Silica: An Essential Nutrient in Wetland Biogeochemistry
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Silica: an essential nutrient in wetland biogeochemistry

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Recent research has emphasized the importance of terrestrial ecosystems in the global biogeochemical cycle of silica (Si). The production, retention, and dissolution of amorphous silica of biological origin in soils and vegetation effectively control terrestrial Si fluxes. However, surprisingly little is known about the role of wetlands in these processes. Wetlands are known hotspots for both nitrogen and phosphorus cycling, and there have been countless studies and numerous reviews on these nutrients worldwide. By bringing together previously scattered results, we show that wetland ecosystems may be as important for Si transport and processing as they are for other important biogeochemical cycles. Yet, the range of studied systems is small and incomplete. This constitutes a serious gap in our understanding of both coastal eutrophication and climate change, issues that are strongly linked to Si biogeochemistry. Ecosystem scientists and wetland biogeochemists around the world need to begin addressing these issues.

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On geological time scales, mineral weathering and volcanic hydrothermal emissions are the ultimate source for all dissolved and biogenically fixed silica (Si) on Earth. However, on biological time scales, this "geo-aspect" of silica biogeochemistry is only one part of the story. The " 'bio' in silica biogeochemistry" (eg Markewitz and Richter 1998) has been studied less intensively, though recent research has shown that processing of Si within ecosystems greatly influences its transport and retention (Conley 2002; Derry *et al.* 2005; Blecker *et al.* 2006). This challenges our ability to predict rates of mineral Si weathering, as the biological contribution is poorly quantified. Assessing weathering rates is important: mineral Si weathering is an important sink for atmospheric CO_2. Furthermore, relative to the well-studied elements nitrogen (N) and phosphorous (P; eg Tiessen 1995; Boyer and Howarth 2002), the export of silica from land is a crucial factor in the occurrence of coastal eutrophication (Ittekot *et al.* 2000). Yet research on wetland Si cycling has been scattered and incomplete, and has never been summarized. This review will emphasize the role of biota (ie vegetation, diatoms, sponges) in Si cycling and show that, based on available data, Si should be included in wetland nutrient budgets.

In a nutshell:

- Wetlands are rich in biologically fixed, amorphous silica, and may exert biological control over the silica cycle
- Hydrology and vegetation control processing of silica in wetlands; human interference has impacts on interactions between wetland Si biogeochemistry on the one hand, and climate change and eutrophication on the other
- Currently, the silica biogeochemistry of several types of wetland, including mangroves, Arctic peatlands, and riparian wetlands, is poorly understood

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The most evident biological sink for Si is diatoms (*Bacillarophyceae*), single-celled organisms abundant in aquatic phytoplankton communities worldwide. Diatoms take up dissolved silicate (DSi = ortho-silicic acid) and deposit it as amorphous silica (ASi), often referred to as biogenic silica (BSi), within the protective coating of the diatom frustule (the cell wall of a diatomic silicate cell). The ocean cycle of diatom ASi is characterized by rapid recycling, with only 3% of yearly diatom ASi production permanently buried in the ocean floor (Van Cappellen 2003). The "biological Si pump" is an important mechanism by which C is transferred from the atmosphere to the deep ocean (Dugdale *et al.* 1995). Ocean food webs would collapse if buried ASi were not replenished by inputs from land, via rivers. Many important global fisheries are dependent on diatom-based food webs (Officer and Ryther 1980).

Another major biological factor in Si cycling is vegetation. Plants take up DSi from soil solution, and deposit it as ASi, mainly in siliceous bodies known as phytoliths (Piperno 1988). Phytoliths are more resistant to decomposition than other plant tissues. They remain buried in large quantities in soil (Clarke 2003), and are often used as paleo-indicators in the reconstruction of past vegetation communities (Blinnikov 2005). Their solubility is still several orders of magnitude greater than that of mineral silicates (Van Cappellen 2003). Conley (2002) has estimated that the global annual fixation of phytolith silica (60–180 Tmol yr^{-1}) is on the same order of magnitude as the amount annually fixed in ocean diatom communities (240 Tmol yr^{-1}), with soils containing orders of magnitude more ASi, primarily buried as phytoliths. As with cycling in the oceans, ASi recycling drives the terrestrial Si cycle.

Wetland ecosystems, which represent a link between terrestrial and aquatic environments, therefore attract special attention. Wetlands interact strongly with river biogeochemistry, and lowland wetlands form large buffers between upstream ecosystems and rivers and estuaries. Wetland systems are characterized by fast plant growth and high biomass, with intense recycling and storage of N and P. Furthermore, wetlands are often dominated by grasses, which are known to accumulate large quantities of ASi (eg Struyf *et al.* 2005). Yet, there has been very little research on Si cycling in these systems, compared to N and P. This is surprising, since the relative input of Si compared to N and P is an essential factor controlling coastal eutrophication.

Here, we summarize previous research on wetland Si cycling, pinpoint its likely importance, and discuss future research possibilities and challenges. We encourage others to include the measurement of Si in their studies of nutrient biogeochemistry within wetland ecosystems, so that our knowledge concerning this important nutrient can catch up with the already abundant literature on N and P.

■ Si in wetland vegetation and soils

A considerable number of wetland plant species, primarily in coastal wetland systems, have been analyzed for their ASi content. We have summarized results for some plants sampled in situ in wetlands, including work by Lanning and Eleuterius (1981, 1983, 1985; WebTable 1). The phylogenetic variability in the ASi deposition by plants has been summarized in Hodson *et al.* (2005). General trends are also recognizable in wetland species: monocots contain more ASi than dicots, and Poaceae (grasses) and Cyperaceae (sedges) are the best represented families among the Si-accumulating species. Exceptionally high values (> 20% of dry weight as ASi) have been found in bamboo (*Arundinaria gigantea*), for instance.

High ASi found in two species of wild rice (*Zizania aquatica* and *Zizanopsis miliacea*) are similar to the high values found in commercial rice (*Oryza sativa*). Years of intensive rice cultivation have depleted some rice fields with respect to Si, and this has been linked to declining rice yield (Savant *et al.* 1997). Silica-rich commercial fertilizers are often applied to help ameliorate the effects of Si limitation (Korndörfer and Lepsch 2001).

Silica accumulation provides plants with several competitive advantages, including enhancement of growth and yield, increased shoot rigidity and protection against physical stress, promotion of photosynthesis, and resistance to disease, herbivores, metal toxicity, and salinity (Epstein 2001). High ASi content has recently been shown to decrease grass palatability for herbivores, and greater levels of herbivory increase investment in defense structures (Massey *et al.* 2007). Efficient use of Si by some plant species or varieties potentially influences competitiveness in dynamic environments. The high silicification of culm sheaths (Lau *et al.* 1978) gives *Phragmites australis* extra rigidity during internodal growth, in contrast to most other grasses, which grow from the top node only. The protective leaf sheath around *P australis* culms could partly explain the ability of this species to invade highly dynamic ecosystems, such as tidal marshes and mudflats. In North America, an invasive, non-native genotype of *P australis* is considered to be a threat to local biodiversity (Saltonstall *et al.* 2002), spreading rapidly and out-competing native species.

The growth of high-biomass plant communities rich in phytolith ASi can result in the burial of abundant ASi in wetland soils. A review by Clarke (2003) shows that phytoliths (but also sponge spicules and diatoms) are a major constituent in the surface soil of wetlands. Swamp soils contained between 3.2% and 4.5% opal (amorphous silica) by grain abundance and alluvial plains contained 2–24% opal, while in seasonal wetlands, opaline material constituted 48%–100% of all grains. Although diatoms and phytoliths are the most studied forms of ASi, the importance of sponges has been confirmed by Andrejko *et al.* (1983) for the Okefenokee Swamp (Florida, Georgia) and by Slate and Stevenson (2000) for the Florida Everglades. In inland peat soils, such as those of the Okefenokee Swamp, biogenic ASi is the predominantly stored mineral, and sponges can comprise a major part of the ASi.

These results do not provide an actual estimate of weight percentage of ASi in soils, obtained by wet-alkaline extraction techniques (Sauer *et al.* 2006; Saccone *et al.* 2007). ASi content in weight percentage of wetland soils has been published for tidal mesohaline marshes (US) and freshwater marshes in Belgium, and for the Everglades (US) in *Cladium* spp and *Typha* spp vegetation. Soils contained between 0.6% and 0.9% ASi by weight (Norris and Hackney 1999; Struyf *et al.* 2005) in tidal marshes, and between 0 and 0.6% by weight in Everglades soil (Jensen *et al.* 1999). Depth gradients in freshwater tidal marshes showed a clear decline in ASi content with depth, indicating gradual dissolution of ASi. Freshwater marsh ASi content per square meter (1500 g Si m^{-2} in upper 30 cm) was similar to the content estimated in tallgrass-dominated inland grasslands (Blecker *et al.* 2006). In grasslands, increased precipitation enhanced phytolith dissolution and Si export; frequent inundation and refreshing of soil water had similar effects in tidal wetlands (discussed below). Initial analyses show that inland sub-Arctic peats dominated by sedges contain 1–5% of amorphous Si by weight percent, which is one order of magnitude above amounts stored in tidal wetlands and the Everglades (E Struyf unpublished), and confirms the capacity of peatlands to accumulate large amounts of ASi.

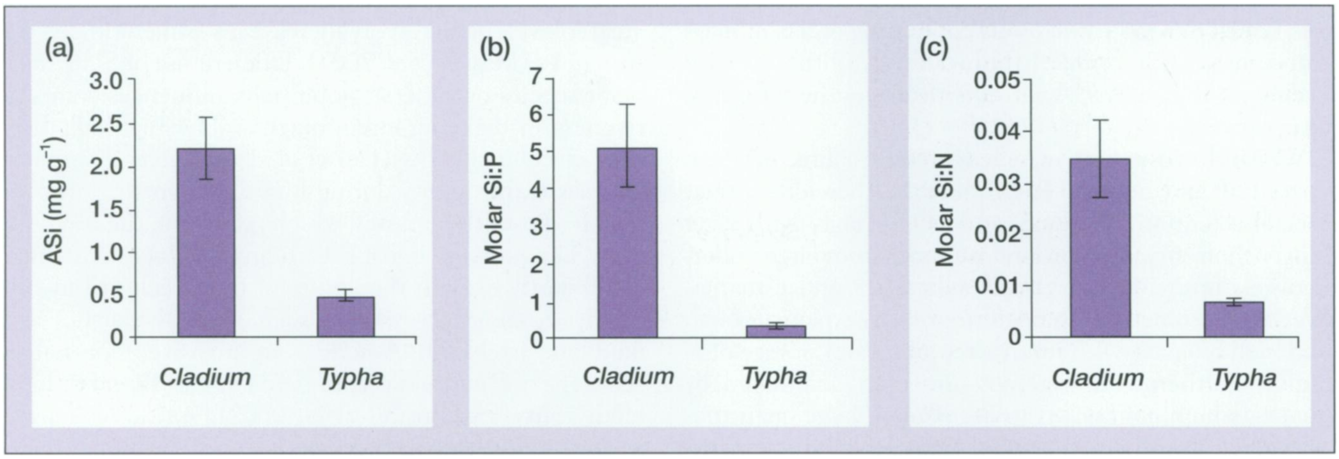

***Figure 1.** (a) Storage of soil ASi in* Cladium *spp and* Typha *spp vegetation types in the Everglades wetlands of Florida, and the relative molar ratio of (b) Si to P and (c) Si to N in the soil in these vegetation types. Error bars represent standard errors on the mean. After data from Jensen* et al. *(1999).*

In Everglades soils, ASi content was four times higher under *Cladium* spp than under *Typha* spp (Figure 1a); this is consistent with plant ASi content found in other studies of these genera (23 versus 4 Si mg [g biomass]$^{-1}$; WebTable 1). This indicates a direct link between soil retention of Si and Si content of vegetation. Retention of Si, relative to N and P, in soils under *Cladium* spp was 4–5 times higher than relative retention in soil under *Typha* spp vegetation (Figure 1 b,c). For P, this was sharpened because *Typha* vegetation also had higher soil P content than did *Cladium* species. Similarly, soils underlying deciduous vegetation in the Hubbard Brook watershed (New Hampshire) had higher ASi content than soils dominated by evergreens; this is also consistent with plant ASi content (L Saccone unpublished). The abundance of phytoliths in peat soils further indicates a probable link between ecosystem structure (eg vegetation) and soil ASi content.

■ Tidal wetlands and Si biogeochemistry

Among wetland ecosystems, tidal marshes have been studied most extensively in terms of their Si biogeochemistry (Gardner 1975; Scudlark and Church 1989; Norris and Hackney 1999; Struyf *et al.* 2005, 2006, 2007 a,b). These systems act as ASi recycling surfaces, importing ASi while exporting DSi. Nevertheless, ASi is not completely recycled; tidal marshes tend to be net sinks for ASi in estuaries. Higher sedimentation rates result in a more efficient burial of ASi (Struyf *et al.* 2007a). Export of DSi is greatest during summer and spring, when DSi concentrations in inundating waters are depleted by diatoms (Scudlark and Church 1989; Struyf *et al.* 2006). Tidal marshes may 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 μM (Hackney *et al.* 2000; E Struyf pers obs). Arndt and Regnier (2007) recently modelled only diffusive fluxes of DSi, and showed that direct diffusive efflux is minor, confirming that the source of observed DSi export in detailed observational studies is advective fluxes (Gardner 1975; Scudlark and Church 1989; Struyf *et al.* 2006).

The sinks and fluxes of Si in a freshwater tidal marsh dominated by *P australis* are summarized in Figure 2. Sediment ASi 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 ASi in *P australis* in the Scheldt freshwater marshes of Belgium (Figure 3) accounts for over 90% of all ASi in vegetation (although biomass accounts for only 50%; Struyf *et al.* 2005a). 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 opal grains were diatomaceous in origin, which is consistent with observed rapid recycling of phytoliths (W Guo and DJ Conley unpublished).

In tidal flats, DSi export to flood water was observed at low elevations, while import was observed higher on the flat, again indicative of porewater seepage and enrichment. In general, export of DSi has been observed from tidal flat sediments, although intense benthic diatom blooms in spring and summer can turn tidal flats into strong sinks for DSi. Export of DSi from tidal marshes was between 0 (in winter) and 20 mg Si m^{-2} ha^{-1} (Scudlark and Church 1989; Struyf *et al.* 2006). In tidal flats, export rose to 67 mg Si m^{-2} ha^{-1}, but on average was 5–10 mg Si m^{-2} ha^{-1} (eg Asmus *et al.* 2000).

■ Non-tidal wetlands

There are very few silica budgets for non-tidal wetlands, as compared to those for N and P. We are aware of only four budget studies that incorporate Si: one in a temperate freshwater marsh, one in a peat bog, and two from a coastal alluvial plain (Table 1). DSi budgets were constructed in three of the four cases and between 6% and 21% of all DSi was retained; such substantial retention warrants further investigation. Interestingly, dissolved inorganic nitrogen retention was between 23% and 61% in the same systems, and soluble reactive phosphate retention was between 46% and 94%, again indicating nutrient ratio shifts through biogeochemical processes in the wetlands. No ASi budgets were found. Data are too scarce for overall conclusions to be drawn for all wetland types. They do, however, confirm that wetlands potentially represent an important yet unquantified factor in Si biogeochemistry, as they are for N and P.

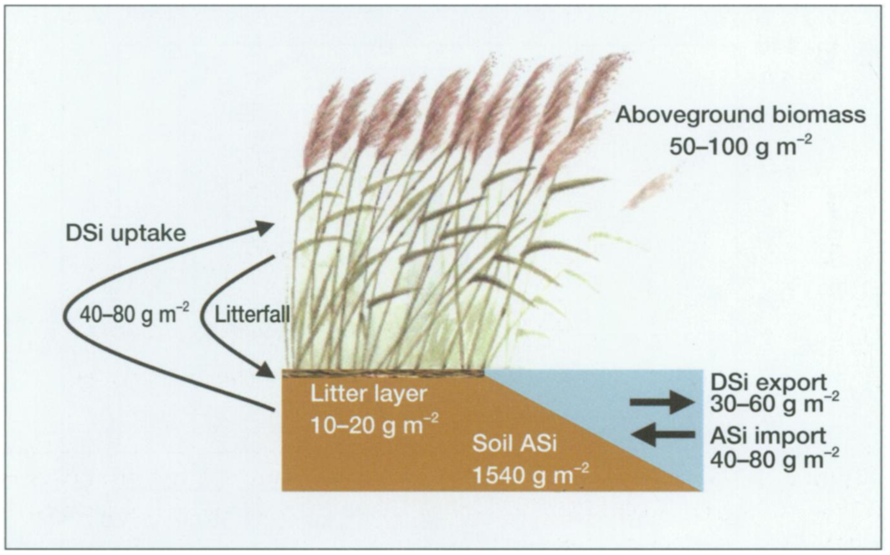

Figure 2. *Stocks and yearly fluxes of DSi and ASi within a Belgian freshwater marsh. Sediment stocks are for the upper 30 cm. Litterfall and DSi uptake by vegetation equal each other on an annual time scale. After Struyf* et al. *(2005, 2006, 2007 a,b).*

Inland wetlands are potential storage zones for DSi transformed into ASi. Because of the important burial of relatively reactive ASi (compared to mineral Si), they also comprise intense ASi recycling zones. Data independently acquired in Swedish boreal rivers by Humborg *et al.* (2004) and in Russia by Zakharova *et al.* (2007) demonstrate a positive relationship between percentage of peat wetland coverage in river basins and DSi concentrations observed in the rivers (Figure 4). The high observed DSi concentration in one Russian basin at 0% wetland was caused by excess subsurface transport of mineral weathering products, due to an exceptionally high river slope. The results clearly show the potential importance of wetlands (and other ecosystems) in governing DSi fluxes through river basins, highlighting the importance of biological processes in Si biogeochemistry.

The paucity of information on Si means that we can only hypothesize about the internal factors influencing Si processing in riparian wetlands, sub-Arctic peat bogs (Figure 5), flooded forests, alluvial plains, non-tidal wetlands, mangroves, and saltwater and brackish tidal marshes. This lack of knowledge is best illustrated by comparing keyword hits among articles published in the scientific journal *Wetlands* (Society of Wetland Scientists) between 1990 and 2007, which provides an indicator of the popularity of studies on Si relative to N and P. In article titles, the keywords "nitrogen" and "phosphorus" delivered 39 and 41 hits, respectively (out of 933 papers), while neither "silicon", "silicate", nor "silica" resulted in a single keyword hit. The results were even more striking for abstracts (1981–2007): "nitrogen" and "phosphorus" had 92 and 88 hits, respectively, while "silicon", "silicate", and "silica" returned just three hits, only one of which was a budget study (Krieger 2003). Another considered saline lake ecology, and was irrelevant to this topic.

The potential for Si retention has previously been demonstrated for forests (Bartoli 1983) and for grasslands (Blecker *et al.* 2006). Forests (Fulweiler and Nixon 2005)

Figure 3. *A typical* Phragmites australis*-dominated tidal freshwater marsh (Scheldt estuary, Belgium).*

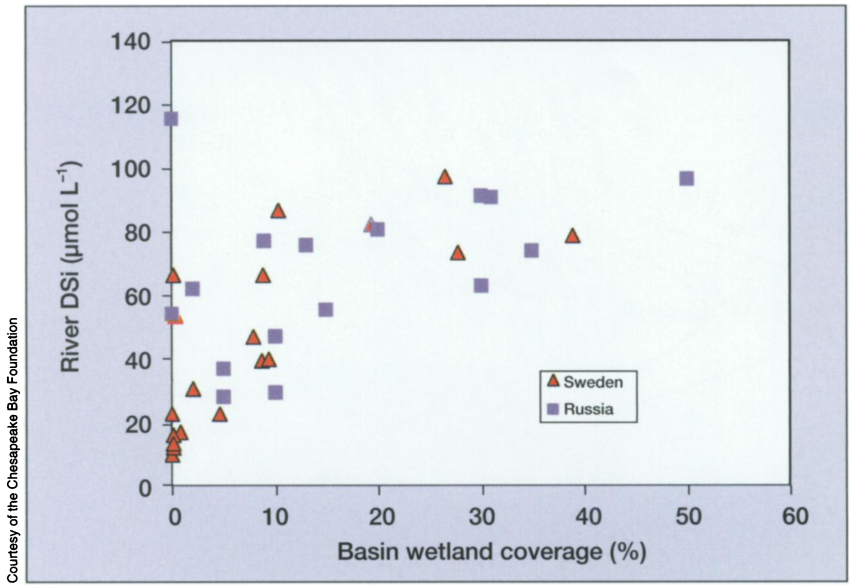

Figure 4. Relation between percentage of peat wetland coverage in river basins and DSi in draining rivers in boreal Sweden (data from Humborg et al. *2004) and Russia (data from Zakharova* et al. *2007).*

have the potential to reduce the transport of DSi by rivers by almost 50% during the growing season. Consistent with studies from other ecosystems, all data in this review indicate that wetlands are major storage and recycling hotspots for ASi.

Conclusions

Retention and recycling potential

Tidal marshes and tidal flats flood on a regular basis, creating a large potential for import, export, and recycling. High ASi concentrations in biomass create ideal conditions for tidal marshes to play a buffering role. Similar observations have been made in grassland ecosystems, with a higher export of DSi in tallgrass wet grasslands relative to drier areas (Blecker *et al.* 2006).

The hydrology of other wetland types can differ greatly from tidal marshes. Sub-Arctic peat bogs, characterized by lengthy water residence times, contained up to 5% of ASi by weight percentage, an order of magnitude more than tidal and fluvial wetlands. We hypothesize that inundation volume, water residence time, and flooding frequency are deciding factors governing ASi retention and recycling in wetlands:

- The regular import of water (flooding frequency) enhances deposition of suspended solids; sediment-associated phytoliths and diatom ASi are imported along with settling sediment.
- Long water residence time increases the potential for ASi retention, as equilibrium concentrations will be reached in soil water for DSi. As a result, ASi recycling will slow considerably, as dissolution is enhanced by the low ambient DSi concentrations (Van Cappellen 2003). High evaporation will further increase retention, as this essentially represents the loss of non-silica-enriched water.
- Ecosystem structure (grass and sedge abundance, abundance of sponges and diatoms) is highly dependent upon hydrology.

Studies in other ecosystems support our hypothesis. Lakes are characterized by continuous import of nutrients, a large volume and low reaction surface (high lake volume relative to sediment area), and a relatively long water residence time. Lakes can retain over 90% of boundary input of Si, buried as ASi in lake sediments (Conley *et al.* 1993). In addition, the creation of artificial lakes behind dams is severely reducing DSi and ASi export to coastal zones, as a result of both ASi burial in sediments (Humborg *et al.* 1997) and reduced water–terrestrial soil contact times (Humborg *et al.* 2002). In Sweden and Finland, relative lake area in river basins is negatively correlated to DSi concentrations in rivers, even though rivers are highly oligotrophic (ruling out phytoplankton burial as an ASi sink; Conley *et al.* 2000). Damming transforms wetlands into permanent lakes and reduces contact efficiency between the water phase and ASi-rich surfaces.

In grasslands, ASi in aboveground vegetation increases with higher precipitation (more water availability and nutrient input). At the same time, recycling of buried phytoliths is much more intensive with increased precipitation (flooding frequency), resulting in less effective burial of ASi and more intense weathering and DSi

Table 1. Net discharge weighted retention (NRDW, %) of DSi, dissolved inorganic nitrogen, soluble reactive phosphate, total nitrogen, total phosphorus, and upstream and downstream concentrations of DSi, after passage through wetland ecosystems

	NRDW (%)					µM			
Type	*DIN*	*DSi*	*SRP*	*Tot N*	*Tot P*	*U DSi*	*D DSi*	*Authors*	*Country*
Alluvial plain/coastal freshwater wetlands	23	6	46	na	34	251	140	Krieger (2003)	USA (Ohio)
Peat bog, dwarf shrubs	na	21	94	63	42	61	36	Emmett *et al.* (1994)	UK (Wales)
Temperate freshwater marsh	61	14	na	na	36	118	102	McCrimmon (1980)	Canada
Coastal brackish wetlands	na	na	na	na	na	106–110	29–67	Lane *et al.* (2004)	USA (Louisiana)

Notes: DIN: dissolved inorganic nitrogen; SRP: soluble reactive phosphate; Tot N: total nitrogen; Tot P: total phosphorus; U DSi: upstream DSi; D DSi: downstream DSi; na: the variable was not measured.

export (Blecker *et al.* 2006). Although recycling intensity is extreme in tidal marshes, storage is still comparable to that in ecosystems such as forests and dryland grass prairies (L Saccone unpublished), suggesting both high storage and recycling potential.

Figure 5. *An example of an unspoiled sub-Arctic peatland (Muddus National Park, northern Sweden).*

Future perspectives

We strongly encourage researchers to include Si in biogeochemical studies of wetlands in the following ways:

(1) Measure import and export of ASi and DSi in wetlands, to determine the size of the net sink or source; Si balances should be constructed for all wetland types, including balances for diatom, sponge, and phytolith ASi.
(2) Characterize the size of ASi pools in wetland soils and vegetation along a wide range of wetland habitat types. Although methods have long been available for the measurement of ASi in aquatic sediments (Demaster 1981), these wet chemical extractions of ASi have recently been shown to be acceptable for the complex mixture of ASi compounds in soils (Saccone *et al.* 2007).
(3) Establish a link between C and Si cycling in wetlands. Arctic wetlands, in particular, are among the most efficient C sinks in the global C cycle. Although Si weathering is closely linked to the C cycle through the uptake of atmospheric CO_2, budgets have not taken into account ASi retention and weathering, potentially biasing C budgets in the Arctic. The abundance of ASi-rich liverworts (Hodson *et al.* 2005) in Arctic marshes increases potential ASi retention.
(4) Conduct comparative studies along hydrological gradients of drainage, evaporation, flooding frequency, and residence time.
(5) Test for the retention of Si in riparian and sewage-treatment wetlands, aimed at reducing nutrient discharge to aquatic systems.

Such research should allow us to move into the next phase of wetland ecosystem science, with the development of mechanistic models of Si cycling, and will help us to predict the influence of wetlands (and loss of wetlands) on Si weathering, and hence climate change and eutrophication.

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