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Anthropogenic impact on biogenic Si pools in temperate soils

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Abstract

Human land use changes directly affect silica (Si) mobilisation and Si storage in terrestrial ecosystems and influence Si export from the continents, although the magnitudes of the impact are unknown. Yet biogenic silica (BSi) in soils is an understudied aspect. We have quantified and compared total biogenic (PSi_a) and easily soluble (PSi_e) Si pools at four sites along a gradient of disturbance in southern Sweden. An estimate of the magnitude of change in temperate continental BSi pools due to human disturbance is provided. Land use clearly affects BSi pools and their distribution. Total PSi_a and PSi_e for a continuous forested site at Siggaboda Nature Reserve ($66\,900 \pm 22\,800$ kg SiO_2 ha^{-1} and 952 ± 16 kg SiO_2 ha^{-1}) are significantly higher than disturbed land use types from the Råshult Culture Reserve including arable land ($28\,800 \pm 7200$ kg SiO_2 ha^{-1} and 239 ± 91 kg SiO_2 ha^{-1}), pasture sites ($27\,300 \pm 5980$ kg SiO_2 ha^{-1} and 370 ± 129 kg SiO_2 ha^{-1}) and grazed forest ($23\,600 \pm 6370$ kg SiO_2 ha^{-1} and 346 ± 123 kg SiO_2 ha^{-1}). Vertical PSi_a and PSi_e profiles show significant ($p < 0.05$) variation among the sites. These differences in size and distribution are interpreted as the long-term effect of reduced BSi replenishment and increased mobilisation of the PSi_a in disturbed soils. In temperate regions, total PSi_a showed a 10 % decline since agricultural development (3000BCE). Recent agricultural expansion (after 1700CE) has resulted in an average export of 1.1 ± 0.8 Tmol Si yr^{-1}, leading to an annual contribution of ca. 20 % to the global land-ocean Si flux carried by rivers. Human activities clearly exert a long-term influence on Si cycling in soils and contribute significantly to the land-ocean Si flux.

1 Introduction

It is well known that the oceanic biogeochemical cycle of Si is driven by biological processes. (Tréguer et al., 1995). Studies on biogenic silica (BSi) dynamics have focused mostly on marine environments (DeMaster, 2002; Ragueneau et al., 2006). In the oceanic and coastal zone, Si is an essential nutrient for diatom production and consequent diatom burial promotes carbon sequestration in the ocean depths (Brzezinski, 1985; Dugdale et al., 1995). The terrestrial and marine Si cycle are linked through the riverine fluxes of Si, which replenish the BSi lost to the deep oceans after burial of diatoms (Laruelle et al., 2009), supporting oceanic primary production.

In parallel to the biological control on oceanic Si cycling, there is growing evidence illustrating the importance of biological Si cycling in terrestrial ecosystems (Meunier et al., 1999; Conley, 2002; Van Cappellen, 2003). Large amounts of BSi are stored in terrestrial soils, primarily in the form of plant siliceous bodies called phytoliths. (Alexandre et al., 1997). BSi in the soil originates from litterfall from vegetation after die-off. Uptake of DSi in the vegetation and dissolution of BSi in soils was shown to control DSi export to rivers from catchments dominated by boreal wetlands (Struyf et al., 2010a), forests (Gérard et al., 2008) and grasslands (Blecker et al., 2006). Due to the terrestrial-ocean link in the global Si cycle, and the increasing evidence of the importance of anthropogenic disturbance on ecosystems in controlling terrestrial Si outputs, the study of BSi in terrestrial soils is now considered a crucial yet understudied aspect in our understanding of global Si cycling (Street-Perrott and Barker, 2008; Struyf and Conley, 2009).

Recent papers have demonstrated that land use changes can have significant effects on Si mobilization from the continents (Conley, 1997; Struyf et al., 2010b). Struyf et al. (2010b) showed that in temperate European watersheds sustained human cultivation led to a two-to threefold decrease in base flow delivery of Si to rivers. A conceptual model was proposed relating changes in Si fluxes to long-term soil disturbance. The model is based on the short-term (< 20 yrs; Conley et al., 2008) and long-term (500–1000 yrs) response of riverine Si fluxes following deforestation and historical agricultural expansion (Struyf et al., 2010b) and is comprised of four different stages: developing forest, climax forest, recently deforested areas and sustained cultivated areas. The authors suggest that developing forests stimulate mineral weathering. The major part of the weathered DSi is taken up by plants and deposited as BSi in biomass. The

amount of BSi annually added to soil is higher than the DSi leaching, creating a strong net BSi sink. As BSi mobilization through dissolution can be assumed to increase with increasing soil BSi stock, a near-equilibrium between BSi production and removal may eventually be reached under climax forest. When deforestation occurs, removal of BSi from the soil system is increased through different pathways. Vegetation water consumption is lowered, thereby increasing soil water and groundwater fluxes promoting leaching, which may be further enhanced by organic matter decomposition. Additionally, increased soil erosion may lead to the physical removal of BSi. After this initial flush, Si fluxes gradually decrease as crop harvesting and continuous soil disturbance prevents replenishment of the BSi stock. A new state with a reduced soil Si stock is reached in heavily cultivated land. The absence of significant soil BSi stocks result in low export fluxes of total Si compared to continuous and early deforested areas.

These findings emphasize the differences in biogeochemical Si cycling between various land uses and the impact of management of land use practices on the global Si cycle. Yet, information about the timescales associated with the transitions between different deforestation stages in the conceptual model is at present lacking. Key data needed to validate the model and to constrain the time scales involved are BSi stocks under different land uses, preferentially with known dates of deforestation or reforestation. However, no systematic surveys on the distribution of BSi in the soil as a function of land use and age of disturbance is available. We therefore aim to quantify and compare the distribution of total biogenic and easily soluble Si pools under different land uses, and compare bio-reactive Si stocks between the land use types. Comparison of different land use types will allow for assessing the response of BSi stocks to human impact. We provide a first evaluation of the concepts introduced by Struyf et al. (2010b) and provide an estimate for the time scale and the magnitude of the changes in continental BSi stocks in temperate regions due to cultivation of the landscape. Finally, we assess how this has impacted the total riverine Si flux from the continents to the coastal zone.

2 Materials and methods

2.1 Study area

Biogenic silica (BSi) pools within soil profiles were assessed under different land use types including pastures, arable land and forests. The sites had similar soil properties, geological history, climate and topography, but differed in land cover history and anthropogenic influences. All sites were located in southern Sweden: one at Siggaboda (continuous forest) and three at Råshult (grazed forest, pasture and arable land), located ca. 30 km northwest of Siggaboda.

Siggaboda is a 71 ha nature reserve in Småland, southern Sweden (56°27′ N, 14°12′ E) that has been continuously forested for at least 2700 years and is co-dominated by beech (*Fagus sylvatica*) and pine (*Picea abies*). Evidence for anthropogenic impact in the past three millenia is lacking. Deglaciation occurred approximately 14 500 years ago. Råshult is a cultural reserve near Älmhult (56°36′ N, 14°11′ E) and is best known as Carl Linnaeus' birth place. The area has a typical infield-outfield structure with traditionally tilled crop fields and hay meadows in the vicinity of the homestead (i.e. infields) and grazing areas, both pasture and forest, at a distance (i.e. outfields) (Lindbladh and Bradshaw, 1998) (Fig. 1). In both areas soils have developed on moraine material overlying granitic to gneissic bedrock and are located within the boreal-nemoral vegetation zone with a mean annual precipitation of ca. 700 mm yr^{-1}. The mean annual temperature is ca. 5 °C, with the July mean lying between 15 and 16 °C, and the January mean lying between −2 °C and −3 °C. Both areas have an undulating topography with slope gradients generally below 5 %.

The agricultural system in Råshult has not undergone any major changes since 1545 (Sweden Land Registry). The oldest indications of human impact are graves and cairns dating to the Bronze Age (1000–500BCE). The landnam was an interplay between periods of deforestation and agricultural expansion and periods of population decline and reforestation. (Lagerås, 2007). The first permanent settlements in southern Sweden were established during the early Iron Age (500BCE–400CE). Farmers abandoned the

area again in the late Iron Age (400–1000CE) and people resettled the area again in the 12th and 13th century. From this point on, two major periods of agricultural settlement and abandonment can be distinguished (Lagerås, 2007). The first coincides with the trans-European occurrence of the Black Death (14th and 15th century) and the second is related to depopulation of the countryside and the introduction of forestry (19th and 20th century). Two reform acts affected agricultural development in the area but were of minor importance in Råshult. The Land Division Reform (mid 17th century), was an unsuccessful attempt to group scattered properties. The Land Enclosure Reform, which started in the 19th century and continued in the 20th century, regrouped properties all over the country. At Råshult , the impact of these reforms was limited to administrative aspects such as property rights, while the Land Enclosure Reform created a strong intensification of agriculture elsewhere in southern Sweden (Lindbladh and Bradshaw, 1995).

2.2 Field sampling

An automatic hammer auger was used to take continuous cores of the soil pedons at the different sites. In total, 29 cores were taken at random places within different land use types including 7 in arable land, 8 in pasture, 8 in grazed forest and 6 in continuous forest. An overview is given in Table 1. Except when stones obstructed augering, cores were taken until the C-horizon (i.e. parent material).

2.3 Laboratory analysis

2.3.1 Soil properties

Soil samples were analysed every five centimetres within each horizon. Cores were cut, oven dried at 50 °C and stored in a cold room (4 °C). Thereafter samples were homogenized by mortar and pestle and sieved through a 2 mm mesh. Carbon contents were measured with a vario MAX CN Macro Elemental Analyzer (Elementar

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Analysensysteme GmbH, Germany). The grain size distribution was determined using a Coulter Counter LS 13 320 (Beckman Coulter, USA). Soil pH was measured using a glass electrode in 0.01 M $CaCl_2$ suspensions at a soil-to-solution ratio of 1:5.

2.3.2 Alkali-Extraction: total biogenic silica pool

The Na_2CO_3 extraction is a weak-base method originating from DeMaster. (1981) who found that (1) alumino-silicates release Si linearly over time and (2) that most BSi dissolves completely in the first 2 h of the digestion. The alkaline (Na_2CO_3) extraction procedure for BSi digests various fractions (i.e. biogenic silica, absorbed silica, non-crystalline amorphous silica); all defined as amorphous silica (Sauer et al., 2006). We therefore refer to the extracted Si pool as the alkali-extractable Si, CSi_a (Cornelis et al., in press). The reliability of the method has been shown for forested soils (Saccone et al., 2007) and wetland soils (Struyf and Conley, 2009). Approximately 30 mg of dried soil (< 2 mm) was mixed in 40 ml of 0.094 M Na_2CO_3 solution and digested for 5 h at 85 °C. A 1 ml aliquot was removed from the sample bottle after 3, 4 and 5 h and neutralized with 9 ml of 0.021 M HCl, before DSi determination (CSi_d) by the automated molybdate-blue method (Grasshoff et al., 1983). The total extracted silica concentration (CSi_t, g SiO_2 kg^{-1}) was calculated for each of the aliquots from:

$$CSi_t = \frac{CSi_d \cdot 0.04 \cdot 60 \cdot 10}{\text{Sample Weight}} \tag{1}$$

where 10 is the HCl dilution factor, 60 is the molecular mass of SiO_2 and 0.04 (litre) is the volume of Na_2CO_3 solution in which the sample is digested. The total CSi_a is then calculated by determining the intercept of the regression between CSi_t and extraction time (DeMaster, 1981). Extrapolating the Si release to the intercept is assumed to correct for mineral dissolution of Si (Clymans et al., 2011).

The distribution of concentrations, the amount of silica per unit soil, provides information on the BSi pools within a soil profile, but provides no information about total silica

pools per horizon. Dry bulk density (ρ_d, kg m^{-3}) samples were taken at different depths. The alkali-extracted pool ($PSi_{a,i}$, kg SiO_2 ha^{-1}) per horizon i was then calculated as:

$$PSi_{a,i} = (CSi_{a,i} \cdot \rho_{d,i} \cdot d_i) \cdot 10 \tag{2}$$

with;

- CSi_a the total alkali-extracted silica concentration (g SiO_2 kg^{-1})
- $\rho_{d,i}$ dry bulk density of horizon i (kg m^{-3})
- d_i depth of horizon i (m)

Total pools were calculated by integration of the pool over depth of the core. The maximum common depth that was reached in field sampling was 0.85 m.

2.3.3 $CaCl_2$-extraction: easily soluble silica

Easily soluble silica (CSi_e) is believed to arise from the dissolution of phytoliths in soils (Farmer et al., 2005) and is an estimate of the availability of DSi to plants. (Haysom and Chapman, 1975). Moreover, CSi_e is a good predictor of the equilibrium Si concentration in soil pore water (Zysset et al., 1999). The weakest extractant (after water) is $CaCl_2$, which only extracts the easily soluble Si pool (Berthelsen et al., 2001). In our measurements, 2 g of dried soil (< 2 mm) was shaken (linear movement) for 16 h with 20 ml 0.01 M $CaCl_2$ extractant (1:10 ratio) in a 50 ml Nalgene tube at 20 °C. After centrifugation at 4000 rpm for 30 min, the supernatant was filtered over 0.45 µm pore size (Chromafil® A-45/25) and analyzed for Si by the automated molybdate-blue method. Total easily soluble pools (PSi_e) were calculated following the same methodology as used for PSi_a calculations.

3 Results

3.1 Distribution of biogenic silica

Under all land uses the maximum CSi_a occurred in the top layer, followed by a general decreasing trend with depth (Fig. 2), despite small variations in distribution between land use types. On arable fields (Fig. 2) the top layer was relatively rich in CSi_a up to a depth of 0.25 m. This depth corresponds with typical plough depths of traditional tillage (Tebrugge and During, 1999). Under continuous forest, grazed forest and pasture the CSi_a rich top layer extended down to 0.15 m. About 75 % of the profiles at pasture sites, 50 % of the profiles in grazed forest, and all profiles in the continuous forest showed a second peak of CSi_a at intermediate depths (0.3–0.6 m), but after averaging, this secondary maximum is only visible for pasture and continuous forest.

CSi_a in the top layer generally followed the trend continuous forest > grazed forest ≥ pasture > arable land. Continuous forest soils were most enriched in CSi_a at depths between 0.1–0.4 m followed by arable land > grazed forest > pasture soils (Table 1). From 0.4 m downwards, continuous forest soils had considerably higher CSi_a, than all other land uses while grazed forest and pasture soils had slightly higher values than arable land.

The total PSi_a (integrated over a depth of 0.85 m) shows a major difference between the continuous forest and all other land uses (Fig. 1). Total PSi_a for the continuous forest site was more than double compared to other land uses ($66\,900 \pm 22\,800$ kg SiO_2 ha^{-1}). The total PSi_a in arable land was $28\,800 \pm 7200$ kg SiO_2 ha^{-1} and was slightly, but not significantly higher than the PSi_a at the grazed forest ($23\,600 \pm 6370$ kg SiO_2 ha^{-1}) and pasture sites ($27\,300 \pm 5980$ kg SiO_2 ha^{-1}).

PSi_a depends on both dry bulk density (ρ_d) and CSi_a. The low ρ_d in the top layer resulted generally in low PSi_a values for the top layers, although CSi_a reached their maxima at these depths (Fig. 2). This difference was most striking for continuous forest, as this highly humic top layer (> 20 % OC) had an extremely low ρ_d (< 200 kg m^{-3}).

For the deeper soil layers, variations in ρ_d were less important and variations in PSi_a coincided with variations in CSi_a.

The differences in total PSi_a and its distribution between the different land use types were tested using a non-parametric ANOVA analysis (Sas-Institute, 2003). Total PSi_a was significantly larger in continuous forests than at grazed forest ($p = 0.0019$), pasture ($p = 0.0018$) and arable ($p = 0.0062$) sites. Although there were differences in PSi_a in the top layer (0–0.1 m), these differences were not statistically significant. By contrast, PSi_a between 0.1–0.2 m in arable profiles were significantly larger then in pasture ($p = 0.024$) and grazed forest ($p = 0.0015$) profiles. Below 0.2 m PSi_a was significantly larger in continuous forest profiles compared to all other land uses (grazed forest ($p = 0.0019$), pasture ($p = 0.0028$) and arable land ($p = 0.0062$))

3.2 Distribution of easily soluble silica

In the top layers the distribution of CSi_e was rather distinct from the CSi_a (Figs. 3 and 4). CSi_e in the top layer were lower in CSi_e than below. Most profiles taken on pasture, grazed forest and continuous forest contained only small amounts of CSi_e at depths between 0.1 and 0.2 m. Further down CSi_e increases again and maximum values were reached at depths varying between 0.25–0.6 m (Fig. 3). Deeper in the soil profile CSi_e decreased again. For arable land CSi_e monotonously increased with depth. CSi_e values were generally lowest in profiles at arable land sites < pasture sites ≤ grazed forest sites ≪ continuous forest sites (Table 1).

All averaged profiles exhibited similar distribution in PSi_e with low pools in the top layer and increasing values at depth with maxima at different levels (Fig. 3). Continuous forest soils contained almost triple (952 ± 16 kg SiO_2 ha^{-1}) the PSi_e than pasture (370 ± 129 kg SiO_2 ha^{-1}) and grazed forest (346 ± 123 kg SiO_2 ha^{-1}) soils, and four times the amount found in arable land soils (239 ± 91 kg SiO_2 ha^{-1}) (Fig. 1). Most important differences were in the top layer and at depths > 0.6 m, where continuous forest has a significant larger pool then the other land uses ($p < 0.05$).

3.3 Physical and chemical soil properties

Soil properties like OC, pH and texture are given in Table 1. Analogous to CSi_a distribution there was (1) generally a progressive decrease of OC with depth, (2) an accumulation of OC in the top layer and (3) a decrease in OC pool from continuous forest over grazed forest and pasture towards arable land. A positive trend suggested the existence of an important relation between OC and CSi_a: $CSi_a = 3.4 + 0.4 \times OC$ ($R^2 = 0.45$, $p < .0001$). Good relationships between variables were found mainly for arable land ($R^2 = 0.65$), pasture ($R^2 = 0.83$) and grazed forest ($R^2 = 0.62$).

pH varied between 3.3 and 4.7 with an average of 4.28 ± 0.45 and is within the range for constant Si solubility (2.5–8) (Dove, 1995). The humic soil top layer under the continuous forest had the lowest pH values. No relationship was found between pH and CSi_a or CSi_e. Texture varied between sand and sandy loam. There was no differentiation with depth, nor with land use.

4 Discussion

4.1 Human impacts

4.1.1 BSi pools

Human activities exert a long-term influence on nutrient cycling and concentrations in soils (Foster et al., 2003), including BSi pools. Although total PSi_a did not change within a three year period following forest clearance at the Hubbard Brook Experimental Forest, a clear redistribution of PSi_a to deeper layers was observed (Saccone et al., 2008). We show that the total PSi_a pool in an undisturbed forest ecosystem, e.g. Sigaboda, was more than twice the size of total PSi_a pools under land uses influenced by human activities for five centuries, e.g. Råshult. The discrepancy between a continuously forested and disturbed sites is due to the long-term effects of reduced BSi input

by litterfall and the increased mobilization of the PSi_a pool in soils with disturbance. Reductions in soil PSi_a stocks after deforestation supports the conceptual model presented by Struyf et al. (2010b).

We expected significantly lower total PSi_a in arable land soils because it experienced the most intensive human impact through the systematic removal of crop residues with harvest and tillage operations. Yet, there were no significant differences in total PSi_a between the three land use types. Deforestation leads to major changes in hydrology (DeFries and Eshleman, 2004) and organic matter dynamics (Wallace Covington, 1981). Larger easily soluble pools (PSi_e) were found under grazed forest and pasture showing that arable fields have experienced a greater mobilisation of the labile BSi pool. Losses of PSi_a also occur with soil erosion and prevents the establishment of a BSi rich surface horizon and replenishment of BSi in the deeper horizons. However, due to the limited relief in the arable fields at Råshult, soil erosion was probably not a significant factor and limited the losses of PSi_a in soils.

4.1.2 BSi distribution

Our data show significant differences in the vertical distribution of PSi_a with disturbance, although total PSi_a pools were not different for all three human land use types. Nutrient leaching and biological (re)cycling determines the vertical distribution of soil nutrients (Jobbágy and Jackson, 2001; Sommer et al., 2006). The accumulation in the top layer and occurrence of a peak at depth (0.25–0.6 m) in CSi_a indicates the influence of both leaching and biological cycling on the Si distribution in our soils. The soil CSi_a profile under continuous forest cover results from the interaction between both processes. Similar PSi_a distributions were observed in temperate forest soils (Cornelis et al., in press). The large PSi_a pool in the top layer is the result of biogenic processes (Blecker et al., 2006). At depth, the increase in CSi_a results from root phytolith input at root depth (Watteau and Villemin, 2001) and pedogenic processes such as the translocation-accumulation of phytoliths and Si adsorption onto Fe oxides and the formation of pedogenic opal (Cornelis et al., in press). The peak was absent under arable land and only slightly visible under pasture and grazed forest. The absence of a PSi_a peak at depth for arable land supports the hypothesis of insufficient BSi replenishment. The transition towards arable land limits biological cycling to the upper soil layer, i.e. root depth. At depth, a decrease in PSi_a has occurred during the last five centuries of cultivation due to continuous dissolution.

PSi_a in the upper 0.25 m of arable land were higher than both grazed forest and pasture, although crop harvest is believed to limit PSi_a input. However, the Si replenishment rate in the topsoil of arable land can be relatively high due to the high root density of crops in this zone. On grazing land, CSi_a is high in the top layer due to the effects of above ground biomass decomposing at the surface replenishing PSi_a pools. The lower subsoil (> 0.4 m) PSi_a pool and PSi_e pool under arable land may indicate that Si leaching under arable land is indeed more intense compared to grazing land.

4.2 Biogenic silica and organic carbon

Plant-available Si is influenced by several factors, such as pH, clay and organic matter (OM) content, Al and Fe oxides, and parent material (Höhn et al., 2008). In contrast to other factors like pH and clay, OC varied between land use types (Table 1). Positive relationships between CSi_a and OC for grazed forest, pasture and arable land confirmed that OC is a good proxy for BSi content, which has been previously shown in grassland soils (Blecker et al., 2006). Nevertheless, variations in CSi_a with depth in continuously forested ecosystems did not reflect variations of soil OC with depth. Several factors such as a varying phytolith content of roots with depth and/or variations of phytolith solubility with depth could create such a profile. Moreover, this indicates a differentiation in processes responsible for BSi and OC storage. Phytolith translocation to deeper depths can occur (Alexandre et al., 1997; Meunier et al., 1999), but translocation of phytoliths does not necessarily imply translocation of OC through the profile. The percentage OC occluded in phytoliths is limited (Parr and Sullivan, 2005), therefore, OC could only be used as an indicator for CSi_a rather than a predictor.

4.3 Historical deforestation: an estimate for temperate regions of the effect on BSi pools

Our data provide an opportunity to estimate historical changes in BSi storage in soils, and the associated Si loss towards the aquatic system, assuming that BSi is converted to DSi and exported from the system. The amount of BSi accumulated in soils depends upon the input, output and recycling of silica within the soil-vegetation continuum. Measurements of BSi pools in soils are rare, especially for temperate regions (Blecker et al., 2006; Saccone et al., 2007). Most studies are constrained to specific vegetation types (forest or grassland), and data for arable lands are lacking. BSi pools typically range between 15 000 and 105 000 $kg\,SiO_2\,ha^{-1}$ (Struyf and Conley, 2011). BSi pools were larger in soils under continuous forest cover ($66\,900 \pm 22\,800\,kg\,SiO_2\,ha^{-1}$) and were lower in grazed forest, pasture and arable land (on average $26\,600 \pm 6520\,kg\,SiO_2\,ha^{-1}$). Our data fall within the range of BSi previously observed. Our study found that PSi_a was reduced by $40\,300 \pm 23\,700\,kg\,SiO_2\,ha^{-1}$, and PSi_e with $634 \pm 199\,kg\,SiO_2\,ha^{-1}$. The first official records from Råshult recording human disturbance date back to 1545 and have persisted until present, e.g. 465 years (Swedish Land Registry), although there are traces of agriculture from Medieval time. We assumed a constant annual loss between 1545 until present providing an average annual loss of $86.7 \pm 51.0\,kg\,SiO_2\,ha^{-1}\,yr^{-1}$ from PSi_a and $1.4 \pm 0.4\,kg\,SiO_2\,ha^{-1}\,yr^{-1}$ from the PSi_e pool. This is higher than the increased Si export seen after deforestation ($16\,kg\,SiO_2\,ha^{-1}\,yr^{-1}$) in Hubbard Brook Experimental Forest (Conley et al., 2008).

Historical arable land and pasture distributions were reconstructed based on statistics combined with satellite information and specific allocation algorithms covering the period 10000BCE to 2000CE (Klein Goldewijk et al., 2011). We assumed that the total area available for land use conversion is constant, and equals the sum of the forested area ($Area_F$) and disturbed area ($Area_D$) in 2005 (World Bank database – http://data.worldbank.org/, last acces: 22 February 2011). We used only two land use types: continuous forest cover and disturbed landscapes (pasture and arable lands). We also assumed that a constant annual Si loss rate occurred between both land use types. Based on these assumptions, total PSi_a (Fig. 5) and PSi_e (Fig. 6) pools were calculated at different time periods in the past in temperate regions covering 70 % of the land surface (Table 2). In 2005CE, soils stored approximately 4010 ± 817 Tmol Si, which represents a decrease of 400 Tmol Si since 3000BCE. Recent land use conversion, after 1700CE, has resulted in major depletion of PSi_a and PSi_e. In temperate regions from 3000BCE onwards PSi_a pools have been lost at a rate of 0.09 ± 0.06 Tmol Si yr^{-1} while recent agricultural expansion (after 1700CE) resulted in an average rate of 1.1 ± 0.8 Tmol Si yr^{-1}. Historical land use changes in temperate regions could annually increase the riverine load by ca. 20 % of the global land-ocean flux of DSi (estimated on 5.6 Tmol Si yr^{-1}). The net contribution will be lower due to retention within rivers and lakes estimated to range from 1.15 Tmol Si yr^{-1} to 2.4 Tmol Si yr^{-1} (Laruelle et al., 2009; Dürr et al., 2011). Our estimate shows the importance of contemporary and historical land use changes on potential Si delivery to the oceans (Conley et al., 2008).

Uncertainties in the land use data are due to the lack of accurate historical data. Furthermore, high standard deviations on Si pools support the necessity of more data on Si pools in soils. Moreover, our arable land use data are from "traditionally" managed arable lands, while under intense cultivated land use used today in industrial agriculture, pools could be depleted even more (Struyf et al., 2010b). In order to improve the estimate special attention needs to be given to variation in land use and land use history. Until now research has focussed mostly on natural ecosystems (Alexandre et al., 1997; Blecker et al., 2006) rather than human influenced systems.

Our estimate is the first to consider the potential of land use changes due to agricultural expansion Si fluxes from the land to the ocean. We show that total PSi_a pools are reduced with 10 % in temperate regions with land use changes. Although a considerable amount is known regarding the impact of temperature, runoff and land area on silicate weathering, to date there are no studies that have considered changes in the

contribution of the terrestrial biosphere on Si fluxes (Conley, 2002; Street-Perrott and Barker, 2008). Removal of vegetation may compensate mineral weathering responses. Recently, silicon isotopes and signatures of Ge/Si have been used in an attempt to gain insight in the dynamics of terrestrial ecosystem pools (Henriet et al., 2008; Derry et al., 2005; Blecker et al., 2006) providing promising tools to track the origin of Si in aquatic systems (Struyf and Conley, 2011).

5 Conclusions

We have shown that total PSi_a in a continuous forest ecosystem was more than twice the size of total PSi_a under human disturbed land uses. We believe long-term disturbance of the vegetation-soil continuum lowered BSi inputs and increased depletion of the PSi_a. These results are consistent with an existing conceptual model describing the effect of human impact on the terrestrial Si-cycle along a deforestation gradient (Struyf et al., 2010b). The absence of a significant difference in total PSi_a for the disturbed land use types conflicts with the idea of a more degraded state under arable land. This is explained by the absence of severe soil erosion in the traditional tilled arable fields. Nevertheless larger PSi_e under grazed forest and pasture indicate that arable fields have undergone a larger mobilisation of the labile BSi pool. Significant differences in the vertical PSi_a and PSi_e distributions result from the affect of deforestation on biogenic and pedogenic processes responsible for the Si distribution in our soils. Along the gradient, the disappearance of the PSi_a peak at intermediate depths implies that land use conversion limited biological cycling and intensified leaching processes at depth. Furthermore historical land use changes in temperate regions decreased BSi storage in soils by 10 % and could contribute ca. 20 % to the global land-ocean Si flux carried by rivers. Despite uncertainties, we clearly show the importance of contemporary and historical human perturbations on Si-cycling in soils and potential Si-delivery to the ocean.

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Table 1. Physical and chemical soil properties of the studied soils.

Land Use	Depth	Silica Concentration CSi_a	CSi_e	OC	Soil Texture Sand	Silt	Clay	pH
	[m]	[g SiO_2 kg^{-1}]		[%]				($CaCl_2$)
Continuous Forest	0 – 0.1	15.0	0.049	ND	ND	ND	ND	ND
(*n* = 6)	0.1 – 0.2	11.4	0.043	20.3	58.2	38.4	3.3	3.3
	0.2 – 0.4	5.3	0.089	4.2	59.1	38.2	2.7	4.3
	0.4 – 0.6	7.2	0.089	2.0	55.9	41.0	3.1	4.5
	0.6 – 0.85	4.3	0.086	1.4	52.7	43.6	3.7	4.5
Grazed Forest	0 – 0.1	9.8	0.026	12.5	73.3	23.9	2.7	3.5
(*n* = 8)	0.1 – 0.2	4.8	0.026	6.1	58.0	37.9	4.1	3.9
	0.2 – 0.4	3.2	0.045	1.8	62.6	34.1	3.3	4.4
	0.4 – 0.6	3.0	0.040	1.2	66.2	30.8	3.0	4.5
	0.6 – 0.85	1.8	0.041	0.8	72.7	24.5	2.8	4.6
Pasture	0 – 0.1	12.1	0.017	10.4	73.5	24.2	2.3	3.9
(*n* = 8)	0.1 – 0.2	3.3	0.025	2.7	63.9	33.0	3.2	4.1
	0.2 – 0.4	2.9	0.041	2.0	65.5	31.3	3.2	4.5
	0.4 – 0.6	3.4	0.037	1.1	74.3	23.3	2.4	4.6
	0.6 – 0.85	2.0	0.030	0.3	77.3	20.3	2.4	4.6
Arable Land	0 – 0.1	7.5	0.013	2.8	57.1	39.8	3.1	4.6
(*n* = 7)	0.1 – 0.2	7.0	0.015	2.3	58.4	38.4	3.2	4.6
	0.2 – 0.4	5.1	0.019	1.4	60.1	36.4	3.6	4.7
	0.4 – 0.6	2.5	0.029	0.7	62.7	33.7	3.5	4.7
	0.6 – 0.85	1.7	0.016	0.2	91.3	7.6	1.2	4.5

ND = No Data.

Table 2. Historical evolution (3000BCE–2005CE) of the biogenic silica (PSi_a) and easily soluble silica pools (PSi_e) for continuous, disturbed and total land area in temperate soils. Standard errors are given in between parentheses. Land use data: Klein Goldewijk et al., 2011 and World Bank database http://data.worldbank.org/, last acces: 22 February 2011.

Year	Area (Mha)	Continuous PSi_a (Tmol)	Continuous PSi_e (Tmol)	Area (Mha)	Disturbed PSi_a (Tmol)	Disturbed PSi_e (Tmol)	Area (Mha)	Total Temperate PSi_a (Tmol)	Total Temperate PSi_e (Tmol)
3000 BCE	3963	4417 (± 1506)	63 (± 1.05)	14	7 (± 1)	0.07 (± 0.04)	3977	4424 (± 1506)	63 (± 1.06)
0 CE	3865	4309 (± 1469)	61 (± 1.03)	112	49 (± 12)	0.59 (± 0.37)	3977	4359 (± 1469)	62 (± 1.10)
1000 CE	3869	4312 (± 1470)	62 (± 1.03)	108	57 (±5)	0.71 (± 0.31)	3977	4369 (± 1470)	62 (± 1.08)
1500 CE	3774	4207 (± 1434)	60 (± 1.00)	203	114 (± 14)	1.37 (± 0.57)	3977	4321 (± 1434)	61 (± 1.16)
1700 CE	3704	4130 (± 1407)	58 (± 1.21)	273	164 (± 5)	2.06 (± 0.69)	3977	4293 (± 1407)	61 (± 1.39)
1800 CE	3546	3954 (± 1348)	56 (± 0.95)	431	318 (± 30)	4.14 (± 0.80)	3977	4271 (± 1348)	60 (± 1.24)
1900 CE	2931	3268 (± 1114)	47 (± 0.78)	1046	943 (± 201)	12.78 (± 1.02)	3977	4211 (± 1132)	59 (± 1.28)
2005 CE	1866	2080 (± 709)	29 (± 0.50)	2111	1932 (± 406)	26.06 (± 1.96)	3977	4012 (± 817)	56 (± 2.02)

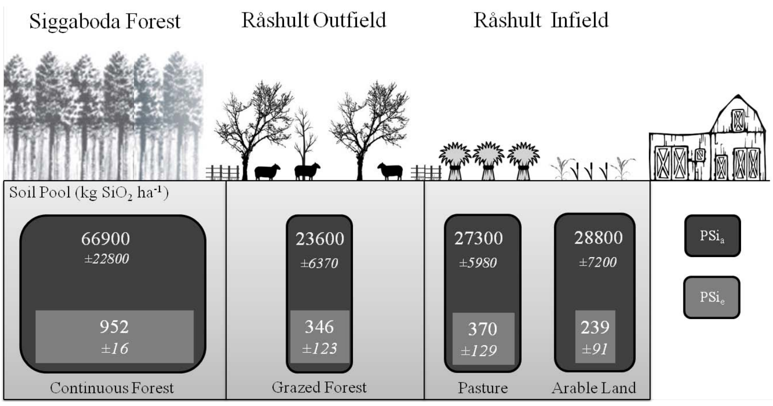

Fig. 1. Representation of the land use sequence in the study area, southern Sweden. Values indicate measured means (±standard errors) for total biogenic silica pool (PSi_a) and easily soluble silica pool (PSi_e) in the soils.

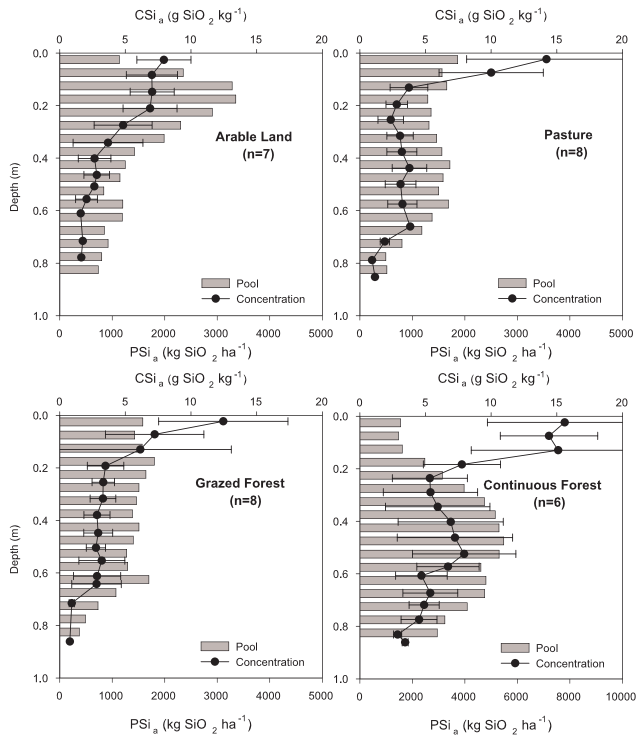

Fig. 2. Average distribution of alkaline (Na_2CO_3) extracted silica (CSi_a, $g\,SiO_2\,kg^{-1}$ dry soil) and total CSi_a-pools (PSi_a, $kg\,SiO_2\,ha^{-1}$) by depth under various land uses in southern Sweden soils. N = number of profiles analysed under specific land use. Scale x-axis not constant.

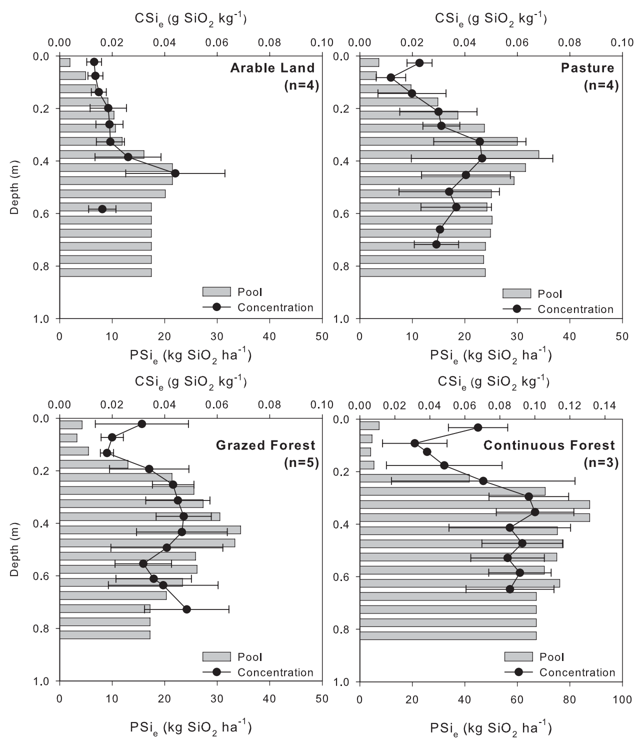

Fig. 3. Average distribution of easily ($CaCl_2$) soluble silica (CSi_e, $g\,SiO_2\,kg^{-1}$ dry soil) and total CSi_e -pools (PSi_e, $kg\,SiO_2\,ha^{-1}$) by depth under various land uses in southern Swedish soils. N = number of profiles analysed under specific land use. Scale x-axis not constant.

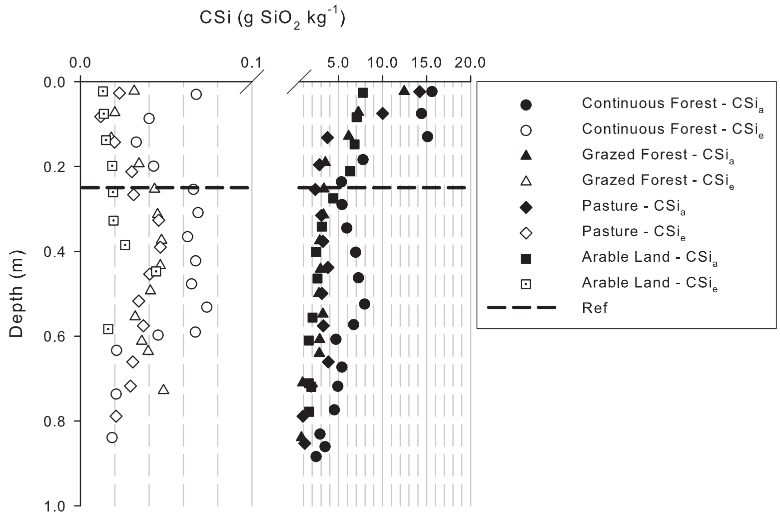

Fig. 4. Average distribution of alkaline extracted silica (CSi_a) and easily soluble silica (CSi_e) in g SiO_2 kg^{-1} dry soil in soils under various land uses in southern Sweden.

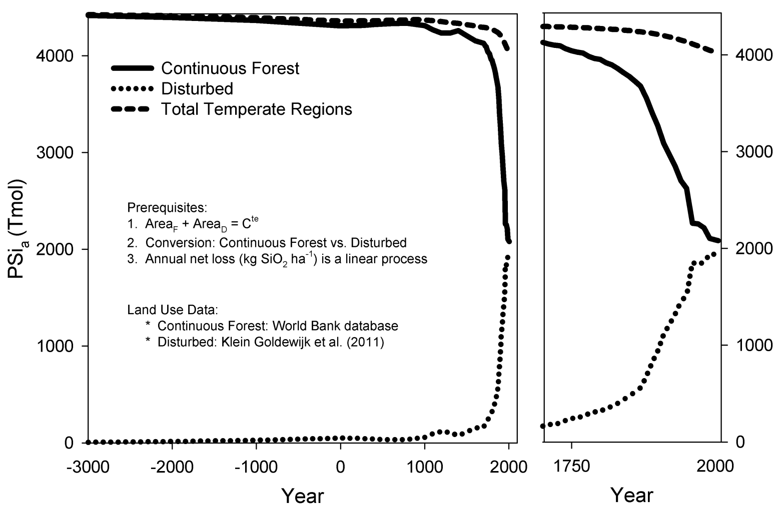

Fig. 5. Historical evolution (3000BCE–2005CE) of the biogenic silica pool (PSi_a, Tmol) for continuous, disturbed and total land area in temperate soils.

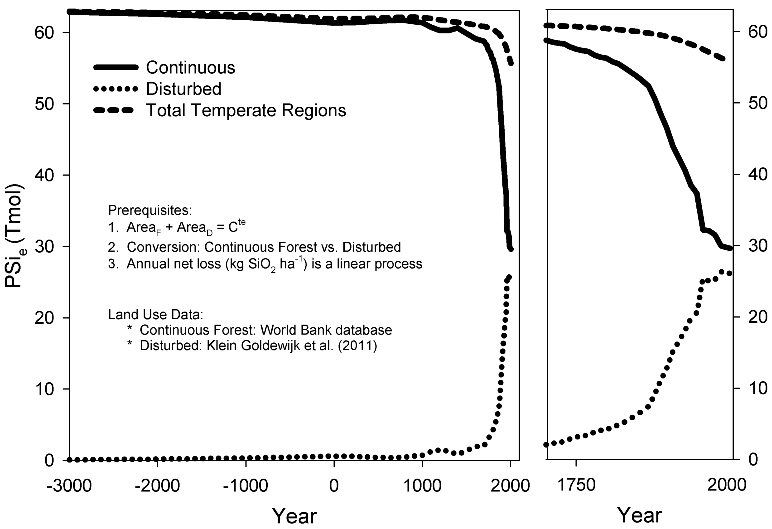

Fig. 6. Historical evolution (3000BCE–2005CE) of the easily soluble silica pool (PSi_e, Tmol) for continuous, disturbed and total land area in temperate soils.