong relation between TLA and dry weight of each abundant species per 0.25 m² plot. Mean R-squared value of all 26 models was 0.81, ranging from 0.36 to 0.99 (Fig. 5.4).

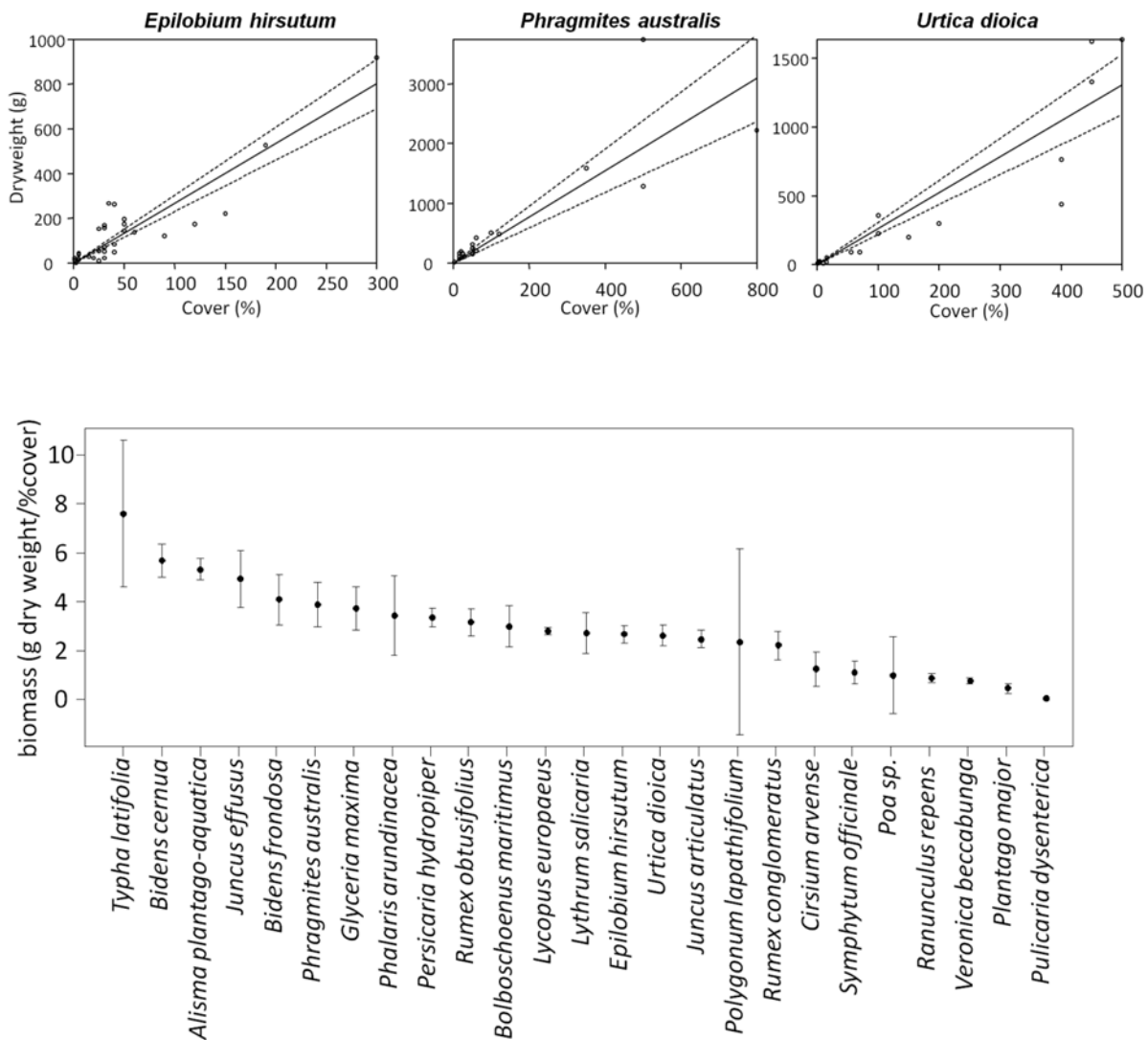


Fig. 5.4: Upper panels: Cover-biomass conversion (CBC) models for three abundant species. R-squared values for *Urtica dioica*, *Epilobium hirsutum* and *Phragmites australis* were 0.89, 0.87 and 0.81, respectively. Mean R-squared value of all 26 models was 0.81, ranging from 0.36 to 0.99. 95% confidence intervals for the model slopes are represented in dashed lines, linear model in solid lines. Lower panel: average CBC per species. Error bars represent minimum and maximum values (based on 95% confidence intervals).

5.4.3 Silica content per species

Some plant species did not accumulate Si, and variation in their Si concentration was generally low (Fig. 5.5). *Phragmites australis* had the highest Si concentration, as

well as the highest individual variation. Other Si-accumulating species were mostly monocots, with some exceptions like the dicots *Symphytum officinale* and *Urtica dioica* (Fig. 5.5). An analysis of variance (ANOVA) on these concentrations yielded significant variation among species ($F= 27,05$; $p < 0.001$). A post-hoc Tukey test distinguished several groups. As can be expected, the species *P. australis*, *Poa* sp. and *Phalaris arundinacea* separated as a group with relatively high Si concentrations and with no significant differences among them. *Bolboschoenus maritimus*, *Poa* sp., *Glyceria maxima*, *P. arundinacea*, and *S. officinale*, formed a second group without internal significant differences. A third bloc with rather low Si concentrations was formed by *S. officinale*, *U. dioica*, all three *Juncus* species, *Cirsium arvense*, both *Bidens* species, *Pulicaria dysenterica* and *Veronica beccabunga*. No significant seasonal changes in Si concentration could be detected within species ($F=1.309$; $p>0.05$).

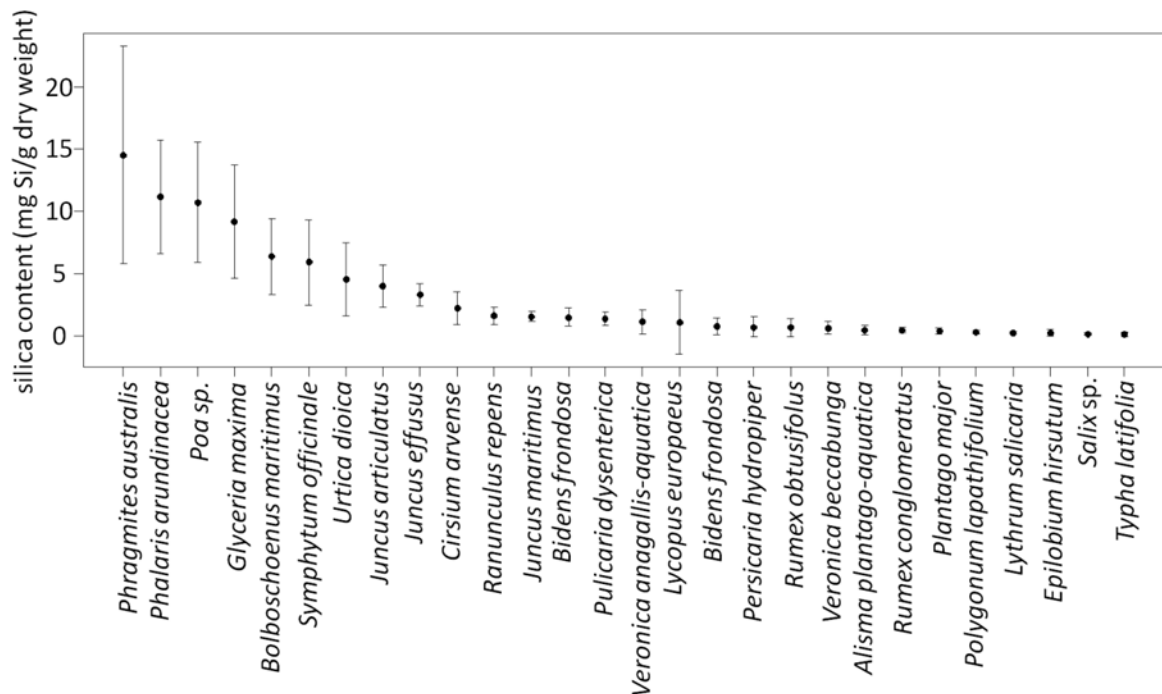


Fig. 5.5: Si content (Si in mg g⁻¹) of the sampled marsh species. Error bars represent standard deviation of the replicates. Apart from the abundant species monitored in the vegetation survey, some additional species (*Symphytum officinale*, *Salix* sp.) were analyzed.

5.4.4 Silica pool in the entire marsh vegetation

The estimated total Si pool amounted to 6.5 t km⁻² in 2012, minimum and maximum estimates being 2.0 and 12.9 t km⁻² respectively, and depicted a clear increase over the seven campaigns (Fig. 5.6). *P. australis* is clearly the biggest contributor to the total vegetation Si pool (Fig. 5.7). During the first growing season (spring 2007 - autumn 2007, Fig. 5.6) the Si pool increased, mainly due to an increase in biomass of *U. dioica* (Fig. 5.7). Between autumn 2007 and spring 2008 the Si pool showed no significant change (Fig. 5.6). A temporary loss in relative contribution of *U. dioica* and *P. australis* was compensated by the increasing contribution of *G. maxima* (Fig. 5.7).

During the subsequent growing seasons (from 2009 to 2012, Fig. 5.6), the increase of the Si pool estimate is mainly governed by an increase in biomass of *P. australis* and to a lesser extent to *G. maxima* (Fig. 5.7).

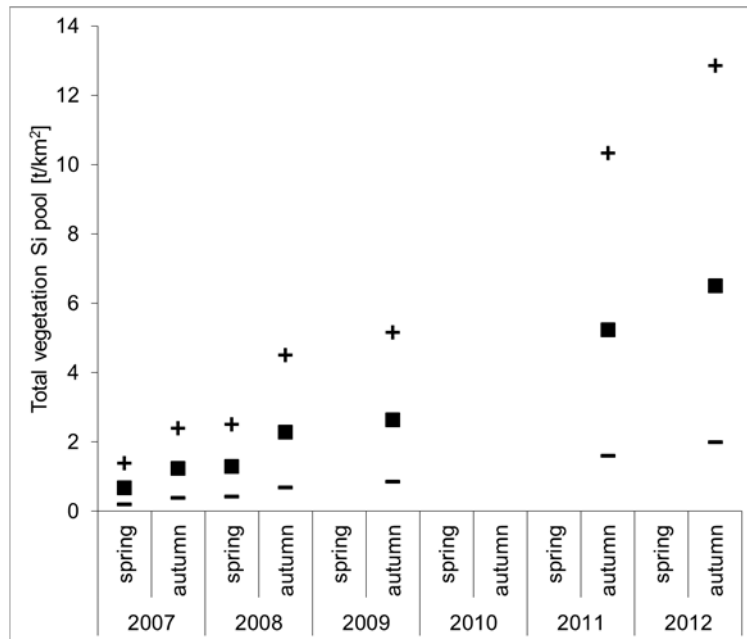


Fig. 5.6: Total Si pool in the marsh vegetation (tonnes elemental Si/km²). ‘+’ and ‘-’ represent standard minimal and maximal estimates calculated as the product of 95% confidence intervals of CBC model and the standard deviations of species’ Si content.

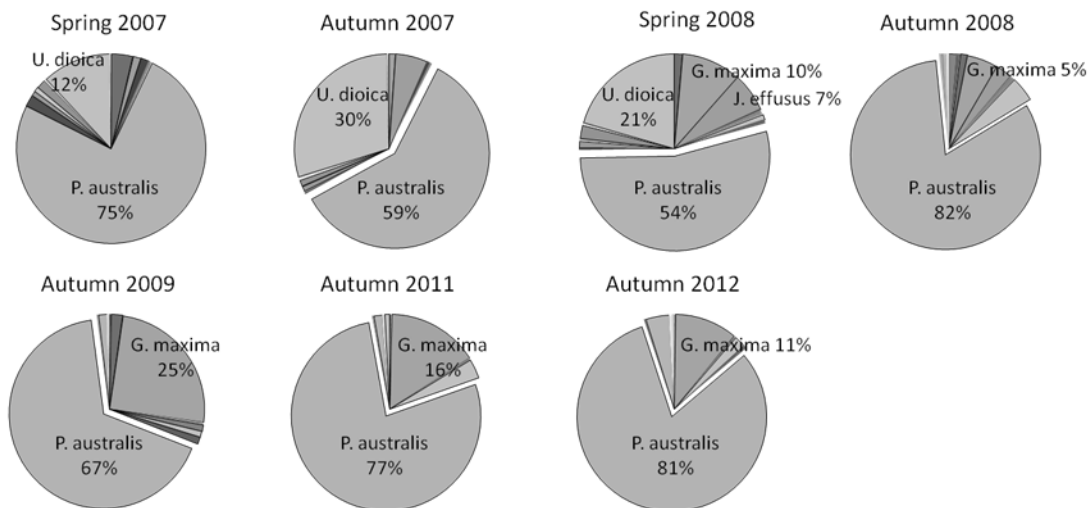


Fig. 5.7: Relative contributions of sampled species to total Si pool in the marsh vegetation for the seven sampling campaigns.

5.5 Discussion

The vegetation Si pool in the restored tidal freshwater marsh built up quickly after restoration. A non-destructive method, which was developed to estimate the size of this pool, showed that the vegetation Si pool has increased five-fold between autumn 2007 and autumn 2012. Although it reached the same order of magnitude as in adjacent tidal freshwater marshes, the vegetation Si pool still remains below its potential maximum.

5.5.1 Estimating the vegetation silica pool

The CBC method proved to be a reliable method to non-destructively estimate vegetation biomass. Firstly, high R-squared values (mean 0.81, range 0.36 - 0.99) for linear models were observed. The lowest R-squared value is an outlier of *Polygonum lapathifolium* (see confidence intervals in Fig. 5.4), which was likely caused by large intra-species variation in growth form (creeping vs. standing). Secondly, R-squared values were taken into account in the final estimates, as 95% confidence intervals are applied for minimal and maximal estimate ranges. CBC thus provides a conservative estimate of vegetation biomass, of which precision can be improved by adding more data points, thus improving the model fits. Similar techniques have been applied before (e.g. Flombaum and Sala 2007). For detailed studies where a wide range in plant biomasses are expected at similar densities, CBC could be a good method to obtain ecosystem-level biomasses. It provides an alternative for methods where allometric equations are scaled with density (e.g. Rittenhouse and Sneva 1977; Johnson et al. 1988; Navar et al. 2004). It is especially useful in multi-species environments with a large amount of abundant species (26 in our study).

The Si content of the sampled plant species was congruent with earlier findings (Hodson et al. 2005; Struyf et al. 2005b; Struyf and Conley 2009). With high Si contents of 1% or more, the monocots *Phragmites australis*, *Phalaris arundinacea*, *Glyceria maxima* and *Poa* sp. were clear Si accumulators. Consistently with other studies, *Typha latifolia* was low in biogenic Si (Borrelli et al. 2011a). Dicots with a relatively high Si content possess hairs (*Urtica dioica*, *Symphytum officinale*) or thorns (*Cirsium arvense*) which are known to often consist of Si (Lucas et al. 2000). Due to their high Si content and large biomass, only a few species contained the majority of the total Si found in the vegetation (Fig. 5.7). Considering only Si accumulators and highly productive species to estimate the total vegetation Si pool could therefore be efficient, provided that newly appearing species are analyzed for their silica content and added if necessary. Including spatial and temporal variations in plant Si content caused by variability in DSi availability would improve the method.

5.5.2 Building up of the vegetation silica pool

The vegetation Si pool built up quickly after restoration. It grew from 1.2 (range 0.4 – 2.4) t km⁻² in autumn 2007 to 6.5 (range 2.0 – 12.9) t km⁻² five years later (Fig. 5.6). This development can mainly be attributed to colonization by tidal marsh species. Due to a good connectivity with the populations in nearby estuarine marshes,

many seeds reached the restored marsh and could establish here (Jacobs et al. 2009). The shift in species was accompanied by an increase in both total biomass and relative abundance of Si accumulators. The main contributor to this increase was *Phragmites australis*. Although a clear overall trend of a yearly increasing vegetation Si pool was observed, relative contributions of species vary between surveys (Fig. 5.7). The Si pool in spring 2008 was as large as in the previous autumn, but smaller than in the subsequent autumn survey. This observation and the fact that Si concentrations did not significantly differ with seasons indicate that the growth rate of the pool was mainly governed by biomass increase. Because of the main focus on development of the vegetation Si pool over the years, spring surveys were not continued after 2008.

The size of the vegetation Si pool was within the range of pools in the aboveground vegetation in other ecosystems. It was slightly larger than earlier reported for dry and humid North American grasslands (2.2 – 5.9 t km⁻²; Blecker et al. 2006). For African grasslands, however, Melzer et al. (2010) found much higher values with a wide range of 9.8 to 55.5 t km⁻². The vegetation Si pool in Lippenbroek was much smaller than vegetation Si pools in the Amazonian rain forest (83.4 t km⁻²; Lucas et al. 1993). However, yearly litter fall in the rain forest system contained only 3.3 t Si km⁻² y⁻¹, which results in a smaller Si turnover than in Lippenbroek, where the total vegetation Si pool is contained in annually recycled aboveground biomass of annual species. For an established, older tidal freshwater marsh, Struyf et al. (Struyf et al. 2005b) showed that the vegetation Si pool ranged between 5 and 85 t /km², depending on vegetation type (lower range in *Salix* forest, higher range in *P. australis* monospecific plots). Our estimate thus shows that even if the Si pool in the vegetation is recovering quickly, it is still below that value.

Depending on the restoration site, it can take between a decade and hundred years until a restored wetland reaches a biological structure comparable to a reference site [e.g. (Craft et al. 2002; Borja et al. 2010; Smith and Warren 2012)]. Fully restoring biogeochemical functioning of a wetland generally takes even longer (Moreno-Mateos et al. 2012). Apart from seed availability, the time span for recovery is largely depending on temperature, soil characteristics, nutrient content and hydrological conditions (Smith and Warren 2012). The comparably quick growth of the primary productivity and the vegetation Si pool at Lippenbroek are good examples of the positive influence the tidal regime has on the restoration success, which was recently described by (Moreno-Mateos et al. 2012).

Vegetation succession at the Lippenbroek site is still ongoing. The competitive outcome of *P. australis* versus *T. latifolia* colonization in particular will impact the amounts of Si pooled in tidal freshwater marsh vegetation. Also further colonization of the low marsh zone by Si accumulators like *P. arundinaceae*, *G. maxima* and *B. maritimus*, could increase total amount of Si pooled in estuarine vegetation. Moreover, management could have a large impact on Si pools in vegetation. Management practices such as mowing to promote reed growth will increase the amount of Si

pooled in the marsh, while on the contrary, succession to willow-dominated forests will most likely cause a decrease of the vegetation Si pool. The water level in the CRT can also be managed. If for instance a larger proportion of high marsh is desired, the inlet culvert can be adjusted to allow less water to flood the marsh per tidal cycle (Jacobs et al. 2009), which would influence vegetation and thus the Si pool.

5.5.3 Contribution of vegetation silica to the estuarine silica cycle

Struyf et al. (2007b) showed that over 98% of the Si in *P. australis* litter dissolved within one year. Dissolution potential from the reed was similar throughout the year and showed no seasonal differences (Vieillard et al. in press). The contribution of the vegetation Si pool to Si export from marshes is thus potentially important: Struyf et al. (Struyf et al. 2007b) estimated an evenly spread DSi release from litter over the seasons, totaling $21.3 \text{ t} \pm 5.7 \text{ t km}^{-2} \text{ y}^{-1}$ for tidal freshwater marshes, which exceeds values found in many other ecosystems (e.g.: 5.8 ± 0.6 to $7.6 \pm 0.7 \text{ t km}^{-2} \text{ y}^{-1}$ for rain forest on ferrasol in Congo, Alexandre et al. 1997; $3.7 \text{ t km}^{-2} \text{ y}^{-1}$ for a temperate forest on till in Canada, Bouchard and Jolicoeur 2000). This indicates the potentially crucial relevance of the vegetation Si pool in the role of tidal marshes as buffers in the estuarine silica cycle.

In 2007, maximal measured DSi export from the Lippenbroek was about 1.5 t km^{-2} in one tide (Jacobs et al. 2008). This maximum was measured on a hot summer day in June 2007 with flood water DSi concentrations below 0.5 mg L^{-1} and ebb water concentrations amounting to 9.27 mg L^{-1} (Jacobs et al. 2008). During the first two years sediment pore water concentrations in the study site ranged from 4.0 to 17.6 mg L^{-1} , strongly varying depending on the time after last flooding and location within the marsh (S. Jacobs, unpublished data). Sediment biogenic Si concentrations ranged from $2.3 - 12.4 \text{ mg Si/kg}$ (S. Jacobs, unpublished data). At that moment the vegetation Si pool was still low ($1.3 (0.4 - 2.4) \text{ t km}^{-2}$ in Fig. 5.6), which points to other, sediment related sources of DSi export from the marsh at that time.

Since then, the vegetation Si pool has increased five-fold, reaching $6.5 (2.0 - 12.9) \text{ t km}^{-2}$ in 2012. Applying recycling rates of Si from litter, as estimated in Struyf et al. (2007b), this would maximally imply a current release rate of 6.4 t km^{-2} from vegetation litter in the Lippenbroek per year.

5.6 Conclusion

Our study shows the rapid and ongoing build-up of the vegetation Si pool in restored tidal marshes, driven by colonization by Si-accumulating species. Succession towards willow forests or (managed) reed-dominated vegetation will be decisive for the size of the vegetation Si pool in the long run. This vegetation is only a temporary sink for Si along the estuary. Dissolution of litter Si in tidal marshes is a rapid process, with most of the Si dissolving within one year after plant collapse. This implies that in reed dominated tidal marshes vegetation could contribute significantly to the buffer capacity of tidal marshes in the estuarine Si cycle. High total amounts of Si delivered

as litter and consequent recycling to DSi in flood water could compensate for the more efficient burial of diatom Si observed earlier in young tidal marshes (Struyf et al. 2007a). However, during times of silica depletion events, net fluxes of DSi out of the Lippenbroek amount up to 25% of the total vegetation BSi pool during one tidal flooding. Earlier studies indicated litter BSi dissolves in two phases, a rapid phase of ca. 14 days, and a slower, long-term release thereafter during about 1 year. Recent litterfall (due e.g. to a summer storm) will therefore be crucial for the contribution of vegetation BSi dissolution to such large DSi delivery events. The 0.08 km² large Lippenbroek area is a pilot project for several large scale restoration projects being implemented along the Scheldt Estuary. Plans include the creation of approximately 18 km² of tidal freshwater marshes in CRT areas by the year 2030 (Van den Bergh et al. 2005). Based on our results, vegetation development in these projects could have a significant influence on the Si cycling in the Scheldt estuary. Still, it is clear it will take several years for the vegetation to attain BSi stocks comparable to natural marshes, with Lippenbroek vegetation currently only containing a total BSi pool comparable to natural marshes low in vegetation BSi.

5.7 Acknowledgements

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6

Silicon-vegetation interaction in various ecosystems: a review

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6.1 Abstract

Silicon (Si) use by plants hasn't always received the research attention of other elements. Yet today, the importance of plant Si function is slowly becoming better understood. However, Si-vegetation interactions can also have far-reaching consequences for both local and global ecological processes, affecting higher levels of ecological organisation, and this field is still less well recognised. In this review, we provide examples of how local vegetation can impact on terrestrial and watershed scale Si fluxes, both directly and indirectly. From river headwaters to estuaries, we provide examples of the importance of linking local processes to larger scale flux consequences in (i) low order streams draining high mountain landscapes, (ii) lowland rivers and wetlands, and (iii) tidal marshes. Next, we discuss the human impact of land-use changes and management practices. Cross-disciplinary studies are strongly recommended to achieve the best understanding of how vegetation can affect the global Si cycle. This is not only crucial for ecosystem ecologists. Si is a crucial element for many plant species, important for decomposition processes, plant competition and stress tolerance. The inclusion of Si uptake as a plant functional trait by vegetation scientists is likely important to assess the link between both plant physiology, and plant distribution and tolerance to environmental changes.

6.2 Background

Silicon (Si) is usually considered a non-essential element for plants, as almost all higher plant families (except for *Equisetaceae*) can grow and reproduce in Si deprived mediums. This has caused few researchers to address Si functioning in plants, vegetation and ecosystems compared to other major elements. However, all plant species contain Si and it can be present in high amounts, for instance 19% of bamboo (*Arundinaria gigantea* (Walter) Muhl.), 8% of rice (*Oryza sativa* L.) and 6% of reed (*Phragmites australis* (Cav.) Trin. ex Steud.) dry biomass (Struyf and Conley 2009). Raven (1983) and Epstein (1994) were among the first to address this discrepancy between Si studies and those on the more “classical” nutrients such as nitrogen and phosphorus. They emphasised silicon’s importance for plant resistance against a number of biotic and abiotic stresses. Si-physiology has been best studied in rice, and several competitive advantages have been highlighted, including increased plant performance under shading and increased resistance against salinity, herbivory or Al, Fe and Mn-toxicity stress (Agarie et al. 1992; Ma and Yamaji 2006; Savant et al. 1996). This is also the reason for its incorporation in a wide range of fertilisers onto agricultural lands (Currie and Perry 2007). Present-day biologists are now learning that plant ecology is actually more siliceous than previously thought, as recently summarised by Cooke and Leishman (2011a). Several plant families, the accumulators of Si, have specialised in using Si to increase their competitiveness, especially grasses and sedges (Epstein 2009). Most research on Si in plants has focused on agricultural species belonging to the grass family, which profit from Si availability to relieve multiple stressors (Cooke and Leishman 2011a; Datnoff et al. 2001).

Research in the last decade has clearly shown that this uptake of Si by plants in natural ecosystems exerts an important control on Si biogeochemistry (Conley 2002; Derry et al. 2005; Struyf and Conley 2009). It is now recognised that vegetation in ecosystems forms an efficient filter between mineral weathering of Si, and transport of Si through rivers to the ocean (Struyf and Conley 2012), with the majority of the weathered Si first passing through vegetation before it can eventually reach rivers and ultimately the coastal zones (Derry et al. 2005). Neotropical grasses for instance, growing on soils with more easily weatherable Si, are more silicified than their paleotropical counterparts (Sarmiento 1992). The turnover and storage efficiency of the vegetation within a watershed are thus prime drivers for eventual fluxes of Si towards rivers. Hence, the vegetation determines the conditions under which Si is released, just like any other filter. In plants, Si is present in the form of hydrated amorphous Si ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), usually referred to as biogenic silica (BSi) and mostly deposited as phytoliths (siliceous plant bodies; Broadley et al. 2012). Diatoms (algae), testate amoebae (single-celled protists) and sponges (animals) also contribute significantly to the terrestrial ecosystem BSi pool, having an amorphous siliceous exoskeleton (Aoki et al. 2007; Smol and Stoermer 2010) or endoskeleton stiffened by (sponge) spicules (Maldonado et al. 2010). The structure of BSi is generally characterised by its relatively low thermodynamic stability which makes its dissolution kinetics an order of

magnitude faster than silicate minerals (e.g. quartz) in water (Cornelis et al. 2011). Due to the efficient uptake of weathered Si into terrestrial biota, large amounts of reactive BSi are currently stored in soils and biomass which are crucial in determining eventual riverine Si fluxes (Struyf and Conley 2012).

To understand the impact of vegetation on the biogeochemical Si cycle, it is essential to establish a link between the uptake, processing and functioning of Si within vegetation and fluxes of Si at the ecosystem level. Hence we must link the plant Si-accumulation rates, plant Si-physiology and the abundance of Si accumulating vegetation, to eventual fluxes into rivers (Bartoli 1983; Conley et al. 2008; Fulweiler and Nixon 2005). Cornelis et al. (2010) showed that differential Si uptake by tree species directly affects BSi content of the soil. BSi in soils is an important factor for pore water dissolved silica (DSi) concentrations (Farmer and Miller 2005), and indirectly for other pedological processes, such as DSi adsorption onto soil particles and neo-formation of secondary silicates (Cornelis et al. 2011). These processes greatly affect Si transport through the watershed.

The understanding of the whole ecosystem Si filtering concept is still at an embryonic stage (Struyf and Conley 2012). We emphasise here that a growing cooperation between researchers focusing on vegetation science and researchers specialising in Si biogeochemistry is essential to establish improved understanding of vegetation-controlled Si fluxes through the continents, but also to improve our understanding of consequent feedback effects on plant competitiveness and functioning. Plant Si processing efficiency, as well as plant Si concentration in different organs, might well be important functional plant traits, determining both response of vegetation to environmental disturbance, and the effect of vegetation on ecosystem functions, such as biogeochemical cycling. Plant Si uptake has, as previously indicated, a strong potential effect on plant competitiveness, but is also correlated factors such cellulose, lignin and phenols affecting decomposition efficiency (Schaller et al. 2012a; Schoelynck et al. 2010) and to uptake of other elements (C, N, P; Schaller et al. 2012b). It hence impacts the remineralisation of crucial resources and soil nutrient turnover rates, and the trade-off between resource efficiency and plant stabilisation/defence (Schaller et al. 2012b). Hence, Si could be an important element for vegetation competition, associated functional traits and ecosystem functioning, but has received little knowledge from vegetation scientists in this context (Diaz and Cabido 1997; Lavorel and Garnier 2002). We provide examples of local vegetation impacting terrestrial, watershed scale Si fluxes, and vice versa, Si availability influencing vegetation dynamics. We have select several ecosystems from river headwater to estuaries; (i) low order upstream ecosystems, (ii) lowland rivers and their floodplains, and (iii) downstream tidal marshes (Fig. 6.1). Our examples demonstrate the importance of linking local vegetation scale processes in the watershed to larger scale flux consequences towards the rivers and ultimately towards the coastal zones. We finish by emphasising the importance of interdisciplinary research and provide a range of examples where interaction will result in a leap forward in our understanding of plant-Si cycle interactions.

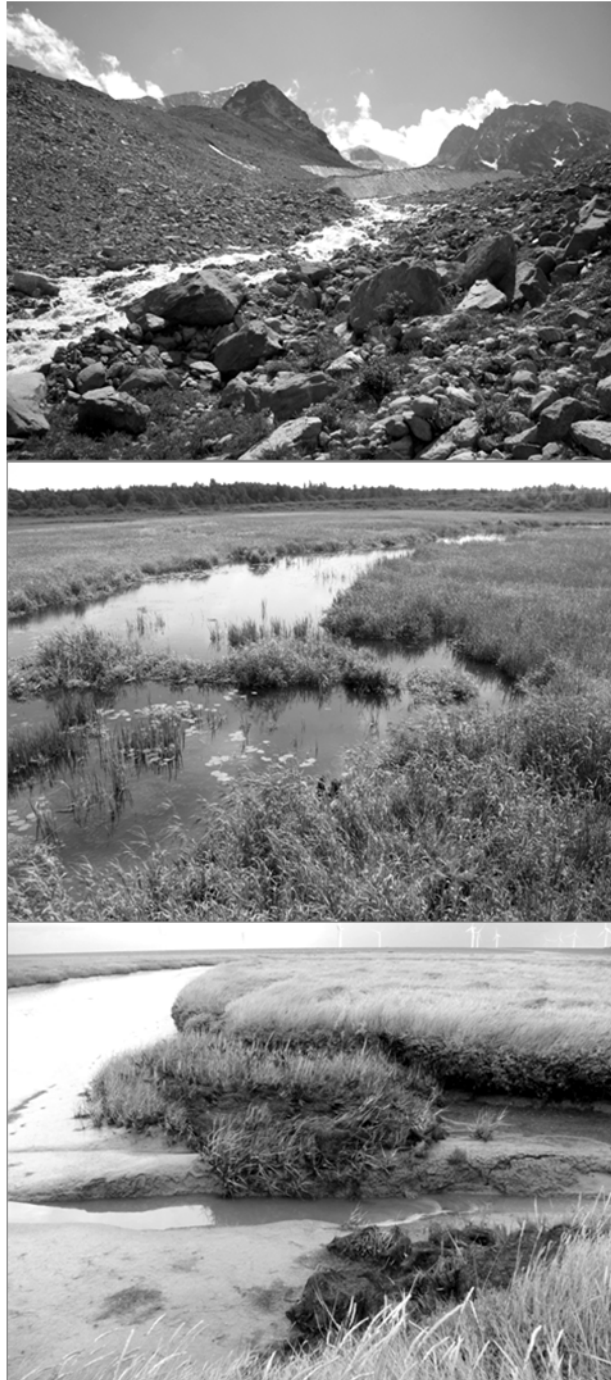


Fig. 6.1: Si weathering, uptake and cycling through vegetation, and fluxes in waterways vary across the river continuum indicating the position in the landscape and vegetation type affect Si fluxes at a site and also further down stream. Top panel: Melt water on a glacial moraine in front of the Tsijiore Nuove glacier in the Alps near Arolla (Switzerland). Vegetation: subalpine (ca. 2250 m) dominated by *Achillea erba-rotta* spp. *moschata* All., *Linaria alpina* Mill., *Saxifraga aizoides* L. and *Saxifraga bryoides* L. Middle panel: Lowland river (Biebrza) at Biebrza National Park near Lipsk (Poland). Vegetation in the river: *Nuphar lutea* Sm. and *Potamogeton crispus* L.; at the floodplain: *Phragmites australis* (Cav.) Trin. ex Steud., *Carex acuta* L. and several other sedges. Lower panel: Ungrazed salt marsh at the Wadden Sea coast at Sönke-Nissen-Koog (Germany). Vegetation at the creek: *Spartina anglica* C.E.Hubb; back and front: *Elymus athericus* L.

6.3 The river continuum: from headwaters to estuary

6.3.1 Low-order upstream catchments

In many headwaters, fast hydrologic flushing rates and minimal soil development limit chemical weathering (Clow and Sueker 2000). Runoff here is negatively correlated with vegetation cover in the watershed, as high rates of evapotranspiration (e.g. in water saturated meadows) and physical slowing of the water current reduce the flushing rates (Clow and Sueker 2000). Vegetation thus prolongs water residence- and contact times, increasing the potential dissolution of Si into flushing water (Hornberger et al. 2001; Scanlon et al. 2001). High-altitude meadows, for instance, have a surprisingly large influence on stream water (Clow and Sueker 2000), despite the small areas covered by this vegetation. Uptake and recycling of Si by vegetation will then be crucial to determine eventual Si fluxes through the rivers.

Average BSi production in subalpine grassland communities can be one order of magnitude higher than that of upper alpine grassland communities, adjacent heaths and nearby conifer forests (Carnelli et al. 2001). At lower altitudes, more intense biological activity leads to rapid mineralisation and humification of organic matter and to quick dissolution of phytoliths, resulting in higher turnover rates of BSi. DSi remineralised from phytoliths is either recycled by the vegetation, or leached from the soil profile to the groundwater (Carnelli et al. 2001). Time-lags between dissolution and uptake are crucial factors for the Si-retention capacity of the ecosystem. A time-lag between vegetation uptake of Si (growing season) and dissolution of litter-associated BSi (autumn) can potentially lead to a large increase in biologically stimulated Si weathering, because of cyclic scarcity of Si as most dissolved Si will not be recycled. This will probably be most pronounced in systems with a strong seasonality in hydrology (e.g. snow melt) and vegetation growth.

Si availability and accumulation capacity of the plant might be an important factor in determining longevity of vegetation (Cooke and Leishman 2011b). Only a limited number of studies have discussed the BSi content of mountain trees growing at similar altitudes (Hodson et al. 1997; Klein and Geis 1978; Wyttenbach et al. 1991). Ge et al. (2011) showed that leaves (needles) and branches of conifers in the Changbai Mountains (China) were more silicified than of broad-leaved species, where phytoliths were scarce and fragile. The proposed explanation for the low Si content in broad-leaved species is that broad-leaved trees have less than 5 months to grow leaves while needles of coniferous species live longer, allowing them to silicify their tissues more strongly (Ge et al. 2011). This could potentially contribute to a reduced foraging on conifers, as Si is an efficient stimulator of food abrasiveness (Sangster and Hodson 2001). In this way, Si content of needles in evergreens potentially provides an important positive feedback loop to sustain needles over multiple years, and could provide conifers with a competitive advantage. It needs to be emphasised that other studies have actually found higher Si content in broad-leaved species compared to gymnosperms: it is thus not a general observation that Si content is highest in conifers.

fers (e.g. Cornelis et al. 2010). To understand the eventual influence on Si fluxes of both the higher retention capacity of Si in the Changbai Mountain conifers (but also potentially higher bio-stimulated weathering) and the higher Si turnover rates in the broad-leaved species (but also reduced biological uptake), vegetation scientists and biogeochemists need to cooperate. Soil Si fractions (both dissolved and solid) and riverine Si fluxes should be linked to processing of Si by the vegetation, and to vegetation functioning and characteristics (competition between conifers and broad-leaved species, biomass production, vegetation seasonality). Research in the eastern Pyrenees e.g. pointed to temperature and rainfall as important factors regulating decomposition rates in high-altitude *Pinus sylvestris* L. (Pausas 1997), but also indicated that other currently unknown factors are important: we hypothesise that Si content could be one (Schaller et al. 2012b).

Major shifts in vegetation are expected in alpine regions due to climate change (Walther et al. 2005; Weber et al. 2007). Plant functional types provide a powerful tool in climate change research, as they bridge the gap between plant physiology, community and ecosystem processes (Diaz and Cabido 1997). We here hypothesise that Si plays an important functional role in vegetation shifts in high altitude and high latitude regions, due to important role in coping with environmental stressors, especially in grasses. Environmental variables (e.g. soil pH), vegetation distribution, water and energy exchange all affect the carbon burial potential (McGuire et al. 2002) at high latitudes, with coordinated studies required to further elucidate how interactions among climate, disturbance, and vegetation distribution influence carbon dynamics and water and energy exchange (McGuire et al. 2002). The potential importance of phytolith for carbon sequestration, the functional role of Si in plants and the resulting impact on export Si fluxes all warrant a coordinated research effort between scientists working at community and ecosystem level, focusing on both vegetation dynamics and biogeochemistry.

Fauna can also impact the transport of Si through rivers through its interaction with vegetation. In a study in the Shenandoah National Park (USA), sudden declines in the DSi concentration in streams, that could not be explained by short-time variations such as differences in hydrological flow paths or mineral contact time, coincided with a gypsy moth (*Lymantria dispar* Linnaeus, 1758) defoliation event (Grady et al. 2007). This species is invasive in North America and can cause intense defoliation and tree dieback. The defoliation event caused a pulse in stream water nitrate. In addition, more light was able to penetrate the vegetation canopy. The authors showed this stimulated diatom populations to bloom year after year, explaining the observed DSi decrease in the streams. This example demonstrates that vegetation can also influence Si dynamics through indirect effects, such as shading and impact on other nutrients.

Herbivory can alter uptake of Si by vegetation, or could cause the vegetation to become dominated by more Si accumulating species (e.g. grasses). Population density of voles was linked to a fluctuating Si content in grazed grass species (Massey et al.

2008). During periods with high vole densities, grasses took up more Si, eventually rendering grazing less efficient and reducing the vole population. Si was therefore hypothesised by these authors to contribute to the cyclic abundance of voles (Massey et al. 2008). In a similar way, high silica levels in perennial savanna grasses of the Serengeti have been explained by long co-evolution between grasses and large grazers (McNaughton et al. 1985), thereby maintaining biotic diversity of both grasses and grazers in the savanna ecosystem. This impacts on storage and recycling of Si in ecosystem soils and thus potentially impacts on transport through rivers. Vegetation-environment relationships are stronger in moderate to heavily grazed situations compared to (near) ungrazed situations (Cingolani et al. 2003), with consumer control (grazing/fire) one of the most important controllers (along with climate) on the distribution of vegetation (Bond 2005). We therefore hypothesise that plant Si metabolism is an important physiological trait to include in multivariate studies exploring response of vegetation to grazing disturbance (e.g. Louault et al. 2005).

These examples clearly show that vegetation, and external impacts on this vegetation, can directly and indirectly change fluxes of Si. Small or large changes in vegetation structure may impact Si fluxes to lower parts of the river basin. Here, a new field is opening for ecologists and biogeochemists: to understand why some ecosystems have far more biological control on the Si cycle and to unravel why certain plant species in a particular ecosystem are specialised in Si uptake, affecting their competitive ability and physiology.

6.3.2 Lowland rivers and floodplains

Rivers and their floodplains are highly dynamic ecosystems, providing a wide range of ecosystem goods and services such as nutrient control, water supply and flood protection (Hoeinghaus et al. 2009; van Diggelen et al. 2006). Vegetation in these ecosystems is an understudied, yet potentially crucial controller in the global Si cycle, with Si playing a role in the potential of vegetation to withstand hydrodynamic stress and therefore, in the occurrence of plants in high-stream flow environments. Common aquatic- and wetland vegetation contains significant amounts of Si (Hodson et al. 2005; Schoelynck et al. 2010; Struyf and Conley 2009), which influences the physical strength. Hydrodynamic forces in the Biebrza River (Poland) were identified as a trigger for BSi incorporation in Yellow Water-Lily (*Nuphar lutea* Sm.), which was also demonstrated experimentally for two submerged macrophytes: *Egeria densa* Planch. and *Limnophila heterophylla* (Roxb.; Schoelynck et al. 2012a). Individuals growing in a hydrodynamic environment (rivers) incorporated more Si than individuals from stagnant water (oxbow lakes), regardless of DSi concentration in the water (Schoelynck et al. 2012a). The Si content of vegetation tissue can be linked to cellulose and lignin contents, two other molecules known to provide structural rigidity to plants (Schaller et al. 2012a; Schoelynck et al. 2010). There is increasing evidence that Si concentration in aquatic species litter is a major factor driving decomposition rates, due to its impact on phenol, cellulose and lignin content and litter stoichiometry (Schaller et al. 2012a; Schaller et al. 2012b). This can have large effects on eco-

system productivity (Hilton et al. 2006) and nutrient availability, which in turn directly affects vascular plant distribution (Bragazza and Gerdol 2002).

Several studies have argued that water velocity is the main factor in regulating aquatic macrophyte distribution, composition, biomass and metabolism in rivers (Franklin et al. 2008; Marshall and Westlake 1990). Macrophytes (partly due to incorporation of Si) withstand the current and physically hamper the flow (de Doncker et al. 2009). This results in the development of self-sustaining vegetation patchiness (linked to occurrence of low- and high flow zones in rivers) with vegetation controlling litter accumulation (Schoelynck et al. 2012b). In many parts of the world, current land-use and increased intensification of agriculture practices force lowland rivers to drain larger water quantities during ever shortening time periods. Drainage, however, is hampered by human artefacts such as dams and bridges as well as by naturally occurring aquatic vegetation. High biomass can lead to river obstructions, rising water levels and increased flooding frequency (Bal and Meire 2009). To avoid flooding and water related problems, river managers opt to remove aquatic vegetation in certain circumstances (Fig. 6.2). Yearly weed cutting may favour the growth of species like *Sparganium emersum* Rehnmann (Riis et al. 2000) because shoots can originate from their basal meristem (Sand-Jensen et al. 1989) giving them a competitive advantage. Analysis showed that *S. emersum* (commelinoid monocot) in the Zwarte Nete (Belgium) contains about twice the amount of BSi than the original eudicot species *Callitriche platycarpa* Kütz. (Schoelynck, unpubl. data). This corresponds to the study by Hodson et al. (2005) who describe the phylogenetic variation in shoot Si concentrations within angiosperms and observed that shoot Si concentrations decreased in the order commelinoid monocots > non-commelinoid monocots > eudicots. This shows how plants' ability to functionally use Si can help it adapt to a dynamically changing environment. Increased obstructions can also increase water residence times in rivers and floodplains, potentially enhancing the trapping of BSi-rich material, as previously observed in lakes and artificial reservoirs. Humborg et al. (2000), among others, showed that these artificial water bodies have the potential to significantly impact river biogeochemistry due to their strong total suspended solids and BSi trapping efficiency as well as reduction on DSi through diatom blooms. This complicated web of interactions between Si, vegetation strength and river flow shows how intricate the range of processes and functions linked to Si uptake by plants can be, showing the need for combined efforts by a wide range of scientists to unravel it.



Fig. 6.2: Management practices may cause a shift in species composition or dominance that may affect the Si-vegetation equilibrium. Left panel: Mowing activities in a lowland river (Belgium) ensures drainage: macrophytes are mechanically removed from the water. Right panel: *Carex appropinquata* A.Schumach. forms tussocks on an unmanaged floodplain meadow along the Biebrza River (Poland). Aboveground biomass has been partly removed revealing tussock structure. These two examples clearly show that management practices may cause a sudden uptake or mobilisation pulse of Si. The activities may also cause a shift in species composition or dominance (resembling invasive plant scenarios) that may affect the Si-vegetation equilibrium.

6.3.3 Tidal wetlands

Many tidal marshes are efficient traps for BSi, which is deposited on the marsh surface during tidal inundations (Hackney et al. 2000; Norris and Hackney 1999; Struyf et al. 2006; Vieillard et al. 2011). With a continuous flow of soil seepage water from these – often water saturated – marsh sediments, DSi can be exported to the estuarine channel, supplying an additional source of dissolved silica to the estuary (Jacobs et al. 2008; Struyf et al. 2006; Vieillard et al. 2011). For a European tidal freshwater marsh, Struyf et al. (2007) found 85% of the BSi contained in *P. australis* dissolved within the first 150 days after dieback/litter formation. The dominance of highly-productive grass species, which generally contain high amounts of BSi (Epstein 1999; Lanning and Eleuterius 1983), combined with the continuous import of nutrients from the estuary, leads to a quick nutrient turnover (Aselmann and Crutzen 1989). The wet soils allow for high transpiration rates, enhancing Si uptake (Jones and Handreck 1967), while frequent flooding provides a continuous hydrological pathway for nutrient import and export.

Compared to ocean surface water, where DSi concentrations are usually $< 2 \mu\text{mol L}^{-1}$ (Tréguer et al. 1995), global average for rivers is relatively high at $160 \mu\text{mol L}^{-1}$ (Dürr et al. 2011). However, in spring and summer, DSi can still be completely depleted in estuaries (Boderie et al. 1993), the key transition zones between rivers and oceans. In

these seasons, discharge from tidal marshes with DSi concentrations of up to $320 \mu\text{mol L}^{-1}$ (Struyf et al. 2006), can become an important nutrient source for diatoms (Bacillariophyceae). As an important food source for primary consumers, diatoms fill a key position in the estuarine food web (Sullivan and Moncreiff 1990). By exporting DSi to the estuary, tidal marshes consequently contribute to the productivity of the system (Hackney et al. 2000). Besides processing and filtering Si in estuarine ecosystems as a whole, BSi accumulation in tidal marshes contributes to the functioning and composition of the vegetation. Si is able to increase the ecological resilience of a marsh by improving the resistance of plants against various stressors (Cooke and Leishman 2011a; Currie and Perry 2007; Liang et al. 2007).

Against a background of rising sea level and further expected constructional changes in estuaries associated with economic development in many regions in the world (Castro and Freitas 2011; Tate et al. 2004), Si induced attributes may become even more valuable for plants. As reported for agricultural grass species, incorporating Si in the tissues makes plants more rigid (Rafi and Epstein 1999) and thus, resistant against waves and currents caused by increased ship traffic and stronger flow surges. Querné et al. (2012), however, did not find increases in BSi concentration in *Spartina alterniflora* Loisel. with increasing abiotic stresses (waves and salinity), but the study did not exclude the possible role of Si in alleviating these stresses either. The impacts of salt water intrusion in the estuary due to dredging activity might be ameliorated by Si-induced salt tolerance (as already observed for e.g. wheat; Ali et al. 2012). It has also been shown that Si can increase resistance of some plants to chemical contaminants (Kidd et al. 2001; Nwugo and Huerta 2008), which are still considered to be one of the major threats to estuaries worldwide (Kennish 2002). In general it could be expected that plants that are able to utilise Si to their benefit would be favoured under changing environmental conditions in estuaries.

Si use might even contribute to the competitiveness and dispersal success of some invasive species. For instance, a non-native genotype of the Si-accumulating *P. australis* is currently invading North-American coastal wetlands, threatening local species composition (Hirtreiter and Potts 2012; Meyerson et al. 2000). The native Si-rich grass *Elymus athericus* (Link) Kerguelen has an invasive behaviour in European salt marshes due to change of land use (Bockelmann et al. 2011; de Bakker et al. 1999; Pétilion et al. 2005) and *Arundo donax* L., a Si-rich bamboo-like grass (Chauhan et al. 2011) known to be one of the world's most invasive alien species (Cooke and Leishman 2011a), is invading sub-tropical wetlands on all continents (Herrera and Dudley 2003). All three plant species have very high biomass production. According to Ehrenfeld (2010), this trait is typical of the majority of invasive species and can lead to substantial changes of soil biogeochemistry and nutrient cycling. In terms of Si, it is conceivable that invaders with high Si-uptake rates will stimulate Si transport from deep soil layers to the surface and therefore promote Si exports to estuaries (Struyf et al. 2007). However, in case of low decomposition rates accompanied by frequent flooding, a considerable fraction of Si could be buried under sedi-

ments, as reported for carbon in *E. athericus*-dominated salt marshes (Valéry et al. 2004). Any change in silica pathways in tidal marshes, due to changes in vegetation with different Si metabolisms, could strongly impact the role of marshes as importers of BSi and exporters of DSi.

Finally Si reaches the coastal zone where it is incorporated in diatom frustules or marine sponges (Maldonado et al. 2010) or in (sub)tropical tidally-driven coastal mangroves, which is a potentially interesting, yet far understudied ecosystem in the Si cycle. Studies in the Bhitarkanika mangrove system at the east coast of India (Chauhan and Ramanathan 2007) and in the mixed *Rhizophora* forests lining Coral Creek on Hinchinbrook Island (Australia; Alongi 1996), show these ecosystems to be a very efficient Si sink. This import may be driven by the consistently high rates of plant growth and productivity within the forests, where Si may serve as stress reliever (Ye et al. 2012).

6.4 Outlook

6.4.1 The human factor

Humans have been modifying natural landscapes and native vegetation for thousands of years. Yet today's growing population and rising food demands are causing land use changes at the expense of natural vegetation systems at unprecedented levels. The implications of land use changes for Si pools and fluxes as well as vegetation Si dynamics are just beginning to be understood and the impacts are significant (Carey and Fulweiler 2011; Clymans et al. 2011; Conley et al. 2008; Struyf et al. 2010a). Croplands and pastures are often dominated by grassy vegetation, hence management and reaction to disturbance is potentially strongly linked to plant Si dynamics. Harvesting of crops containing high levels of Si, reduces the amount of Si that is released into soil biogenic Si pools, with large amounts of BSi annually exported through agricultural production (Vandevenne et al. 2012). Persistent cropping of winter wheat straw in the UK decreases available Si in top soils, whereas a re-building of soil phytolith storage is seen in reforested fields, due to slower litter decomposition under acidic conditions (Guntzer et al. 2011). Applying artificial Si fertilisers to enrich Si-depleted cultivated soils is one solution to this problem (Currie and Perry 2007). A similar effect can be achieved using economical crop species like bamboo that have the ability to actively uplift Si from deeper layers to the surface (Parr et al. 2010). In Indonesia, local farmers have been practicing the "bamboo-kebun" crop rotation system, consisting of annual food or cash crops (kebun) alternating with tree crops (i.e. clumps of bamboo species). Bamboo plays a key role in both the cycling and retention of organic matter (Christanty et al. 1997) and nutrients (Mailly et al. 1997), restoring fertility during the fallow period of shifting cultivation systems. The traditional belief of Indonesian farmers "without bamboo the land dies" hints at the tremendous importance of bamboo for soil Si stores and pathways. First estimations for temperate regions point at a 10% reduction of BSi storage in soils since historical land use changes occurred (Clymans et al. 2011). These land use changes are respon-

sible for up to 20% of the global riverine Si flux from land to ocean (Clymans et al. 2011).

Although pastures and meadows are (often) cultural ecosystems, traditional management methods result in large plant diversity and mosaic landscapes with high species richness (Weibull et al. 2003). Cessation of traditional management in such mosaic landscapes can result in species shifts towards generalist species, at the expense of specialists, due to landscape homogenization (Dullinger et al. 2003; Eriksson et al. 2002). In the Biebrza National Park in Eastern Poland, unreclaimed low productive meadows have traditionally been mown for hay, but abandonment began in the 1970's. Around 1981-1983, ca. 30000 ha was still mown annually (Banaszuk 1994), while today less than 5000 ha of meadows within the park boundaries is still mown or grazed. On abandoned parcels, the original succession restarts growing monocots, especially grasses (Poaceae) and sedges (Cyperaceae) of which many form tussocks. Tussock formation in wet meadow plants is a fairly common occurrence and is observed in several (Si accumulating) graminoids (Costello 1936; Taylor et al. 2001). It appears to be a stress avoidance strategy for plants to escape waterlogging and associated low oxygen levels and soil toxicity by elevating their rooting substrate (van de Koppel and Crain 2006). Inside these tussocks, apparent aerobic conditions may enhance nutrient cycling (Olde Venterink et al. 2002), including Si cycling (Fig. 6.2). In a study comparing the BSi stock in the above ground biomass of *Carex appropinquata* A.Schumach. of unmanaged (tussock) parcels and managed parcels, 6 times more BSi was found in the unmanaged parcels (Opdekamp et al. 2012). This could partly be ascribed to the repetitive removal of biomass (and hence BSi) from the mown fields, causing a degradation of the stock, but also to the tussocks' engineering capacity; living vegetation traps dead material and its own litter and stimulates an intense internal recycling of nutrients from which almost no Si leaks out. This could provide the tussock-formers with a competitive advantages; it creates a strong availability of Si for the tussock grasses, which in turn helps them to sustain their rigidity in a dynamic environment.

6.4.2 Recommendation

Si delivery from the continents plays an essential role in the occurrence of eutrophication problems in the coastal zone: the ratio in which Si, N and P are delivered is a determining factor for the occurrence of nuisance algal blooms (which usually occur when increased N and P input coincide with Si-limitation; Cloern 2001). The direct impact of Si dynamics on three of the major global carbon sinks is even more compelling (Ragueneau et al. 2006; Street-Perrott and Barker 2008). First, the weathering of mineral silicates is an important sink for atmospheric CO₂ on geological time-scales as CO₂ is absorbed in the weathering process to form carbonate and release silicate (Struyf et al. 2010b). Secondly, organic carbon occluded within phytoliths is highly resistant to decomposition compared to other soil organic carbon components. Its accumulation within the soil is an important process in the terrestrial sequestration of carbon (Parr and Sullivan 2005). Thirdly, the import of Si into coastal zones from

the terrestrial environment is essential to sustain diatom growth. Dead frustules and associated carbon are ultimately reincorporated into sediments and plays a key role in the oceanic C-sink (Rabosky and Sorhannus 2009).

Multi-disciplinary studies are required to better understand the broader effects of local Si-vegetation interaction. We conclude this review with a list of diverse scientific scenarios (Tab. 6.1) that such studies could address. The questions are grouped according to three themes: natural ecosystems, agricultural ecosystems and environmental management. All examples have worldwide significance because of ever-growing human environmental pressures. Other disciplines than those mentioned in the table maybe indispensable (e.g.: hydrology, geology, and microbiology). To facilitate interpretation of the table, two of the scenarios are briefly elaborated here as examples. In a first example, the effect of grazing by insects and large herbivores on the Si cycle is proposed. The expertise of ecologists, plant physiologists and biogeochemists are needed to understand plant response to herbivory (such as induced Si accumulation), the resultant changes in plant productivity and altered Si mobilisation potential from faecal matter vs litter fall. The Si flux rate is expected to be relatively slow as it depends on many factors (hydrology, in-field recycling). In a second example, the effect of fire as management technique is discussed. An accidental fire at the Kalmthoutse Heide (Belgium) in 1996 (and again in 2011) destroyed many hectares of *Erica* species and resulted in the encroachment of *Molinia caerulea* L. (a high Si accumulating species; Jacquemyn et al. 2005). It requires a combined scientific effort from ecologists (vegetation shift), physiologists (Si accumulating species emerge, but also fire resistant species) and biogeochemists (shifted abiotic conditions and altered Si mobilisation potential from the ash) to quantify the impact of this fire on the Si cycle, and to elaborate how Si could potentially play a role in vegetation resistance to fire stress and invasion rates after the fire. The subsequent Si flux rate is initially expected to be fast as a lot of stored BSi becomes suddenly available from ash (parallel to other elements N, P, Ca, Mg, K; Kucerova et al. 2008).

Tab. 6.1: Examples of scenarios that could affect Si transformation and export from an ecosystem together with an indication of scientific specialisations required to tackle these new research horizons (indicated with +) and an indication of the expected rate of the Si flux. The requirement of a scientist is based on its field of interest covering the various key factors that primarily determine ecosystem Si dynamics (based on Struyf and Conley 2012).

	Ecologist	Biogeo- chemist	Physiolo- gist	Si flux rate
<i>Key factors:</i>	<i>Ecosystem biodiversity</i>	<i>Abiotic conditions</i>	<i>Within plant response</i>	
Natural ecosystem				
<i>Invasive plant species:</i> An invasive Si-accumulator may impact abiotic conditions and Si dissolution rates because of increased Si uptake by the vegetation.	+	+	0	slow
<i>Invasive animal species:</i> Native vegetation is affected by an invasive herbivore that may also trample or burrow in the soil. BSi processing may increase due to herbivory, but the vegetation increase Si uptake as herbivore defense.	+	+	+	fast
<i>Abiotic stress:</i> Increased UV radiation, salinity, drought or heavy metal pollution may cause plant stress that can be relieved by Si. Plant reaction may involve Si uptake, resembling macrophyte reaction to hydrodynamic stress (Schoelynck et al. 2012a), ultimately reducing output of Si to rivers.	+	+	+	slow
<i>Eutrophication:</i> Increased nutrient availability will increase vegetation production and will induce a shift towards fast-growing species, with potentially higher uptake of Si and faster turnover (e.g. high productive grasslands or nettles which are relatively Si rich; Struyf et al. 2005b).	+	+	0	slow
Agricultural ecosystem				
<i>Genetically modified organisms:</i> Biofuels are less efficient with more BSi in biomass material. Industry prefers highly productive crops with low BSi content. This might alter vegetation control on Si fluxes.	0	0	+	slow
<i>Grazing:</i> Pastures are grazed by insects and large herbivores. The grass will show several growth cohorts, influencing the systems' productivity and the system will shift towards species with higher Si content (Garbuzov et al. 2011; Reynolds et al. 2009).	+	+	+	slow
<i>Reduced soil stability (erosion):</i> In high-productivity arable farming the potential for soil erosion is high, leading to high exports of soil BSi in suspended material resulting in soils depleted in plant available Si.	+	+	0	fast
<i>Water management:</i> To increase productivity, hydrology is managed. Still, abiotic conditions can shift abruptly. Pulse fluxes of Si are associated with flooding/drainage events.	+	+	0	fast
Nature management				
<i>Succession fixation:</i> Natural succession is prevented. Soil biogeochemistry is kept stable artificially.	+	+	0	slow
<i>Fire:</i> Fire rejuvenates succession. Abiotics suddenly shift, causing abrupt Si mobilization (ash). A new dominant vegetation appears (e.g. <i>Molinia caerulea</i> L. (Poaceae) encroachment in heath lands (Jacquemyn et al. 2005).	+	+	0	fast
<i>Mowing:</i> Dominant vegetation is mown to increase rare species diversity (e.g. (Metsoja et al. 2012). Si is exported in harvest. Plants may invest in Si uptake (see herbivory).	+	0	+	fast
<i>Topsoil removal:</i> Topsoil is removed, suddenly changing abiotic conditions. Rapid Si export flux occurs (as BSi in removed soil). Dominant vegetation completely shifts.	+	+	0	fast
<i>Rewetting:</i> To restore wetlands, hydrology is managed. Hydrological connections are re-established, allowing increased exchange fluxes. With abrupt shifts in abiotic conditions, and vegetation shifts entirely.	+	+	0	fast

Table 6.1 is testimony to the lack of knowledge that currently exists on interactions between plant Si metabolism and whole ecosystem Si cycling. The scenarios addressed here could appear straightforward to scientists specialising in other major elements, but they are not to the scientists aiming to predict effect of land use changes or vegetation shifts on the Si cycle, or aiming to predict how vegetation Si metabolism can and will respond to these environmental changes. We emphasise that multidisciplinary studies are potentially of high scientific value: they could change our understanding of ecosystem Si cycling, and hence of linked element cycles. As described above, the terrestrial and aquatic Si cycle is strongly linked to important carbon sinks. However, research now also shows that the availability of Si impacts on plant nutrient and metal uptake, and hence also potentially alters plant decomposition (Schaller et al. 2012a; Schaller et al. 2012b), which largely depend on e.g. C/N ratios (Taylor et al. 1989). Only a concerted effort bringing scientists together from a broad array of disciplines as suggested above will allow providing this new direction to research on plant and ecosystem Si cycling.

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Box 1 Surface elevation change

In the face of a rising sea level, monitoring of surface elevation change (SEC) in salt marshes is of great importance. A dense vegetation cover can increase sediment deposition rates in marshes (Baustian et al. 2012). Consequently also grazing management can affect sedimentation processes in salt marshes. The hypothesis of this study was therefore that ungrazed salt marshes have a higher SEC than grazed sites.

The study was conducted at Dieksanderkoog (DSK) and Sönke-Nissen-Koog (SNK) in the Schleswig-Holstein Wadden Sea National Park, Germany. In October 2009, 16 sedimentation erosion bars (SEB; see section 1.4.4) were installed; eight per study site and four per grazing treatment. Per study site, four of the SEBs were placed at locations close to the marsh edge ('seawards') and four close to the land ('landwards'). Until March 2012, SEC was measured each spring and autumn. Wilcoxon-test and Pearson's correlation coefficient were used to determine the influence of study site, treatment, location, distance to marsh edge, distance to the next creek and elevation.

Over the whole period of 2.5 years, a mean SEC of 6.8 mm yr⁻¹ was documented. At one location, no SEC could be determined over the whole period, at other locations, rates of up to 14.0 mm yr⁻¹ were reached. No significant differences were found among study sites, locations, or grazing treatments (Fig. Box 1.1).

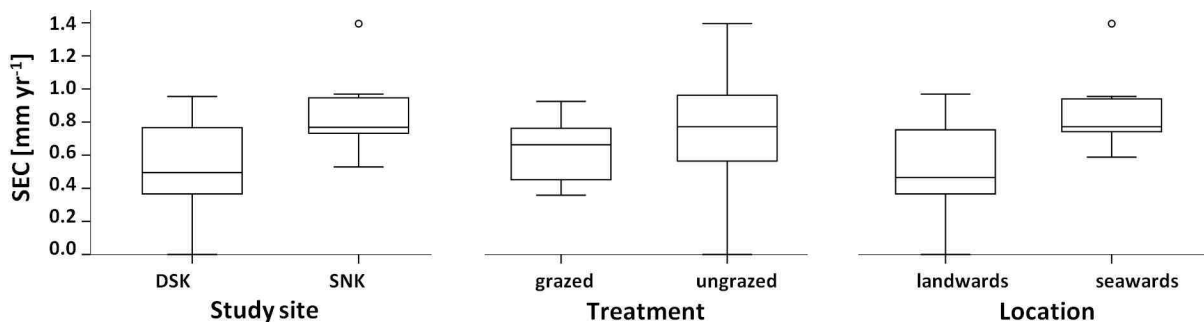


Fig. Box 6.3: Surface elevation change (SEC) measured with 16 sedimentation erosion bars. DSK=Dieksanderkoog; SNK=Sönke-Nissen-Koog. After Bonferroni corrections statistical significance was determined with the probability $p < 0.017$. Statistics for study site: $Z = -1.8$; $p = 0.074$, location: $Z = -2.1$; $p = 0.036$ and treatment: $Z = -1.1$; $p = 0.26$. Boxplots represent medians, quartiles and outliers. SEC was significantly correlated to distance to the marsh edge ($r_s = -0.54$; $p < 0.05$) and to distance to the next creek ($r_s = -0.51$; $p < 0.05$), but not to elevation ($r_s = -0.28$; $p = 0.28$).

The determined SEC can be considered to let the marshes keep pace with current projections of sea-level rise (1.8 mm yr⁻¹ between 1961 and 2003; IPCC 2007). Up to 70% of the total SEC was registered in the winter 2011/12, underlining the importance of storm surges in the sediment deposition. Only a tendency of a higher SEC on ungrazed sites was observed. However, tendencies were stronger for factors such as study site and location. For an assessment of the consequences of management on surface elevation change of Wadden Sea salt marshes, a larger data set would be necessary to draw broader conclusions.

7

Does livestock grazing influence salt marsh resilience to sea-level rise in the Wadden Sea?

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7.1 Abstract

Sea-level rise (SLR) can be a major threat to coastal ecosystems, such as salt marshes. The resilience of salt marshes to SLR is largely determined by their ability to respond with increased accretion rates. In European salt marshes, livestock grazing is common practice, but its effect on marsh accretion has hardly been studied. Grazing by livestock might influence accretion rates directly, by increasing soil compaction through trampling, and indirectly, by reducing aboveground biomass and thus decreasing sediment deposition rates. We therefore expect accretion to be lower in grazed compared to ungrazed salt marshes. In four study sites along the mainland coast of the Wadden Sea, accretion rates, sediment deposition rates and soil compaction of grazed and ungrazed marshes were analysed by using the ^{137}Cs radionuclide dating method. At each study site, landward and seaward locations were differentiated. Accretion rates were on average 11 mm yr^{-1} during recent decades and thus higher than current and projected rates of SLR. Neither accretion (mean: grazed 9.9 and ungrazed 13.7 mm yr^{-1}) nor sediment deposition rates (mean: grazed 6.61 and ungrazed $7.01 \text{ kg m}^{-2} \text{ yr}^{-1}$) were significantly different between grazing treatments, but both were higher on the seaward than on the landward location (mean accretion: seaward 13.7 and landward 9.3 mm yr^{-1} ; mean sediment deposition: seaward 8.03 and landward $5.39 \text{ kg m}^{-2} \text{ yr}^{-1}$). Compaction was clearly affected by grazing with signifi-

cantly higher values of compactibility on the grazed parts of the marshes (mean compactibility: grazed 5.9% and ungrazed 9.5%; seaward 6.3% and landward 8.9%). We conclude that the interplay of grazing with other factors might be of great importance to evaluate the resilience of salt marshes to SLR.

7.2 Introduction

Many coasts of the world show an enhanced rate of sea-level rise (SLR) over the last century, and studies predict it to accelerate even faster in the future (IPCC 2007). Global SLR was 3.1 mm yr⁻¹ between 1993 and 2003 (IPCC 2007). For the Wadden Sea, a long-term SLR of 1-2 mm yr⁻¹ was reported for the last 50 to 100 years while mean high tide (MHT) even increased by 2-2.5 mm yr⁻¹ (Oost et al. 2009, citing several authors). As a consequence of SLR, 5-20% of all coastal wetlands will be lost until 2080 (Nicholls 2004). Among these coastal ecosystems are for example mangroves (e.g. Krauss et al. 2010), tidal freshwater forests (e.g. Craft 2012) and salt marshes (e.g. Morris et al. 2002). Salt marshes provide many ecosystem services (Short et al. 2000), such as improving coastal protection by attenuating wave energy (Möller 2006), carbon sequestration (Callaway et al. 2012), and harbour a unique flora and fauna (Schmidt et al. 2012).

The resilience of salt marshes to SLR is largely determined by their ability to compensate higher water levels by increased accretion rates: Only if accretion rates are sufficiently high, will a salt marsh be able to keep pace with relative SLR. Salt-marsh accretion is defined as the increase in surface elevation relative to a marker horizon or a local measuring device (Cahoon et al. 1995; Van Wijnen and Bakker 2001). The accreted material on top of the marker horizon is subject to shallow subsidence caused, for instance, by autocompaction (Bartholdy et al. 2010). Even if many studies have already investigated accretion rates in salt marshes (e.g. Cahoon and Turner 1989; Belluci et al. 2007; Baustian et al. 2012) and a number of models exist to predict the future development of salt marshes (e.g. Allen 1990; Temmerman et al. 2003; Bartholdy et al. 2004), the question if current accretion rates in salt marshes are sufficiently high to outpace SLR is still a point of discussion (e.g. Suchrow et al. 2012).

In general, important factors influencing accretion rates in tidal marshes are distance to the sediment source (creek or marsh edge; e.g. Esselink et al. 1998; Reed et al. 1999; Bartholdy et al. 2004), elevation affecting flooding frequency and duration (e.g. Richard et al. 1978; Stoddart et al. 1989; Temmerman et al. 2003), and suspended sediment concentration (SSC) of the inundating water (Temmerman et al. 2004). An important mechanism for the spatial variability of sediment deposition rates is the reduction of the flow velocity above the vegetated marsh surface (Temmerman et al. 2012), which can lead to increased sediment deposition at sites with higher biomass (Morris et al. 2002) and/or in the vicinity of tidal creeks or the marsh edge (Christiansen et al. 2000; Temmerman et al. 2004; van Proosdij et al. 2006).

Whether and how grazing management affects accretion rates on these marshes is scarcely studied (e.g. Andresen et al. 1990; Neuhaus et al. 1999; Stock 2011, Suchrow et al. 2012). Mainland salt marshes at the Wadden Sea coast represent 10% of all European temperate salt marshes (Bakker et al. 1997). Here, livestock grazing for agricultural purposes used to be common (Esselink et al. 2000). Since the 1980s, however, grazing was reduced in many of these salt marshes primarily for nature conservation reasons (Esselink et al. 2009). We expect grazing livestock to influence accretion rates in salt marshes in different ways: directly, by increasing soil compaction through trampling (Olsen et al. 2011); and indirectly by reducing aboveground biomass (e.g. Kiehl et al. 1996) and thus lowering the input of mineral sediments.

We studied effects of livestock grazing on the resilience of salt marshes to SLR by quantifying accretion and sediment deposition rates as well as soil compaction in grazed and adjacent ungrazed parts of four salt marshes along the mainland coast of the Wadden Sea. To account for within marsh variation, landward and seaward locations were sampled at each study site.

We tested the following hypotheses:

- 1) Vertical accretion rates are lower in grazed compared to ungrazed salt marshes. To prove this we calculated accretion rates by radionuclide dating of sediment horizons in soil cores.
- 2) Sediment deposition rates are lower in grazed compared to ungrazed sites. This was investigated by calculating the yearly amount of settled sediment per unit area.
- 3) Soil compaction is higher on grazed compared to ungrazed sites. This hypothesis was tested by comparing the compactibility and the bulk density of the soil.

7.3 Material and methods

The study was carried out on four different salt marshes in the Netherlands and Germany along the mainland coast of the European Wadden Sea, a shallow depositional coastal system, stretching from the Netherlands to Denmark (Fig. 7.1). The three German study sites are part of the Schleswig-Holstein Wadden Sea National Park, which was established in 1985. The Dutch study site is protected as a national nature conservation area. Traditionally, all study sites were used for intensive livestock grazing and are characterised by a history of coastal engineering. The construction of ditched sedimentation fields, enhancing sediment deposition and establishment of salt-marsh vegetation, led to an even distribution of ditches and a relatively flat topography (Esselink et al. 1998). With increasing importance of nature conservation aims, drainage and grazing were reduced or stopped in many Wadden Sea salt marshes since the 1980s (Esselink et al. 2009). Each of our study sites is subdivided into a grazed and an ungrazed part. Grazing treatments were underway at least 20 years before sampling and have been maintained ever since. The change in grazing

treatment led to a change in vegetation composition in most of the ungrazed and in some of the grazed parts of the study sites between 1988 and 2010 (Tab. 7.1). Salt marsh vegetation types are regularly surveyed for the whole Wadden Sea coast in the framework of the Trilateral Monitoring and Assessment Program (TMAP; Esselink et al. 2009). Vegetation on ungrazed parts of the study sites generally developed from *Puccinellia maritima* or *Festuca rubra* types to the *Elymus athericus* type, which typically implied a development from rather short to high and biomass-rich canopies (Kiehl et al. 2001). Vegetation on grazed parts of the marshes often developed from *Puccinellia maritima* to *Festuca rubra* types or stayed the same (Esselink et al. 2009). The elevation of sampling locations was measured using a levelling instrument (Spectra precision® laser LL500 and laser receiver HR500 by Trimble) or extracted from a digital elevation model using the Software ArcGIS 10 (Tab. 7.1). The same Software was used to assess distance to the next creek and the distance to the marsh edge by means of an aerial photograph.

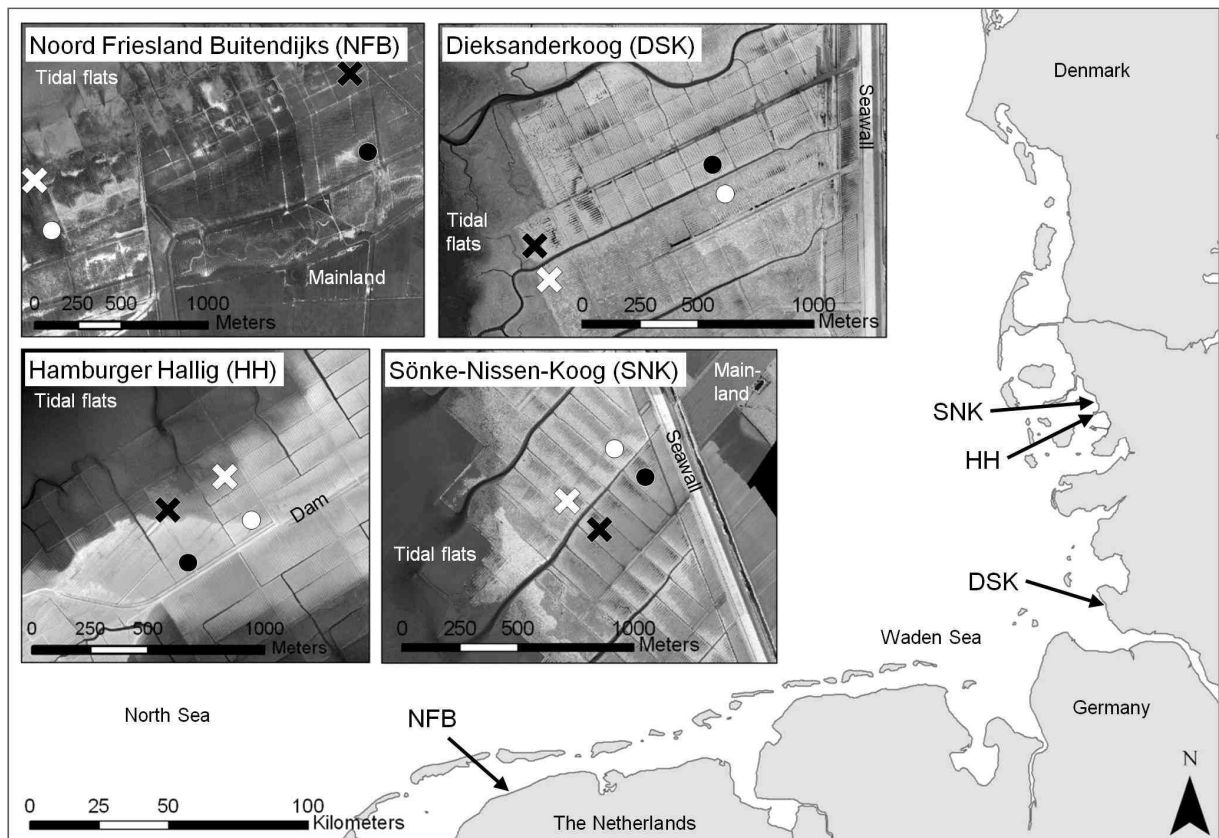


Fig. 7.1: Location of the four study sites on the Wadden Sea mainland coast. Black markers=grazed salt marsh; white markers=ungrazed salt marsh; crosses=seaward sampling locations; dots=landward sampling locations; base maps: Amtliche Geobasisdaten Schleswig-Holstein, © VermKatV-SH and Ministry of Agriculture, Nature and Food Quality, Copyright Slagboom en Peeters 2009.

The salt marsh Noord-Friesland Buitendijks (NFB), the Netherlands ($53^{\circ}20'11''$, $5^{\circ}43'40''$), is exposed to a tidal amplitude of about 2.1 m. The sedimentation fields leading to marsh development were installed in the years 1952 to 1960. Large parts of

the area have been purchased by the NGO ‘It Fryske Gea’ for nature conservation. Drainage ditches have not been maintained since the year 2000 (Dijkema et al. 2011). Today, the part of the site where sampling took place is moderately grazed by horses (Dijkema et al. 2011). The ungrazed part was abandoned approximately 30 years ago and lies at a distance of 1.8 km to the grazed part.

Dieksanderkoog (DSK) at the mouth of the Elbe estuary, Germany, is a wide salt marsh, which stretches up to 2,000 m from the seawall to the intertidal flats (53°58'23", 8°53'8") and is exposed to a tidal amplitude of 3 m. The marsh started to develop after 1935, when the present seawall and a system of sedimentation fields were constructed (Kohlus 2000). One part of the salt marsh is intensively grazed by sheep and an adjacent part remained ungrazed since the early 1990s (Stock et al. 2005). On the latter part, maintenance of the ditches was stopped after the abandonment of grazing. On the grazed part, however, ditches are still renewed every five years.

Tab. 7.1: Key parameters of the study sites. Tidal amplitude data was retrieved from BSH (2011); NAP= Normal Amsterdam Peil (Dutch Ordnance Datum); NHN=Normalhöhennull (German Ordnance Datum); MHT=mean high tide; TMAP=Trilateral Monitoring and Assessment Program; SEB=sedimentation erosion bar; *= elevation data was extracted from a digital elevation model. TMAP vegetation types were coded as follows: Agr (*Agrostis stolonifera* type), Atr / Puc (*Atriplex portulacoides* / *Puccinellia maritima* type), Ely (*Elymus athericus* type), Fes (*Festuca rubra* type), Puc (*Puccinellia maritima* type), Spa (*Spartina anglica* type).

Site	Location	Treatment	Elevation		TMAP vegetation		Grazing		Distance to		Reference accretion rates		
			absolut	above MHT [m]	in 1988	in 2010	Animals	Inten-sity	creek [m]	marsh edge [m]	[mm yr ⁻¹]	Method	Reference
NFB	Landwards	Ungrazed	1.55 m NAP	0.57	<i>Puc</i>	<i>Ely</i>	-	-	50	380	23.8	Plate	Nolte et al.
		Grazed	1.74 m NAP	0.76	<i>Puc</i>	<i>Agr</i>	Horses	moderate	50	630	7.2		
	Seawards	Ungrazed	1.29 m NAP	0.31	<i>Puc</i>	<i>Puc</i>	-	-	68	100	28.6		unpubl. data
		Grazed	1.49 m NAP	0.51	<i>Puc</i>	<i>Puc</i>	Horses	moderate	100	160	9.2		
DSK	Landwards	Ungrazed	2.11 m NHN	0.49	<i>Fes</i>	<i>Ely</i>	-	-	14	955	3.4	Levelling	WSV 2012
		Grazed	1.91 m NHN*	0.29	<i>Puc</i>	<i>Fes</i>	Sheep	intensive	48	920	5.2		
	Seawards	Ungrazed	2.40 m NHN	0.78	<i>Puc</i>	<i>Ely</i>	-	-	74	290	9.1		
		Grazed	2.25 m NHN*	0.63	<i>Spa</i>	<i>Ely</i>	Sheep	intensive	85	205	9.2		
HH	Landwards	Ungrazed	2.13 m NHN	0.54	<i>Puc</i>	<i>Ely</i>	-	-	55	250	3.3-4.8	SEB	Stock 2011
		Grazed	2.09 m NHN	0.5	<i>Puc</i>	<i>Fes</i>	Sheep	moderate	95	230			
	Seawards	Ungrazed	1.92 m NHN	0.33	<i>Atr/Puc</i>	<i>Atr/Puc</i>	-	-	35	35	3.2-6.3		
		Grazed	1.92 m NHN	0.33	<i>Puc</i>	<i>Fes</i>	Sheep	moderate	40	40			
SNK	Landwards	Ungrazed	2.00 m NHN	0.41	<i>Puc</i>	<i>Ely</i>	-	-	46	525	7.7	Leveling	Suchrow et al. 2012
		Grazed	2.07 m NHN	0.48	<i>Puc</i>	<i>Puc</i>	Sheep	intensive	51	685			
	Seawards	Ungrazed	2.04 m NHN	0.45	<i>Puc</i>	<i>Ely</i>	-	-	47	340	7.7		
		Grazed	2.04 m NHN	0.45	<i>Puc</i>	<i>Puc</i>	Sheep	intensive	48	450			

The study site Hamburger Hallig (HH) is situated behind a small remnant of a former island 3 km off the coast (54°36'8", 8°49'27"). The tidal amplitude at this site is 3.4 m. After the construction of a dam connecting the island with the mainland in 1874, salt marshes began to expand alongside the dam (Palm 2000). The whole salt marsh was intensively grazed by sheep until 1991. Since then, 26% of the area are

moderately grazed and 21% are still intensively grazed, while grazing was abandoned on 53% of the area (Esselink et al. 2009).

The study site Sönke-Nissen-Koog (SNK) is situated 3.5 km north of HH (54°38'4", 8°50'2") and experiences the same tidal amplitude (3.4 m). After the construction of the present seawall and adjacent sedimentation fields in 1925 (Kunz and Panten 1997), a salt marsh developed with a current extent of approximately 1,000 m. The study site is part of a grazing experiment (Kiehl et al. 1996), which started in 1988 and guarantees a continuous intensive grazing on the grazed part. The ungrazed part of the marsh is situated adjacent to the grazed one.

7.3.1 Core processing and soil properties

In the laboratory, each core was cut twice along its side in order to remove one half of the tube. For NFB and HH, processing of the cores was carried out at Groningen University. Here, the cores were cut into 2 cm sections. Each section of soil was weighed, dried in the oven at 105 °C to constant weight, and then weighed again to determine soil moisture. Dry weight and volume per section was used to calculate dry bulk density (g cm^{-3}). The dried material was ground using a Culatti rotor mill to disaggregate the soil particles. The grain size was then analysed by laser diffractrometry (Mastersizer S – long bench MAM 5005) assessing volumetric concentrations of different grain-size classes. Organic matter content was determined as the weight loss after ignition of a 5 g subsample of each section at 550 °C for four hours. For DSK and SNK, processing of the cores was carried out at Hamburg University. Here, the cores were cut into 1 cm sections in the upper 24 cm and into 2 cm sections below. For SNK, sections below 40 cm were cut to 5 cm. Soil moisture, dry bulk density, and organic matter content were determined as described for NFB and HH, and samples were manually ground afterwards. Grain size distribution was analysed using a laser diffraction sensor (HELOS H2249).

In order to measure the activity of the radionuclide ^{137}Cs , the ground soil material of all samples was filled into 120 ml containers. Measurements were performed in the Laboratory for Radioisotopes at Göttingen University, Germany, for a minimum counting time of 250,000 seconds using a low-background coaxial Ge(Li)detector (Schuerch et al. 2012). Because ^{137}Cs sorbs strongly on to small particles, the ^{137}Cs activity was normalised to the mean organic matter content and mean percentage of grain sizes smaller than 20 μm (Kirchner and Ehlers 1998).

7.3.2 The ^{137}Cs dating method

The ^{137}Cs radionuclide ($t_{1/2} = 30.2$ years) is anthropogenic in origin and produced by nuclear fission. In Europe, sediment cores usually show two peaks of increased ^{137}Cs activity, which can be attributed to two historic nuclear events: The upper peak is usually related to the accident at the Chernobyl nuclear power plant in 1986, while the lower peak is caused by the nuclear bomb tests during the 1960s with its maximum in 1963 (Kirchner and Ehlers 1998). In cases where only one peak is present,

the ^{137}Cs activity below the peak was considered to relate the peak to either 1963 or to 1986. If ^{137}Cs activity was approaching zero below the peak, the peak was regarded as resulting from 1963 and not from 1986 since anthropogenic emission of ^{137}Cs only started in the 1950s (Pennington et al. 1973).

7.3.3 Accretion and sediment deposition rates

Before calculating salt-marsh accretion rates we corrected each core for sampling compaction (see below). Then, marsh accretion rates (mm yr^{-1}) were derived from the depth of the identified ^{137}Cs -peak by dividing the respective depth by the time period since 1986 or 1963 (see Dyer et al. 2002).

To determine the input of sediment to a site, we calculated the sediment deposition rate ($\text{kg m}^{-2}\text{yr}^{-1}$; Callaway et al. 1996). For this, dry bulk density (ρ) and thickness of each section (a) above the soil depth with the identified ^{137}Cs -peak were multiplied, summed up and divided by the years passed (t ; Eq. 1). The sediment deposition rate includes both mineral sediment deposition and organic sediment deposition.

$$\text{sediment deposition rate} = \frac{\sum_{i=1}^n (a_i * \rho_i)}{t} \quad (\text{Eq. 1})$$

7.3.4 Soil compaction and dry bulk density

As proxies for soil compaction, dry bulk density and sampling compaction were used. Sampling compaction was measured while taking the cores in the field. For doing this, the actual length of each soil core (distance upper to lower end of the core) was related to its original length (distance soil surface to lower end of the core) resulting in sampling compaction in %. A smaller sampling compaction indicates a higher degree of soil compaction by e.g. trampling. We further compared mean dry bulk densities above the identified ^{137}Cs -peaks. Grazing-induced compaction is assumed to be an important parameter in influencing dry bulk density as found amongst others by Schrama et al. (2012) in salt marshes.

7.3.5 Data Analysis

Site and core characteristics such as elevation in relation to MHT, distance to marsh edge and to the next creek as well as mean organic matter content and percentage of grain sizes smaller than $20 \mu\text{m}$ were compared between sites, grazing treatments and sampling locations using Wilcoxon signed-rank and Kruskal-Wallis tests.

Differences in accretion rates, sediment deposition rates, sampling compaction, and dry bulk density between grazed and ungrazed parts were analysed with a Wilcoxon signed-rank test. The same test was used for analysing differences between seaward and landward sampling locations. Differences between the four study sites were analysed with Kruskal-Wallis tests.

The relation of accretion rate, sediment deposition rate, sampling compaction and dry bulk density to mean organic matter content, mean percentage of grain sizes smaller than $20 \mu\text{m}$ in the upper 50 cm of soil, elevation in relation to MHT, distance to the

next creek and distance to the marsh edge was tested with Spearman's rank correlations. 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.

7.4 Results

7.4.1 Peak identification

In 14 out of the 16 cores, peaks of ^{137}Cs -activity could be identified. Seven cores showed the expected pattern with two peaks (Fig. 7.2), which could be identified as 1986 and 1963, respectively. In five cores, we found a single peak in the core which was identified as 1986. In two further cores, single peaks were found and identified as 1963 because the ^{137}Cs -activity approached zero below the respective peak. No peak could be detected in the core of the seaward ungrazed sampling location at NFB. Here, it is likely that both the 1986- and 1963-peak were below the sampling depth of 80 cm. In the core of the landward ungrazed sampling location at HH, a high activity of ^{137}Cs in a layer close to the marsh surface was found. This peak could not be clearly identified; its position was too shallow to be identified as the 1986-peak. We assume some disturbance in this core and excluded it from the calculation of accretion and sediment deposition rates and of mean dry bulk densities above the ^{137}Cs -peak.

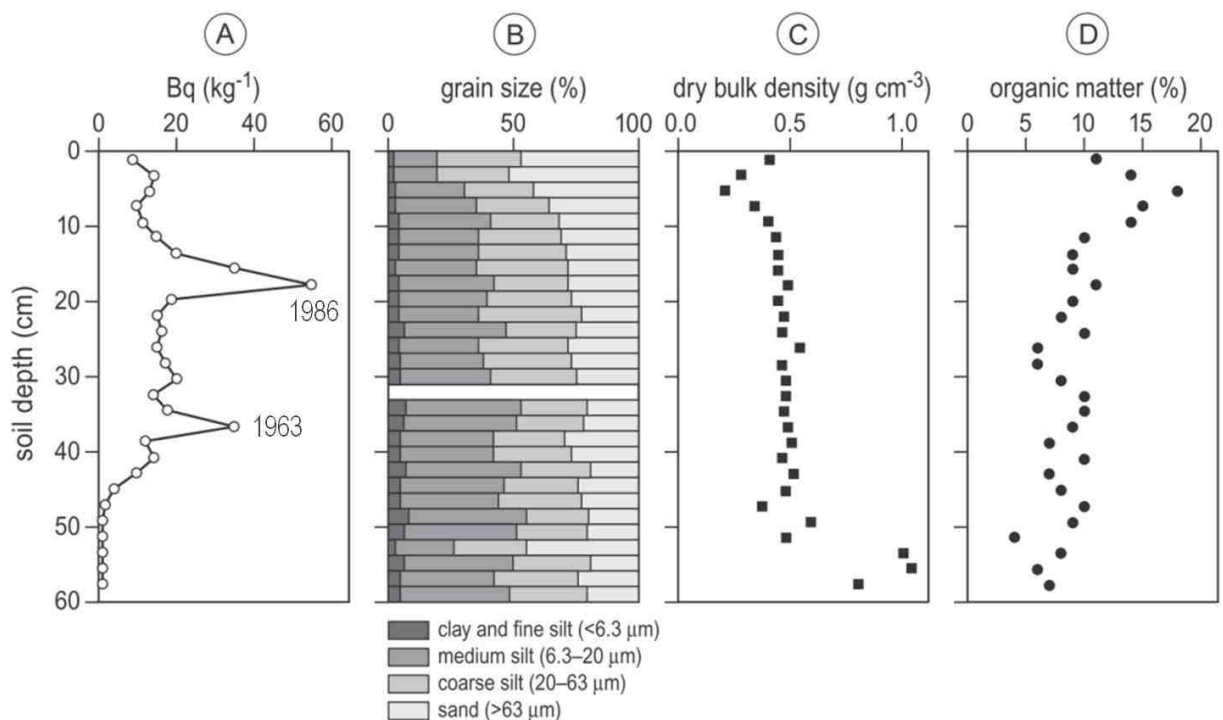


Fig. 7.2: An example for the ^{137}Cs -activity (A), grain size distribution (B), dry bulk density (C) and organic matter content (D) for all depths in the core from the landward grazed sampling location.

7.4.2 Site and core characteristics

Organic matter content, elevation in relation to MHT and distance to the marsh edge did not differ significantly between grazed and ungrazed parts of the marshes (Tab.

7.2). The only difference was observed for the average distance to the next creek, which was slightly smaller for ungrazed parts (median 49 m, range 14-74 m) compared to grazed parts (median 51 m, range 40-100 m; $Z = -2.371$; $p < 0.05$; $N = 16$; Wilcoxon-Test). Beside distance to the marsh edge, which is of course smaller for the seaward location, none of the abovementioned factors differed significantly between seaward and landward sampling locations.

Tab. 7.2: Depth of the ^{137}Cs peaks and mean proportion of grain sizes smaller than $20\ \mu\text{m}$ and mean organic matter content in the upper 50 cm of each core.

Site	Orientation	Treatment	mean percentage		^{137}Cs peak depth		Accretion		Sediment deposition $[\text{kg m}^{-2} \text{yr}^{-1}]$	Sampling compaction [%]	Mean dry bulk density above peak $[\text{g cm}^{-3}]$
			grain size $< 20\ \mu\text{m}$ [%]	organic matter [%]	1986 [cm]	1960 [cm]	Reference year	Rate $[\text{mm yr}^{-1}]$			
NFB	Landwards	Ungrazed	45.8	9.7	56.1	none	1986	23.4	9	10	0.38
		Grazed	40.4	9.4	17.9	36.8	1986	7.5	3	5	0.38
	Seawards	Ungrazed	37.7	8.8	none	none	1986	34.6	11.9	5	0.34
		Grazed	41.4	9.3	46.4	none	1986	19.3	8.5	0.3	0.43
DSK	Landwards	Ungrazed	6.5	2.9	none	43.3	1963	8.7	8.9	11	0.98
		Grazed	22.6	6.4	14.4	26.7	1963	6.1	5.7	6.7	0.91
	Seawards	Ungrazed	22.4	5.4	19.4	47.6	1963	10.1	9.2	10.7	0.89
		Grazed	10.6	3.4	none	46.8	1963	10.4	11.6	4.1	1.09
HH	Landwards	Ungrazed	31.0	5.1	3.3	none	1986	1.4	0.7	8.7	0.38
		Grazed	30.8	5.5	17.9	30.5	1986	7.5	3.5	5.1	0.44
	Seawards	Ungrazed	21.9	3.7	18.9	none	1986	7.5	4	11.1	0.48
		Grazed	23.8	4.2	31.1	none	1986	12.9	7.5	7.2	0.56
SNK	Landwards	Ungrazed	40.9	10.2	12.9	none	1986	5.4	2.8	12.4	0.52
		Grazed	32.5	7.3	15.2	53.4	1986	6.3	4.8	12.4	0.75
	Seawards	Ungrazed	30.3	6.9	14.5	33.7	1986	5.6	3.3	7.1	0.56
		Grazed	27.0	7.5	21.4	49.7	1986	8.9	8.3	4.6	0.93

7.4.3 Accretion rates

The mean accretion rate was $11.6\ \text{mm yr}^{-1}$ and ranged from 5.4 to $34.6\ \text{mm yr}^{-1}$ (Tab. 7.3). Rates did not significantly differ between the grazing treatments (Fig. 7.3). Generally, highest values were achieved at the Dutch site NFB, where rates on the ungrazed parts were twice as high as on the grazed parts (medians $29.0\ \text{mm yr}^{-1}$ and $13.4\ \text{mm yr}^{-1}$, respectively). The three German sites had all lower accretion rates of on average $8.2\ \text{mm yr}^{-1}$. Accretion rates differed significantly between landward and seaward locations (Fig. 7.3). We also found a negative correlation with distance to the marsh edge ($r_s = 0.54$; $p < 0.05$; $N = 15$). No significant correlations were found between accretion rate and distance to the next creek or to elevation above MHT.

Tab. 7.3: Mean accretion rate, sediment deposition rate, sampling compaction and dry bulk density of the four study sites.

Site	Accretion rate [mm yr ⁻¹]	Sediment deposition rate [kg m ⁻² yr ⁻¹]	Sampling compaction [%]	Dry bulk density [g cm ⁻³]
NFB	21.2 ± 11.2	8.1 ± 3.7	5.0 ± 4.0	0.38 ± 0.04
DSK	8.9 ± 2.0	8.8 ± 2.4	8.1 ± 3.3	0.97 ± 0.09
HH	9.4 ± 3.1	5.0 ± 2.2	8.0 ± 2.5	0.47 ± 0.08
SNK	6.6 ± 1.6	4.8 ± 2.5	9.1 ± 3.9	0.69 ± 0.19

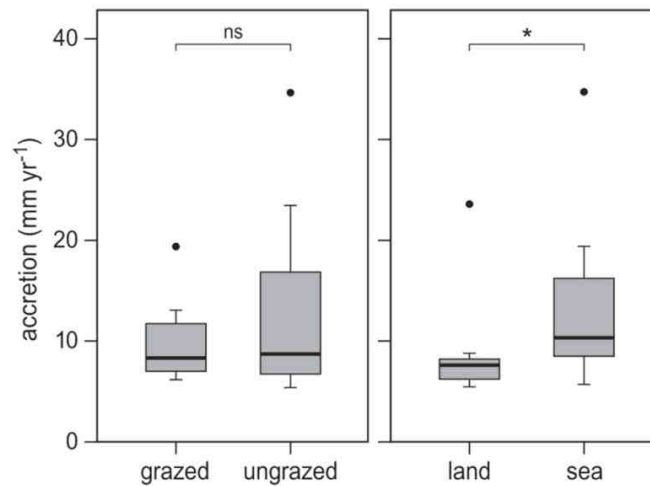


Fig. 7.3: Accretion rates of grazed and ungrazed and landward and seaward locations. Boxplots represent: median (middle line), 25–75% (box), top and bottom quartile (whiskers) and outliers (dots). The grazing treatment had no significant effect ($Z=0.34$; $p=0.74$; $N=15$; Wilcoxon-Test), while accretion rates were significantly higher in seaward compared to landward locations ($Z=-2.37$; $p<0.05$; $N=15$; Wilcoxon-Test).

7.4.4 Sediment deposition rates

The mean sediment deposition rate was $6.6 \text{ kg m}^{-2} \text{ yr}^{-1}$ and ranged from 2.8 to $11.9 \text{ kg m}^{-2} \text{ yr}^{-1}$. It did not differ between the grazing treatments (Fig. 7.4). Also differences between the study sites were not significant ($H=6.57$; $p=0.09$; $N=15$; Kruskal-Wallis-Test). However, we found a trend of higher values at NFB. Here, a median of $10.4 \text{ kg m}^{-2} \text{ yr}^{-1}$ was deposited on ungrazed and $5.8 \text{ kg m}^{-2} \text{ yr}^{-1}$ on grazed parts. At all four study sites, sediment deposition rates were found to be higher at seaward compared to landward sampling locations (medians 8.4 and $4.8 \text{ kg m}^{-2} \text{ yr}^{-1}$, respectively; Fig. 7.4).

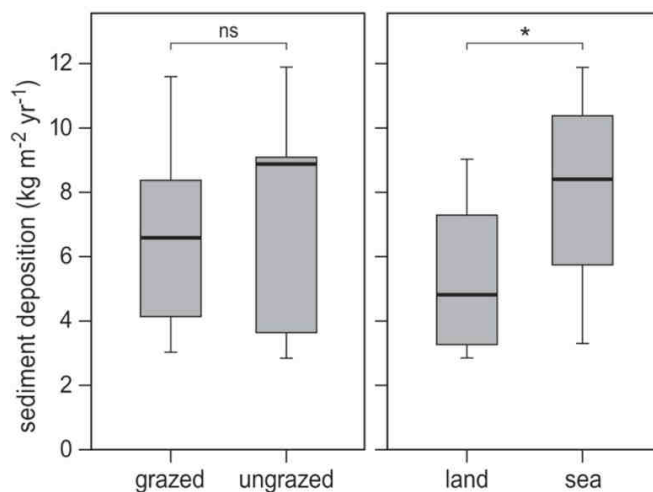


Fig. 7.4: Comparison of sediment deposition rates between grazed and ungrazed and between landward and seaward locations. Box plots represent: median (middle line), 25–75% (box), top and bottom quartile (whiskers). The grazing treatment had no significant effect ($Z=0.00$; $p=1.0$; $N=15$; Wilcoxon-Test), while sediment deposition rates were significantly higher in seaward compared to landward locations ($Z=-2.37$; $p<0.05$; $N=15$; Wilcoxon-Test).

7.4.5 Compaction

The mean sampling soil compaction was 7.5% and ranged from 0.3 to 12.4%. It was twice as high at ungrazed compared to grazed parts (medians 10.4 and 5.1%, respectively; Fig. 7.5). An extremely low sampling compaction of only 0.3% was found for the landward, horse-grazed part at NFB. There were no differences in sampling compaction between the study sites ($H=2.85$; $p=0.42$; $N=16$; Kruskal-Wallis-Test), but generally, highest values were observed at SNK (median 9.8%) and lowest at NFB (median 5.0%).

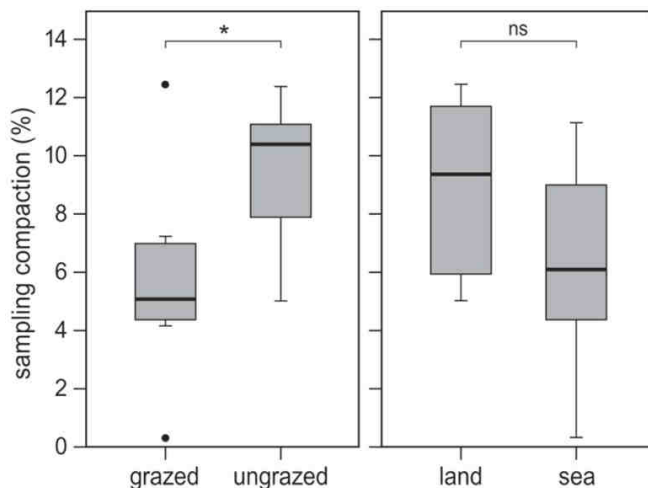


Fig. 7.5: Comparison of sampling compaction between grazed and ungrazed and between landward and seaward locations. Box plots represent: median (middle line), 25–75% (box), top and bottom quartile (whiskers) and outliers (dots). A low sampling compaction indicates that the soil is already compacted by trampling. Median sampling compaction was found to be significantly higher in ungrazed locations ($Z=-2.38$; $p<0.05$; $N=16$; Wilcoxon-Test), while no significant difference was found between landward and seaward locations ($Z=-1.82$; $p=0.07$; $N=16$; Wilcoxon-Test).

Mean dry bulk density of sediment above the identified ^{137}Cs peak ranged from 0.34 to 1.10 g cm^{-3} and did also depend on the grazing treatment; it was significantly higher on grazed compared to ungrazed parts (medians 0.65 and 0.52 g cm^{-3} , respectively; Fig. 7.6). Mean dry bulk density increased with decreasing mean organic matter content in the upper 50 cm of the soil cores ($r_s=-0.68$; $p<0.01$; $N=15$). It further increased with decreasing mean percentage of soil particles smaller than 20 μm ($r_s=-0.76$; $p<0.001$; $N=15$).

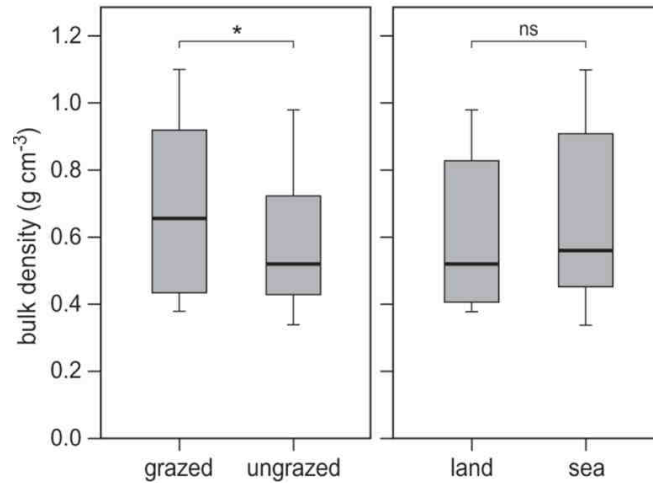


Fig. 7.6: Comparison of mean dry bulk density above the identified ^{137}Cs -peak between grazed and ungrazed and between landward and seaward locations. Peaks were identified to originate from 1986 (NFB, HH and SNK) and from 1963 (DSK). Box plots represent: median (middle line), 25–75% (box), top and bottom quartile (whiskers). Median dry bulk density was found to be significantly lower in ungrazed locations ($Z=-2.01$; $p<0.05$; $N=15$; Wilcoxon-Test), while no significant difference was found between landward and seaward locations ($Z=-1.82$; $p=0.069$; $N=15$; Wilcoxon-Test).

7.5 Discussion

Few studies have analysed effects of livestock grazing on the resilience of salt marshes to SLR so far (e.g. Stock 2011; Suchrow et al. 2012). To our knowledge, this is the first study in which salt marsh accretion and sediment deposition rates as well as soil compaction have been quantified for grazed and ungrazed salt marshes using the same methodological approach for sites representing the whole geographical range of the Wadden Sea coast. Our results show that salt marsh soils were compacted by grazing, while accretion rates and sediment deposition rates were not affected. In areas with high minerogenic deposition rates like the Wadden Sea, the resilience of salt marshes to SLR seems thus not to be negatively influenced by livestock grazing.

Generally, we found that the accretion rates calculated by ^{137}Cs -dating were in accordance with literature data, except for a small number of differences (Tab. 7.1). The average accretion rate in four salt marshes at the Wadden Sea coast was 11 mm yr^{-1} . For the sampling site in the Netherlands we found a mean accretion rate of 21 mm yr^{-1} , which is in line with values reported in other studies of the Dutch coast (7–43 mm yr^{-1} ; Dijkema 1997; Esselink et al. 1998; Hazelden and Boorman 1999;

Dijkema et al. 2010). In comparison, the mean accretion rate in Germany was lower (8.1 mm yr^{-1}) and comparable to most reference data we found for the German coast ($6\text{-}26 \text{ mm yr}^{-1}$; Dittmann and Wilhelmsen 2004; Stock 2011; Suchrow et al. 2012). Higher SSC at the Dutch Wadden Sea coast compared to the Eastern Wadden Sea coast (Eisma and Kalf 1987) probably led to the generally higher sediment deposition rates at NFB. Higher sediment loads in the Western Wadden Sea can be explained by the proximity to sediment sources like the North Atlantic ocean and rivers discharging to the Southern Bight (Eisma and Kalf 1979), the anti-clockwise direction of the tidal wave, and anthropogenic changes like the closure of lake IJssel (Kragtwijk et al. 2004).

Our hypotheses that accretion and sediment deposition rates would be higher on ungrazed compared to grazed salt marshes was not supported by our results. All accretion rates of grazed and ungrazed salt marshes were well above long-term local SLR ($1\text{-}2 \text{ mm yr}^{-1}$), the rise in long-term MHT ($2\text{-}2.5 \text{ mm yr}^{-1}$), and the short-term local SLR of the years 1995-2010 (0.7 mm yr^{-1} and 2.3 mm yr^{-1} , with and without correction for the lunar nodal cycle, respectively; Baart et al. 2012). Thus, it seems to be likely that most mainland Wadden Sea salt marshes outpace rates of current and projected future SLR. Furthermore, if sea level rises, the frequency of inundations increases as well, initiating a positive feedback loop of enhanced sediment deposition on salt marshes (French 2006). However, if the rate of SLR would highly accelerate in the future, salt marshes in tidal basins with low sediment supply such as in Denmark (Flemming and Bartholomä 2002) might be endangered in the long term.

Rather than depending on the grazing treatment or on elevation, which was found to be an important factor in other studies (e.g. 1978; Stoddart et al. 1989; Temmerman et al. 2003), accretion and sediment deposition rates depended on the distance to the marsh edge and were, in our study, always higher at seaward than at landward sampling locations. Distance to the marsh edge was also identified as a determining factor explaining large scale patterns of sediment deposition in other accretion studies (e.g. Esselink et al. 1998; Reed et al. 1999; Bartholdy et al. 2004; but see Craft 2012 for a contrasting result). At NFB, where grazed sampling locations were situated nearly twice as far from the marsh edge as the ungrazed sampling locations, the grazed part of the marsh had a far lower sediment deposition than the ungrazed part (Fig. 7.4). This difference in distance to the sediment source might thus be one reason why at NFB, in contrast to most of the German marshes, the hypothesis of higher accretion and sediment deposition rates on the ungrazed part was supported.

Another explanation for the unexpected result of lower accretion and sediment deposition rates in ungrazed compared to grazed marshes in Germany might be the relative importance of small scale patterns of sediment deposition. In contrast to NFB, where ditches are silted up, inundating water enters the study areas in Germany mainly from the still intact ditch system. In the case of flooding, the inundation of the marsh surface will start perpendicular to these ditches (Temmerman et al. 2012). Consequently, sediment deposition is highest along the ditches, thereby increasing

small-scale variation in these sites and leading to the formation of a levee close to the ditch. This small-scale pattern of sediment deposition might even be amplified by vegetation patterns, which in turn is affected by grazing management. As outlined earlier, vegetation can slow down currents and enhance sedimentation (e.g. Christiansen et al. 2000; Baustian et al. 2012; Temmerman et al. 2012). The grazed and ungrazed parts of the study sites differed considerably in their vegetation types (Tab. 7.1): Ungrazed salt marshes were covered by nearly mono-dominant patches of *Elymus athericus*. This species is known for its high biomass production, tall canopy and thick litter layers (Groenendijk 1984), which can be expected to trap large amounts of sediment. According to Temmerman et al. (2012), flow velocities at the creek edge are 2-4 times lower on a vegetated marsh than on a marsh with no or only short vegetation. Therefore, in a marsh with tall vegetation, more sediment settles close to the ditch and does not reach the central part of the marsh, where the cores for this study were taken.

The hypothesis that compaction is higher on grazed sites than on ungrazed sites was supported by our findings. Sampling compaction was expected to be higher on ungrazed sites since these are less compacted by trampling and thus probably have a higher compactibility. Indeed, sampling compaction was twice as high on ungrazed compared to grazed sites. Additionally, mean dry bulk densities, which were used as an additional indicator for soil compaction, were significantly higher on grazed sites. Olsen et al. (2011) and Schrama et al. (2012) came to a similar conclusion. In general, also organic matter content and grain size distribution can influence dry bulk densities (Kolker et al. 2009). Since the mean organic matter content and the mean percentage of grain sizes smaller than 20 μm did not differ significantly between grazed and ungrazed parts of the marsh, these do, however, not explain differences of mean dry bulk densities between the grazing treatments.

Soil compaction was especially pronounced at NFB, where the soil core of the grazed landward sampling location showed hardly any sampling compaction which indicates a highly compacted soil. This very clear outcome might be caused by the livestock species used for grazing. While the German marshes are grazed by sheep, the study site at NFB is grazed by horses, which are likely to differ in their ability to cause compaction. Frame (1976, as cited in Jensen 1985) estimated the pressure caused by a (standing) cow to be 1.56 kg cm^{-2} , which is likely to be similar to a horse, while the pressure caused by a sheep is estimated to be 0.94 kg cm^{-2} . Furthermore, horses are known to be more active in comparison to cattle and sheep (Menard et al. 2002), which increases their impact on the soil.

7.6 Conclusions

To conclude, accretion rates of the four investigated study sites were higher than the current rise in both sea level and MHT. No effect of grazing treatments on salt marsh resilience to SLR measured as accretion and sediment deposition rates was found. Instead, these parameters were most affected by the distance to the marsh edge and

were significantly higher at seaward sampling locations. However, salt-marsh soils were clearly affected by grazing. Soil compaction was significantly higher on grazed compared to ungrazed marshes. For this reason, the role and interplay of abiotic and biotic factors for accretion rates and how these factors are altered by livestock grazing should be further studied. This might especially be important in organogenic coastal systems, where grazing animals might cause a larger degree of compaction compared to the minerogenic Wadden Sea marshes. In salt grasslands at the Baltic Sea coast, for instance, accretion is mainly organic (Callaway et al. 1996), and livestock grazing is used as a tool to increase biodiversity (Sammul et al. 2012). In addition, small scale patterns of sediment deposition should be considered in future studies. Small scale spatial patterns could not be detected in this study due to its low spatial resolution. If a prediction should be made about the marshes' future development, these should take the entire marsh into account (de Groot et al. 2011). This could be done by combining methods with a high temporal resolution, such as ^{137}Cs -dating, with methods with a high spatial resolution, such as levelling or a high number of sediment traps. In the face of a rising sea level, the question whether or not grazing as a tool for salt marsh management might influence sedimentation processes, is crucial to make sustainable management decisions. Models which aim to predict future marsh development therefore should seek to include the interplay between grazing and other factors influencing marsh accretion with respect to spatial patterns.

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8

Synthesis

8.1 Key findings

This thesis addressed three main research objectives: quantifying the relevance of silica cycling in tidal marshes for estuarine silica budgets, quantifying sedimentation processes in Wadden Sea marshes and assessing the influence of nature management on these ecosystem functions. The thesis had a focus on salt marshes, but regarding the silica cycling, research on tidal freshwater marshes and the river continuum as a whole was included. Key findings of the research are:

- Seepage water from salt marshes was highly enriched with DSi; concentrations were between 1.7 times (spring) and 7.6 times (autumn) higher than in flood water.
- The total amount of silica supplied from Wadden Sea salt marshes to coastal waters was mainly driven by discharge and was therefore higher for ungrazed sites. On ungrazed salt marshes, thick layers of aboveground biomass and litter absorb flood and rain water, thereby increasing the potential enrichment with silica, which was gradually released during the ebb tide.
- Import of BSi in fresh sediments deposited on salt marshes largely exceeded silica exports with the seepage water. The investigated salt marshes were thus sinks for silica.
- One third of the annual BSi imports to the investigated salt marshes occurred during one major flooding event. Omitting the impact of rare events like storm surges on the silica balances has most likely caused an underestimation of silica imports to tidal marshes thus far.
- The DSi export per km² from European salt marshes are nearly four times as high as the DSi export per km² from European river catchments. However, due to the small relative surface area compared to riverine catchments, total DSi exports from salt marshes were up to two orders of magnitude smaller compared to river total export.

- Six years after restoration of a tidal freshwater marsh, the vegetation BSi pool has quickly built up and reached the size of the vegetation BSi pool in salt marshes. However, it was still one order of magnitude smaller than the vegetation BSi pool in a reference tidal freshwater marsh.
- Radionuclide dating in four salt marshes revealed that accretion rates and sediment deposition rates were not significantly different between grazed and ungrazed salt marshes. They were, instead, influenced by distance to the sediment source. Differences in compaction indicate that an influence by grazing on accretion rates might be present but was not detectable with the applied method.
- SEB measurements in two salt marshes showed a tendency for higher surface elevation change on ungrazed compared to grazed salt marshes.

8.2 Silica cycling

The following section evaluates the relevance of salt marshes in supplying silica to the coastal zone. The results of chapter 2 show that DSi concentration in the seepage water from salt marshes at the Wadden Sea coast (on average $324 \pm 70 \mu\text{mol l}^{-1}$ in summer and $416 \pm 53 \mu\text{mol l}^{-1}$ in winter) was relatively high compared to other tidal marshes (Tab. 8.1). Total exports, on the contrary, were slightly lower than reported by most of the few existing studies on DSi exports from salt marshes (Dankers et al. 1984; Scudlark and Church 1989; Struyf et al. 2006) and slightly higher than one study reported (Vieillard et al. 2011). On average, $72 \pm 59 \text{ kmol km}^{-2} \text{ yr}^{-1}$ DSi and $8 \pm 9 \text{ kmol km}^{-2} \text{ yr}^{-1}$ BSi leached to the adjacent coastal waters from the two investigated salt marshes. These exports were mainly driven by discharge and less by the silica concentrations in the seepage water. This finding was obtained by comparing two study sites with each other; where discharge was higher, export rates were higher as well. It was further supported by a comparison with a more regularly flooded tidal freshwater marsh, on which Struyf et al. (2005a) measured both higher discharge and higher DSi exports (200 to 13,000 $\text{kmol km}^{-2} \text{ yr}^{-1}$).

The export per km^2 from European salt marshes was 3.6 times higher than the global DSi export per km^2 from river catchments (chapter 6). It is therefore likely that the reduction of salt marsh area by diking during recent centuries significantly reduced the DSi supply to coastal waters, particularly in the summer season. Despite these high area specific exports and although results from chapter 2 and 3 indicate a high local importance of DSi exports from salt marshes, the overall regional relevance of DSi exports from salt marshes might be limited. Compared to the annual DSi export from rivers, the silica supply function to coastal waters is estimated to be only 0.5% in salt marshes compared to annual river DSi exports (chapter 6). On the other hand, these values are not directly comparable since rivers constitute an original silica source to the coastal zone, whereas marshes only contribute to silica transformation which had already reached the area.

Tab. 8.1: DSi concentrations in the seepage water of salt marshes and tidal freshwater marshes; sorted for lower boundary of the concentration range. Note that concentrations in the seepage water of European marshes generally exceed those in the seepage water of North American sites.

Study site	$\mu\text{mol l}^{-1}$		Reference
	Range	Average	
Salt marsh, Crommet Creek, New Hampshire, USA (whole year)	35-50		Daly and Mathieson 1981
Salt marsh, Rowley Marsh, Massachusetts, USA (before neap tide; summer)		44	Vieillard et al. 2011
Salt marsh, Rowley Marsh, Massachusetts, USA (before mid tide; summer)		58	Vieillard et al. 2011
Salt marsh, Rowley Marsh, Massachusetts, USA (before spring tide; summer)		65	Vieillard et al. 2011
Salt marsh, Carmel Polder, France (outflow, but no seepage water; whole year)	40-130		Struyf et al. 2006
Restored tidal freshwater marsh, Scheldt Estuary, Belgium	40-240		Jacobs et al. 2008
Salt marsh, Dollard, The Netherlands (winter, spring, summer)	60-100		Dankers et al. 1984
Salt marsh, Dollard, The Netherlands (autumn)	120-180		Dankers et al. 1984
Salt marsh, Het Zwin, Belgium (summer)	128-273	215	Müller et al. under review
Tidal freshwater marsh at the Elbe estuary, Germany (whole year)		270	Weiss et al. accepted
Tidal freshwater marsh, Tielrode, Belgium, January	220-270		Struyf et al. 2005a
Tidal freshwater marsh, Tielrode, Belgium, July	270-330		Struyf et al. 2005a
Tidal freshwater marsh, Tielrode, Belgium (whole year)	290-390		Struyf et al. 2006
Salt marshes, Wadden Sea coast, Germany (summer)	158-432	324	Müller et al. under review
Brackish marsh, Elbe estuary, Germany (whole year)		350	Weiss et al. accepted
Salt marsh, Elbe estuary, Germany (whole year)		380	Weiss et al. accepted
Salt marshes, Wadden Sea coast, Germany (winter)	276-527	416	Müller et al. under review

If silica exports from salt marshes are discussed, also their imports and silica pools should be considered. In chapter 3, the first integrated study considering silica concentrations, pools, fluxes as well as the different compartments of a tidal marsh (soil, aboveground biomass, pore water, fresh sediments and seepage water) is presented. Pools differed considerably in size, and the upper 60 cm of soil constituted the largest silica pool (ranging from 85,000 to 171,400 kmol km⁻²). Pore water DSi and vegetation BSi pools were up to four orders of magnitude smaller than the soil BSi pool. The budget calculation of import and export silica fluxes revealed that the investigated salt marshes were clear sinks for silica, with BSi imports ($1,334 \pm 1,019$ kmol km⁻² yr⁻¹) exceeding the abovementioned exports by far. This result especially underlines the relevance of storm surges for silica cycling. One third of annual BSi imports were deposited during only one major storm event in September 2009. Omitting such 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 imports with sediments rates should hence be considered.

Since not only salt marshes matter as biological buffers in the silica cycle, a review is presented in chapter 6 that discusses the effects of silica-vegetation interactions along the river continuum. Effects can reach far through higher levels of ecological organisation, affecting both local and global ecological processes. The chapter provided a non-exhaustive overview of how local vegetation can impact biological silica cycling, in both direct and indirect pathways. For low order streams in high altitudes, it was discussed that fauna can also indirectly affect DSi concentrations. Here, a gypsy moth outbreak led to defoliation of a whole forest and to a subsequent bloom of diatoms, which reduced DSi concentrations for several years (Grady et al. 2007). For lowland

rivers and floodplains, it was hypothesised that by increasing stiffness and rigidity of plants (Schoelynck et al. 2010), silica can enhance the facilitation effect for other plant species by lowering the velocity of flood water and thus increasing sedimentation rates. Patches of silica rich grasses and sedges can reduce the flow currents in the stream and increase retention time during flooding events (Bal and Meire 2009). For tidal wetlands finally, the role of silica in abating current and future environmental threats to estuaries was discussed. It was shown earlier that silica plays a key role in different mechanisms against various environmental stressors (e.g. Liang et al. 2007). We therefore hypothesised that plants which are able to utilise silica to their benefit could be favoured in terms of resisting sea level rise, stronger currents, increasing salinities, chemical contaminants or introduced pathogens, thereby ensuring the ecosystem's functioning.

8.3 Sedimentation processes

The aim of this section is to characterise sedimentation processes in Wadden Sea salt marshes. Long-term accretion rates, measured with the ^{137}Cs radionuclide dating method in four Wadden Sea salt marshes, were on average 11.0 mm yr^{-1} (chapter 7). Sampling locations close to the marsh edge had higher accretion rates compared to locations further inland. In addition, low surface elevation had a positive influence on accretion rates. Short-term SEBs measurements between 2009 and 2012 (displayed in box 1) revealed that the current surface elevation change was slightly lower compared to the accretion rates, resulting of radionuclide dating in the same sites (for terminology see introduction). On average, surface elevation change was 6.9 mm yr^{-1} . Again, sites close to the sediment source and sites low in elevation achieved higher values.

The average rate of surface elevation change was above the current relative sea-level rise of 3.6 mm yr^{-1} , which Wahl et al. (2011) reported for the German Bight. It is therefore not to expect that whole salt marshes in the Wadden Sea area would drown in the near future. However, especially some of the landward sampling locations showed a surface elevation change below this threshold (chapter 7); these locations might become subject to re-wetting. Certainly, if sea level rises, the frequency of inundations increases as well, initiating a positive feedback loop of enhanced sediment deposition on salt marshes. Still, the question is whether the supply with suspended sediments will be sufficient to keep pace with sea-level rise. Already today, tidal basins in the Wadden Sea differ in their sediment budgets (Dittmann and Wilhelmssen 2004). Salt marshes situated at tidal basins with a negative sediment balance (e.g. at the Danish or Northern Schleswig-Holstein coast) might be more endangered by an ever accelerated sea-level rise as are those with a positive balance (e.g. at the Dutch or Lower Saxony coast; Flemming and Bartholomä 2003). However, the Dutch government recently commissioned a study on high-end climate change scenarios. If the calculated maximum sea-level rise of 1.20 m until 2100 (Vellinga et al. 2009) would become a reality, salt marshes in tidal basins with high sediment supply might also be threatened in the long term.

As for the BSi imports, a closer look at the SEB results presented in box 1 reveals that rare events like storm surges largely determine the import of sediment to tidal marshes. Half of the total surface elevation change of 2.5 years occurred during winter 2011/12, and at single locations even up to 71% were caused by sedimentation in that period. This finding highlights the importance of rare events like storm surges for the ability of salt marshes to keep pace with sea-level rise, as it was recently discussed by Schuerch et al. (2012).

8.4 Influence of grazing and restoration management on silica cycling and sedimentation processes

This section discusses the influence of grazing and restoration management on estuarine silica cycling and on sedimentation processes. By altering species composition, vegetation structure and soil characteristics, grazing management can influence the silica cycling of an ecosystem (chapters 2, 3). Although vegetation composition changed considerably since the abandonment of grazing in the investigated salt marshes (Stock et al. 2005), no congruent differences in BSi concentrations of soil and aboveground biomass were observed between grazed and ungrazed sites. Only the pore water DSi was found to be affected by grazing management. In winter, pore water DSi concentrations in upper soil layers were significantly lower on ungrazed ($307 \pm 51 \mu\text{m l}^{-1}$) compared to grazed ($406 \pm 72 \mu\text{m l}^{-1}$) sites. The seepage water, which originates from pore water, showed an opposite pattern. Especially in spring, seepage water DSi concentrations were lower on grazed ($169 \pm 66 \mu\text{m l}^{-1}$) compared to ungrazed sites ($289 \pm 38 \mu\text{m l}^{-1}$). The pattern nearly diminished in winter, suggesting biological control on the values. Diatoms are known to regulate nutrient fluxes across the sediment water interface (Sigmon and Cahoon 1997). Although diatom abundance is not directly influenced by the grazing regime, fewer diatoms can be expected to colonise in creeks on ungrazed sites due to shading vegetation and steeper creeks. It was hypothesised that these organisms were responsible for the low DSi concentrations. Weiss et al. (2012) found evidence for diatom involvement in decreasing DSi concentrations during a supplemental 12h-sampling campaign in the same study site.

Not only silica concentrations can be affected by grazing management, the influence on pools and fluxes of silica is even more relevant in terms of supplying silica to the coastal zone. In chapter 3, it was shown that especially the aboveground vegetation BSi pool was significantly affected by grazing management. Due to a larger standing stock of biomass, BSi pools on ungrazed sites ($467 \pm 464 \text{ kmol km}^{-2}$) exceeded those on grazed ($68 \pm 45 \text{ kmol km}^{-2}$) sites by far. A similar difference was described for silica fluxes in chapter 2. Here, larger silica exports were observed from ungrazed sites, because discharge was higher. It was hypothesised that thick litter layers on ungrazed sites (resulting from dense *Elymus athericus* patches) have led to increased retention times of flood and rain water, as it was earlier described for terrestrial grasslands (Naeth et al. 1991). Also the import of BSi in freshly deposited sediments appeared

to be influenced by grazing management. BSi imports were measured to be higher on grazed sites, but this pattern might also be an artefact related to the employed methodology. Based on the episodic nature of sedimentation events and its possible dependence on grazing management (see also chapter 7), it can be concluded that short-term sedimentation measurements should be supplemented by long-term approaches to estimate BSi imports to salt marshes.

Besides grazing management, restoration management also influences silica cycling. As outlined in chapter 6, a recently restored tidal freshwater marsh was able to quickly build up a considerable vegetation BSi pool. With a size of 230 kmol km^{-2} , the pool was in the range of the vegetation BSi pool in salt marshes which was between 76 and 660 kmol km^{-2} (chapter 3). However, it was not clear if and when the pool will reach the size of a BSi pool in a natural tidal freshwater marsh. Six years after restoration, it was still one order of magnitude smaller than a reference vegetation BSi pool, which was as large as $3,030 \text{ kmol km}^{-2}$ (Struyf et al. 2005b). This difference in BSi pools between salt marshes and young tidal freshwater marshes compared to mature tidal freshwater marshes can be attributed to the dominance of *Phragmites australis* in the latter system. This grass has both a high BSi content and a high above-ground biomass production. To estimate the vegetation BSi in an efficient way, a novel non-destructive method was applied that converts cover estimates of abundant plant species to biomass data and multiplies it with the silica content of the plant tissue. This method could be helpful to estimate the annual salt marsh vegetation BSi pools without harvesting.

In chapter 7, we aimed at clarifying whether a possible influence of grazing management on long-term accretion rates was rather caused by less soil compaction or by increased sediment trapping on ungrazed sites. We found compaction to be significantly higher on grazed sites, but this pattern did not determine accretion rates; no significant influence of grazing management on accretion rates was observed. Instead, abiotic factors appeared to be the driving forces for accretion rates. Both sediment deposition rates and accretion rates increased with declining distance to the marsh edge (i.e. the sediment source). From these findings, it can be concluded that the effect of grazing might be present but will only be visible in a study design with a larger sample size. SEB measurements presented in box 1 revealed no significant differences in surface elevation change between the two grazing treatments. At the most, a tendency of higher surface elevation change for ungrazed compared to grazed sites could be observed. Also in case of these short-term measurements, abiotic factors such as distance to the marsh edge superimposed management effects.

8.5 Future work

Salt marshes are often considered to be particularly valuable wetland ecosystems because they fulfil various ecosystem functions and services (Costanza et al. 1989). Against the background of current environmental threats, the ecological and economical quantification of ecosystem functions is of rising significance worldwide. In Eu-

rope, for instance, different directives, such as the Water Framework Directive or the Marine Strategy Framework Directive aim at achieving a “good environmental status” in European rivers and seas (BfN 2012). So far, the supply of silica to the coastal zone is not necessarily included in the assessment of ecosystem functioning in Europe, although earlier studies indicated that silica recycling in tidal marshes might reduce harmful algae blooms (Conley et al. 1993) and stabilise coastal food webs (Kristiansen and Hoell 2002). Also sedimentation processes in salt marshes are not yet regularly monitored on a European level (Esselink et al. 2009), even though sediment deposition is known to be a prerequisite to ensure that salt marshes keep pace with a rising current sea level (Reed 1989).

The pool and budget calculations presented here constitute a first step in quantifying the relevance of salt marshes in coastal silica cycling. As a next step, findings on silica cycling in salt marshes should be up-scaled. BSi in salt marsh vegetation is a highly reactive pool of silica. To assess the role of salt marshes as suppliers of DSi to the coastal zone, it would therefore be important to estimate the size of the vegetation BSi pool on a larger scale. If the calculation was extended to vegetation types instead of single species, it would be possible to estimate BSi pools for the whole Wadden Sea coast using existing and regularly updated TMAP surveys (such as presented in Esselink et al. 2009).

BSi import fluxes are highly variable (chapter 3). Studies on nutrient cycling in tidal marshes often consider only the imports via the creek water, whereas this thesis demonstrates the significance of BSi imports with sediments during storm tides. To avoid a vast underestimation, future studies should not further omit this significant import path. While chapter 4 presents large-scale export fluxes, future studies could extend on this and assess large-scale imports. Because of the high spatial and temporal variability of BSi imports with sediments, it will be useful to include existing long-term data on sedimentation processes. So far, sedimentation data is not included in the official TMAP monitoring scheme, but Esselink et al. (2009) give an overview of current measurement activities along the Wadden Sea coast.

However, in order to assess the relevance of ecosystem functions, is it not only important to quantify these functions, but also to gain knowledge about the underlying processes. A lack of knowledge exists, for instance, in our understanding of regional transformation processes in silica cycling. It is known that the silica concentration in ocean water can become a limiting factor for diatom growth (Conley et al. 1993). At the same time, this thesis and other recent studies (e.g. Vieillard et al. 2011; Carey and Fulweiler 2013) show that salt marshes deliver dissolved silica to the coastal zone. However, it still remains unclear if the silica supply of tidal marshes can effectively reduce silica limitation in the oceans. In the Wadden Sea, large areas of tidal flats lie between the salt marshes and the open North Sea. Processes of silica transformation in the transition from terrestrial over coastal to marine systems should be addressed in future research.

In terms of sedimentation processes, it is not yet clear, if and under which circumstances, livestock grazing on salt marshes can influence the vertical growth of the marsh surface. For minerogenic salt marshes at the Wadden Sea, we were not able to supply evidence for reduced accretion rates under grazing. If existing, the influence of grazing on accretion rates is probably minor compared to factors related to marsh geomorphology. Future studies should, therefore, approach this research question with a larger sample size. Particularly in organogenic coastal systems, the question if livestock grazing leads to reduced accretion rates might be of high relevance. In salt grasslands at the Baltic Sea coast, for instance, accretion is mainly organic (Callaway et al. 1996), and livestock grazing is commonly used in these systems to increase local biodiversity (Sammul et al. 2012). In the face of a rising sea-level, future studies should shed light on the question if the low rates of annual surface elevation change in salt grasslands (e.g. Vestergaard 1997 for a Danish site) are further reduced by livestock grazing.

The question whether silica supply from salt marshes is indeed able to stabilise coastal and marine food webs and whether grazing management has an influence on accretion rates is ultimately also important for a realistic assessment of the ecological and economical value of salt marshes.

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Eidesstattliche Versicherung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertationsschrift selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Hamburg, den 30.11.2012

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28th November 2012

Re: Frauke Müller

To whom it may concern,

as a native English speaker and experienced proof-reader, I do hereby declare that the PhD thesis: "Management effects on ecosystem functions of salt marshes: silica cycling and sedimentation processes" has been written in concise and correct English (UK).

Yours sincerely,

A handwritten signature in black ink, appearing to read 'Tom Maxfield', written in a cursive style.

Tom Maxfield
English Proof-reader, University of Edinburgh