

### 3. N and Si cycling in freshwater tidal marshes

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#### **Abstract**

Tidal marshes have high sediment surface areas, promoting processes affecting nutrient speciation, transformation and retention. In this project we performed whole-ecosystem  $^{15}\text{NH}_4^+$  tracer addition experiments to quantify the fate and transport of ammonium through a tidal freshwater marsh. Combined with a mass-balance study, this approach allowed a simultaneous examination of transport and processing of nitrogen. We also performed additional studies on Si cycling in parallel to the N-labeling experiment.

Our work shows that the large reactive surface of the tidal freshwater marsh vegetation is crucial for nitrogen transformation and assimilation. It clearly revealed the dominant role of microbes in initial nitrogen retention in marsh ecosystems. Parallel study of silica cycling revealed that tidal marshes act as biogenic Si recycling surfaces, importing biogenic Si while exporting dissolved Si. Export of dissolved Si is greatest during summer and spring, when dissolved Si concentrations in inundating waters are depleted by diatoms. Tidal marshes thus buffer estuarine dissolved Si in times of limitation. We can conclude that the studied marsh had an increasing effect on the Si:N ratio in flooding waters. Export of DSi and import of total dissolved nitrogen (DIN) contributed about equally to the increase of the Si:N ratio.

#### **i. Problem and aims**

Estuaries are well known to modify and attenuate nitrogen (N) transfer from rivers to the coastal sea (Billen et al., 1991). Specifically tidal marshes have been reported to play a major role in nitrogen retention (Van Damme et al., 2009). Marshes have high surface areas of sediment and bio-films in contact with the water, promoting processes that affect nitrogen speciation and remove dissolved inorganic and organic nitrogen while increasing deposition of particulate nitrogen. There is considerable interest in exploiting this nitrogen filtration capacity of wetland ecosystems in order to improve estuarine and coastal marine water quality. However, despite the widely held belief that wetland systems are important nutrient sinks, the literature regarding the influence of tidal freshwater wetlands on water quality is remarkably small (Merrill and Cornwell, 2000).

The importance of freshwater marshes to the estuarine nitrogen budget is most often estimated with a mass-balance approach (e.g., Van Damme et al., 2009). This technique, however, is subject to considerable error and yields little information regarding the role and spatial and temporal distribution of the underlying processes. In this project we performed whole-ecosystem  $^{15}\text{NH}_4^+$  tracer addition experiments to quantify the fate and transport of watershed-derived ammonium through a tidal freshwater marsh system. Combined with a mass-balance study, this approach allowed a simultaneous examination of transport and processing of nitrogen in an intact ecosystem, something that is impossible to achieve in traditional bottle, enclosure, or mesocosm experiments.

The whole-ecosystem  $^{15}\text{N}$  labeling experiment was conducted in a tidal freshwater marsh fringing the nutrient-rich Scheldt River (Fig. E-3.1, Belgium). Although many tidal marshes of the Scheldt basin have been reduced to very small size today, they are still a prominent feature of the Scheldt, and the surfaces of the 4.5 km<sup>2</sup> of tidal freshwater marshes could represent important potential N sinks. We defined project goals that were specifically aimed at assessing the role of these marshes as nitrogen sinks and transformers:

- to quantify different processes within the marsh: N-uptake and N-loss, nitrification and denitrification
- to identify the main N-compartments
- to estimate the retention time of different N-forms and its spatial distribution

It should be emphasized that nitrogen cycling within estuaries cannot be considered independently from the cycle of other nutrients. It is in fact the N-P-Si ratio that eventually reaches coastal waters through estuaries that affects phytoplankton productivity. High anthropogenic inputs of N and P can induce Si limitation in diatoms and cause a succession of the phytoplankton community to non-diatom species, which are less available to higher trophic levels (e.g., *Phaeocystis* sp). Apart from this negative effect on estuarine and coastal food webs, increased non-diatom phytoplankton production can have several other negative consequences, including increased water turbidity, anoxic conditions, and the appearance of toxic algal blooms (Cloern, 2001).

Especially silica cycling in tidal marshes had so far remained unstudied. Yet both diatoms and reed, both biological silica accumulators, are abundant in tidal freshwater marshes. As such, these areas have a high potential to also affect silica cycling in estuarine ecosystems. Therefore, we performed the most detailed study on Si cycling in a tidal marsh so far in parallel to the N-labeling experiment. Specifically, we aimed to quantify biogenic Si (BSi) stocks in freshwater marsh vegetation and sediment, internal recycling rates of both sediment and vegetation associated BSi and exchange of DSi and BSi between the marsh and adjacent estuarine waters.



**Fig. E-3.1:** A typical *Phragmites australis*-dominated tidal freshwater marsh (Scheldt estuary, Belgium).

## ii. Results

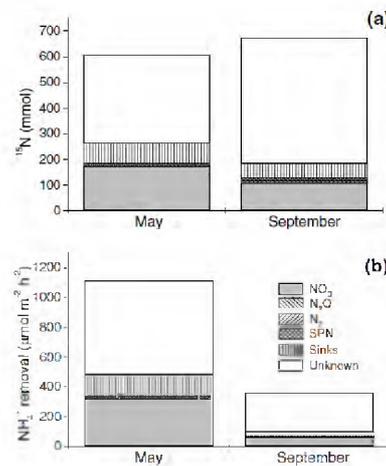
### Nitrogen

In spring (May 2002) and late summer (September 2003), we added  $^{15}\text{N-NH}_4^+$  to the flood water entering a  $3477 \text{ m}^2$  tidal freshwater marsh area, and traced the ammonium processing and retention in four subsequent tide cycles. Changes in concentration and isotopic enrichment of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{NH}_4^+$  and suspended particulate nitrogen (SPN) were measured. All analyzed N-pools were labeled: in May 31 % and in September 49 % of the added  $^{15}\text{N-NH}_4^+$  was retained or transformed. The most important pool for  $^{15}\text{N}$  was nitrate. The temporal and spatial patterns of  $^{15}\text{N}$  transformation in the water phase component of the system were remarkably similar during both periods: however, the absolute ammonium transformation rate was 3 times higher in May. While the marsh surface area was crucial for nitrification in May this was less pronounced in September. Denitrification on the other hand was more intense in September compared to May.

Although the total amount of  $^{15}\text{N}$ , and the relative distribution of  $^{15}\text{N}$  recovered in the various compartments was quite similar between the two campaigns (Fig. E-3.2a), the corresponding total ammonium processing rates on a marsh surface area basis varied greatly (Fig. E-3.2b). This is mainly due to a combination of a 5 times lower total in situ flood water ammonium pool and a higher relative  $^{15}\text{N}$  (4.5 % of the ammonium pool) concentration in September. Thus, the absolute amount of ammonium processed in the marsh was 3 times higher, and >5 times more ammonium was nitrified, in May compared to September. These findings suggest that flood water ammonium concentration is the key determinant for ammonium removal in tidal freshwater marsh ecosystems.

The specific study of the sinks, as in Figure E-3.2, revealed that that leaf litter and ruderal vegetations are more important in nitrogen uptake and retention than the prominent reed (*Phragmites australis*) meadows. Moreover, short-term nitrogen retention in these nutrient rich marshes occurs mainly via microbial pathways associated with the litter and sediment. Rather than direct uptake by macrophytes, it is the large reactive surface area provided by the tidal freshwater marsh vegetation that is most crucial for nitrogen transformation, assimilation and short term retention in nutrient rich tidal freshwater marshes. Our results clearly revealed the

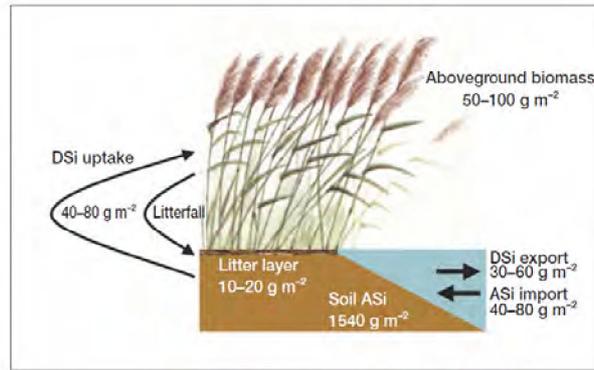
dominant role of microbes in initial nitrogen retention in marsh ecosystems. However, our whole ecosystem labeling study did not allow us to elucidate in detail the dynamics within the microbial compartments; e.g. we do not know whether eukaryotes (benthic algae or fungi) or prokaryotes contribute most to nitrogen retention.



**Fig. E-3.2:** (a) Amount of recovered  $^{15}\text{N}$  in the various pools after  $T_0$  in May and September (not exported as  $^{15}\text{NH}_4^+$ ), and (b) average total marsh ammonium transformation rates based on recovery of  $^{15}\text{N}$  label after one tide. The “unknown” compartment is probably mainly denitrification and export of dissolved organic N (Gribsholt et al., 2006).

## Silica

Our parallel study of silica cycling revealed that tidal marshes act as significant BSi recycling surfaces, importing BSi while exporting DSi. Nevertheless, BSi is not completely recycled; tidal marshes tend to be net sinks for BSi in estuaries. Higher sedimentation rates result in a more efficient burial of BSi. Export of DSi is greatest during summer and spring, when DSi concentrations in inundating waters are depleted by diatoms. Tidal marshes thus buffer estuarine DSi in times of limitation, when recycling can exceed freshwater runoff. Export of DSi is most strongly connected to the slow advective (horizontal) release of water retained in the marsh after high tide, both from interstitial water and puddles, which contain DSi concentrations of 100–600  $\mu\text{M}$ . The sinks and fluxes of Si in the freshwater tidal marsh (dominated by *Phragmites australis*) are summarized in Figure E-3.3. Sediment BSi pools are large compared to vegetation. In practice, most export of DSi occurs during only a few months in summer and spring. The vegetation is, in essence, self-sufficient for Si. Nevertheless, the abundant litter layer has an important role in the Si buffering capacity of tidal marshes. The storage of BSi in *Phragmites australis* in the Scheldt freshwater marshes of Belgium accounts for over 90 % of all ASi in vegetation (although its biomass accounts for only 50 % of total biomass). Decomposition experiments have shown that recycling of reed ASi is very efficient, with over 85 % dissolving within a year after culms collapse. In Scheldt marsh sediment, approximately 80 % of all BSi was diatomaceous in origin, which is consistent with observed rapid recycling of phytoliths.



**Fig. E-3.3:** Stocks and yearly fluxes of DSi and ASi (amorphous Si ~ BSi) within the 3477 m<sup>2</sup> Belgian freshwater marsh. Sediment stocks are for the upper 30 cm. Litterfall and DSi uptake by vegetation equal each other on an annual time scale (Struyf & Conley, 2009).

### iii. Conclusions and recommendations

Our work has revealed new insights in the cycling of N (Gribsholt et al., 2005, 2006, 2007) and Si (Struyf et al., 2005a,b, 2006, 2007a,b) within freshwater tidal marshes. The studied marsh had an increasing effect on the Si:N ratio in flooding waters. Export of DSi and import of total dissolved nitrogen (DIN) contributed about equally to the increase of the Si:N ratio. The marsh had a counteracting effect on the long term trend of nutrient ratios in the estuary, which could be identified as a positive effect within an estuary that has experienced high N inputs during the past decades. Low Si availability compared to N and P has resulted in frequent occurrence of Si-limitation events within freshwater and saltwater parts of the Scheldt estuary.

However, it should be noted that our results also reveal that tidal freshwater marshes contribute little to the overall yearly N and Si cycling of the Scheldt estuary, which is mainly governed by main-stream water column processes. This is likely due to a combination of the small surface of marshes relative to the overall surface of the estuary, very high nutrient loading, and short water residence time. Still, marshes can play an important role in silica transport through the estuary during specific time-periods when DSi limitation is occurring (especially spring and summer). Moreover, if the large areas of brackish and saltwater marshes in the Scheldt estuary transform N and Si at similar rates compared to our freshwater marsh site, as much as 19 % of the yearly ammonium load to the Scheldt is potentially nitrified in tidal marshes.

We can conclude that coupled research of different element cycles (e.g. N, P, Si) is recommendable for future studies in tidal marshes, as the effect of marshes on estuarine biogeochemical functioning is mainly situated in their interaction. We can also conclude that whole-ecosystem labeling studies are a promising approach to trace importance of internal compartments in nutrient cycling, complementing classical mass-balances. Finally, we recommend research to focus on recently restored tidal marshes. These areas are often implemented to improve estuarine habitat quality, yet especially their role in estuarine nutrient cycling and the evolution of this role with age is poorly quantified.

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