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Anthropogenic impact on amorphous silica pools in temperate soils

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Abstract. Human land use changes perturb biogeochemical silica (Si) cycling in terrestrial ecosystems. This directly affects Si mobilisation and Si storage and influences Si export from the continents, although the magnitude of the impact is unknown. A major reason for our lack of understanding is that very little information exists on how land use affects amorphous silica (ASi) storage in soils. We have quantified and compared total alkali-extracted (PSi_a) and easily soluble (PSi_e) Si pools at four sites along a gradient of anthropogenic disturbance in southern Sweden. Land use clearly affects ASi 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 ASi replenishment, as well as changes in ecosystem specific pedogenic processes and increased mobilisation of the PSi_a in disturbed soils. We have also made a first, though rough, estimate of the magnitude of change in temperate continental ASi pools due to human disturbance. Assuming that our data are representative, we estimate that total ASi storage in soils has declined by ca. 10 % since the onset of agricultural development (3000 BCE). Recent agricultural expansion (after 1700 CE) may have resulted in an average additional export of 1.1 ± 0.8 Tmol Si yr^{-1} from the soil reservoir to aquatic ecosystems. This is ca. 20 % to the global land-ocean Si flux carried by rivers. It is necessary to update this estimate in future studies, incorporating differences in pedology, geology and climatology over temperate regions, but data are currently not sufficient. Yet, our results emphasize the importance of human activities for Si cycling in soils and for the land-ocean Si flux.

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1 Introduction

It is well known that the oceanic biogeochemical cycle of Si is driven by biological processes (i.e. diatom uptake) (Tréguer et al., 1995). Studies on biogenic silica (BSi) dynamics, i.e. biologically precipitated Si, have focused mostly on marine environments (DeMaster, 2002; Ragueneau et al., 2006). In the oceanic and coastal zone, dissolved silica (DSi) is an essential nutrient for diatom production and consequent diatom BSi 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 due to the diatom burial (Laruelle et al., 2009) and are therefore a key element in maintaining the ocean's primary productivity. Evidently, the ultimate control on riverine Si fluxes is the rate at which silicate minerals are weathered on the continents. However, Si weathering and riverine Si fluxes are not directly coupled. 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; Derry et al., 2005). Large amounts of Si are stored in terrestrial soils in a more soluble amorphous form than mineral Si. The amorphous Si (ASi) constitutes mainly of biogenic silica (BSi), primarily in the form of plant siliceous bodies called phytoliths (Alexandre et al., 1997), but also as different pedogenic Si forms (Sauer et al., 2006). This implies that riverine Si fluxes will be affected by biological and pedological processes. Uptake of DSi in the vegetation and dissolution of ASi in soils has been shown to be an important factor for the 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).

Recent papers have also 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 yr; Conley et al., 2008) and long-term (500–1000 yr) 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, deposited as ASi in the biomass and is finally incorporated in the soil through litterfall and vegetation die-off. The amount of ASi annually added to soil is higher than the DSi leaching, creating a net ASi sink. As ASi mobilization through dissolution can be assumed to increase with increasing soil ASi stock, a near-equilibrium between ASi production and removal may eventually be reached under climax forest. When deforestation occurs, removal of ASi 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 ASi. After this initial flush, Si fluxes will gradually decrease as crop harvesting and continuous soil disturbance prevent the replenishment of the ASi stock. Finally a new equilibrium state with a reduced soil Si stock will be reached. At this stage, the soil ASi stock and DSi export fluxes are low in comparison to those occurring under forest or just after deforestation.

The model proposed by Struyf et al. (2010b) provides a conceptual framework for the interpretation of the limited observational data on the effect of land use and land use change on Si cycling. Yet, information about the timescales associated with the transitions between different stages in the conceptual model is at present entirely lacking. Key data needed to validate the model and to constrain the time scales involved are ASi stocks under different land uses, preferentially with known dates of deforestation or reforestation. However, at present no systematic surveys on the distribution of ASi in the soil as a function of land use and age of disturbance are available. We therefore aim to quantify and compare the distribution of total alkali-extracted Si and easily soluble Si pools under different land uses, and compare Si stocks between the land use types. Comparison of different land use types will allow for assessing the response of ASi stocks to human impact. We provide a first evaluation of the concepts introduced by Struyf et al. (2010b) and provide a first estimate for the time scale and the magnitude of the changes in continental ASi stocks in temperate regions due to cultivation of the landscape. Finally, we illustrate how this may have impacted the total riverine Si flux from the continents to the coastal zone.

2 Materials and methods

2.1 Study area

Silica (Si) pools within soil profiles were assessed under different land use types including pasture, arable land and forests. 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. The sites had similar soil properties, geological history, climate and topography, but differed in land cover history and anthropogenic influences.

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* L.) and pine (*Picea abies* L.). 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 arable 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). Arable fields are tilled using a system called *ensäde*, which means fields are sown every year without fallow periods (M. Mikaelsson, personal communication, 2010). Crops include barley (*Hordeum vulgare* L.), rye (*Secale cereal* L.), oats (*Avena sativa* L.) and flax (*Linum usitatissimim* L.). Pastures are dominated by herbaceous species such as viper's grass (*Scorzonera hispanica* L.), common milkwort (*Polygala vulgaris* L.), matt grass (*Axonopus fissifolius*), bitter vetch (*Vicia ervillia* L.) and others. The forest component includes major deciduous tree species such as lime (*Tilia cordata*), hornbeam (*Carpinus betulus* L.), hazel (*Corylus avellana* L.) and beech (*Fagus sylvatica* L.). 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 %.

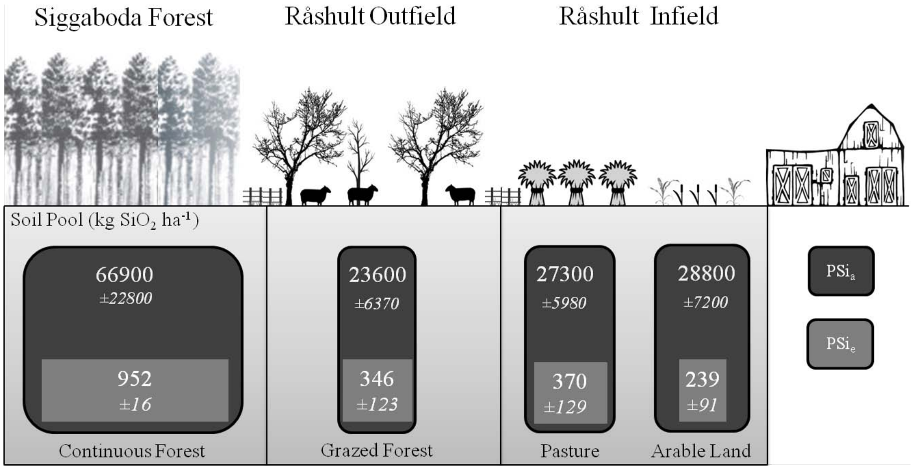

Fig. 1. Representation of the land use sequence in the study area, southern Sweden. Values indicate measured means (± standard errors) for total amorphous silica pool (PSi_a) and easily soluble silica pool (PSi_e) in the soils.

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 (1000–500 BCE). 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 (500 BCE–400 CE). Farmers abandoned the area again in the late Iron Age (400–1000 CE) 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 pan-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 content was measured with a vario MAX CN Macro Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). The grain size distribution was determined using a Coulter Counter LS 13320 (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. Cation Exchange Capacity (CEC) and Base Saturation (BS) were measured using NH_4OAc (Warncke and Brown, 1998).

2.3.2 Alkali-extraction

The Na_2CO_3 extraction is a weak-base method originating from DeMaster (1981) who found (1) that alumino-silicates release Si linearly over time and (2) that most ASi dissolves completely in the first 2 h of the digestion. The alkaline (Na_2CO_3) extraction procedure digests various Si fractions (i.e. biogenic and pedogenic silica, absorbed silica, poorly crystalline forms) (Sauer et al., 2006). Given their origin and the acidic conditions in our soils, poorly crystalline mineral forms such as allophane and imogolite are not important in this study. The alkali-extractable Si pool can therefore be considered as equivalent to the amorphous Si pool. We therefore refer to the extracted Si pool as the amorphous Si pool (PSi_a) and to the equivalent Si concentration as the amorphous Si concentration, (CSi_a). A generally higher

Table 1. Physical and chemical soil properties of the studied soils (ND = No Data).

Land Use	Depth	Silica Concentration		OC	Soil Texture			CEC	BS	pH
		CSi_a	CSi_e		Sand	Silt	Clay			
	[m]	[$g\,SiO_2\,kg^{-1}$]			[%]					($CaCl_2$)
Continuous Forest ($n=6$)	0–0.1	15.0	0.049	ND	ND	ND	ND	21	6.7	ND
	0.1–0.2	11.4	0.043	20.3	58.2	38.4	3.3	18	9.9	3.3
	0.2–0.4	5.3	0.089	4.2	59.1	38.2	2.7	9.0	13	4.3
	0.4–0.6	7.2	0.089	2.0	55.9	41.0	3.1	6.8	13	4.5
	0.6–0.85	4.3	0.086	1.4	52.7	43.6	3.7	3.8	11	4.5
Grazed Forest ($n=8$)	0–0.1	9.8	0.026	12.5	73.3	23.9	2.7	17	16	3.5
	0.1–0.2	4.8	0.026	6.1	58.0	37.9	4.1	6.3	14	3.9
	0.2–0.4	3.2	0.045	1.8	62.6	34.1	3.3	4.5	16	4.4
	0.4–0.6	3.0	0.040	1.2	66.2	30.8	3.0	3.1	8	4.5
	0.6–0.85	1.8	0.041	0.8	72.7	24.5	2.8	1.6	10	4.6
Pasture ($n=8$)	0–0.1	12.1	0.017	10.4	73.5	24.2	2.3	12	15	3.9
	0.1–0.2	3.3	0.025	2.7	63.9	33.0	3.2	4.3	11	4.1
	0.2–0.4	2.9	0.041	2.0	65.5	31.3	3.2	6.3	12	4.5
	0.4–0.6	3.4	0.037	1.1	74.3	23.3	2.4	5.5	13	4.6
	0.6–0.85	2.0	0.030	0.3	77.3	20.3	2.4	5.3	13	4.6
Arable Land ($n=7$)	0–0.1	7.5	0.013	2.8	57.1	39.8	3.1	6.7	46	4.6
	0.1–0.2	7.0	0.015	2.3	58.4	38.4	3.2	5.9	39	4.6
	0.2–0.4	5.1	0.019	1.4	60.1	36.4	3.6	1.7	53	4.7
	0.4–0.6	2.5	0.029	0.7	62.7	33.7	3.5	1.5	34	4.7
	0.6–0.85	1.7	0.016	0.2	91.3	7.6	1.2	ND	44	4.5

solubility of the amorphous Si fraction as compared to the mineral phase makes it more easily available for biological (re-)cycling on shorter time scales (Sommer et al., 2006). The reliability of the method has been shown for forested soils (Saccone et al., 2007), arable soils (Clymans et al., 2011) 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:

$$CSi_t = \frac{CSi_d \cdot 0.04 \cdot 60 \cdot 10}{\text{Sample Weight}}. \quad (1)$$

where 10 is the HCl dilution factor, 60 is the molecular mass of SiO_2 and 0.04 (l) 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 (Koning et al., 2002).

The distribution of concentrations, the amount of silica per unit soil, provides information on the ASi 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:

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

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 (CSi_e) is an estimate of DSi available 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 this easily soluble Si pool (Berthelsen et al., 2001). In our measurements, 2 g of

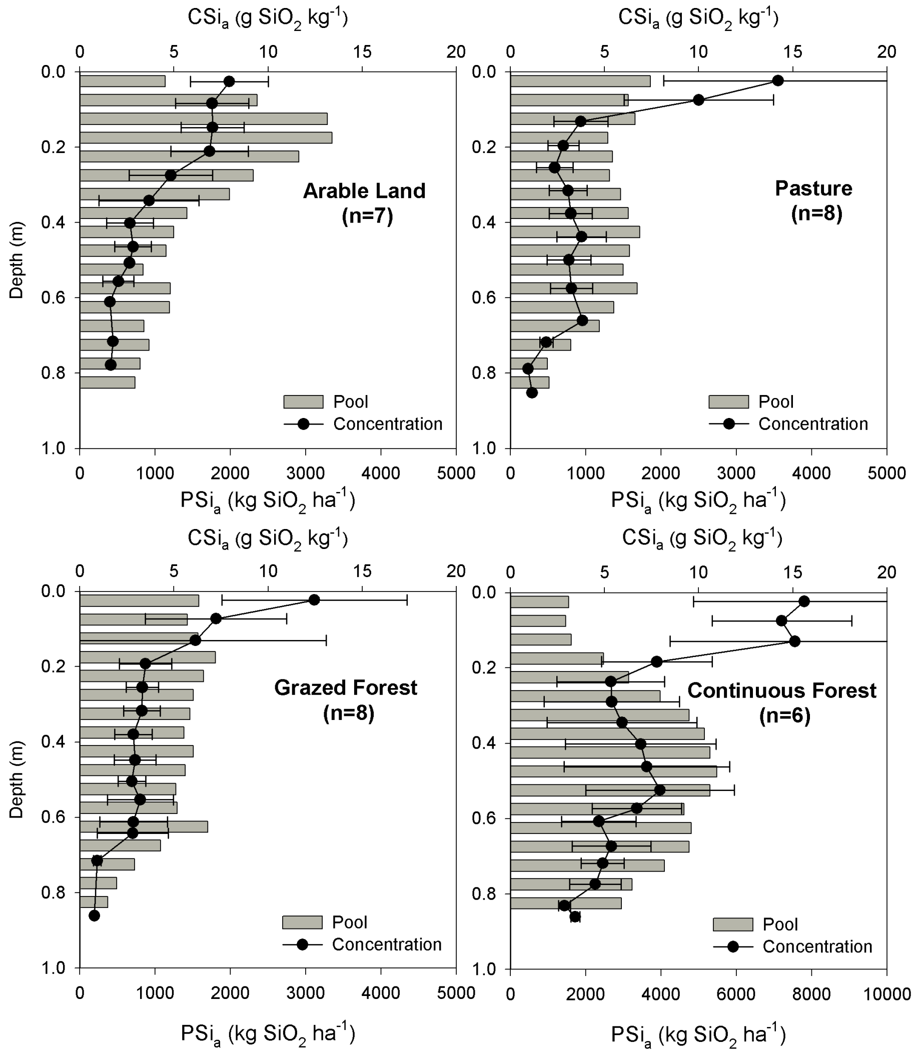

Fig. 2. Average distribution of alkaline (Na_2CO_3) extracted silica (CSi$_a$, g SiO_2 kg^{-1} dry soil) and total CSi$_a$-pools (PSi$_a$, kg SiO_2 ha^{-1}) by depth under various land uses in southern Sweden soils. N = number of profiles analysed under specific land use. Scale x-axis not constant.

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 (Höhn et al., 2008). 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 amorphous 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, 2002–2003). 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). While the maximum CSi_a occurred in the top layer (0–0.1 m) under all land uses, CSi_e did not reach its maximum here. 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 $\leq$ grazed forest sites $\ll$ 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 amount of PSi_e in pasture soils (370 ± 129 kg SiO_2 ha^{-1}) and grazed forest soils (346 ± 123 kg SiO_2 ha^{-1}), 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, CEC, BS, pH and texture are given in Table 1. The soils for each land use type are classified as a typical Cambisol (ISSS-ISRIC-FAO, 1998). 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 these two 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 systematic differentiation with depth, nor with land use.

4 Discussion

4.1 Human impacts

4.1.1 ASi pools

Human activities exert a long-term influence on nutrient cycling and concentrations in soils, including ASi pools (Foster et al., 2003). 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. Siggaboda, 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 ASi input by litterfall and the increased mobilization of the PSi_a pool in soils due to soil disturbance and the change in hydrological regime. The reductions in soil PSi_a storage 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 anthropogenic land use types. Larger easily soluble pools (PSi_e) were found under

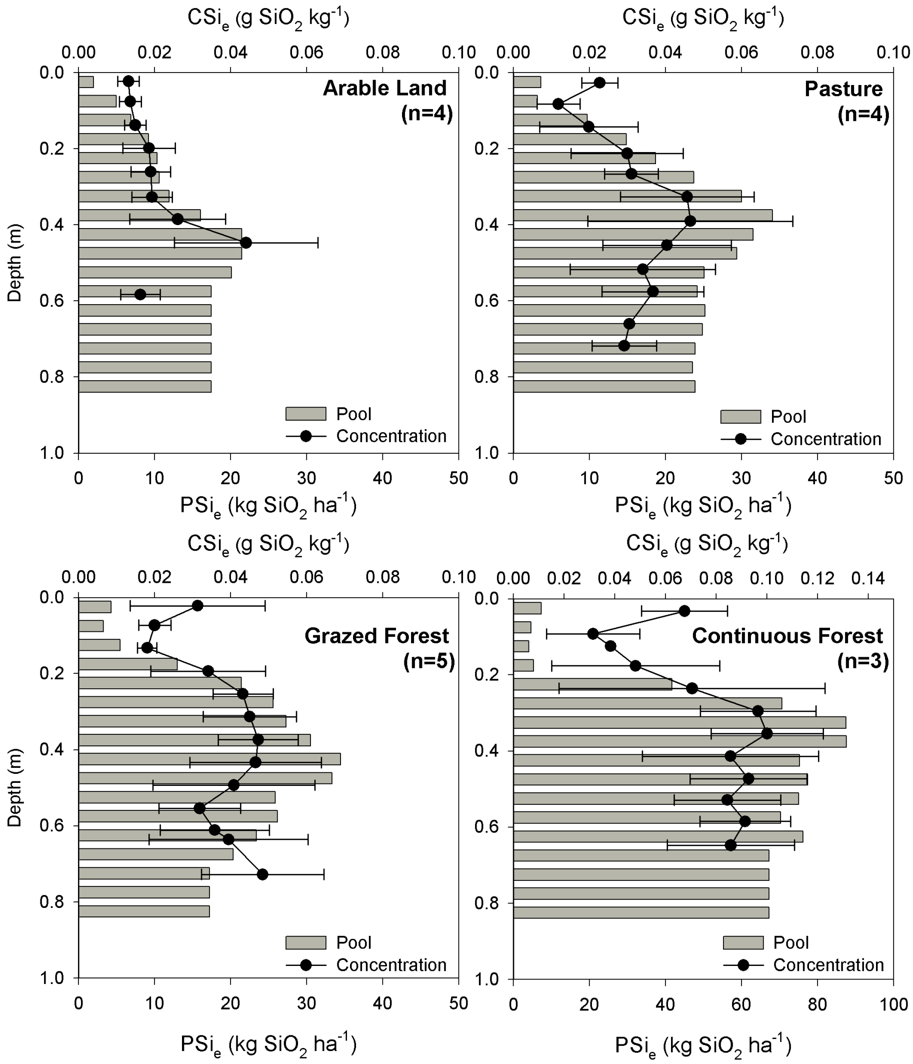

Fig. 3. Average distribution of easily ($CaCl_2$) soluble silica (CSi$_e$, g SiO_2 kg^{-1} dry soil) and total CSi$_e$-pools (PSi$_e$, kg SiO_2 ha^{-1}) by depth under various land uses in southern Swedish soils. *N* = number of profiles analysed under specific land use. Scale x-axis not constant.

grazed forest and pasture showing that arable fields have experienced a greater mobilisation or conversion to less soluble Si phases of the labile ASi pool. Losses of PSi$_a$ may also occur due to soil erosion which can prevent the establishment of ASi rich surface horizons and replenishment of ASi 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 ASi distribution

Nutrient leaching, biological (re)cycling and pedogenic processes determine 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., 2011a). The large PSi$_a$ pool in the top layer is the result of biogenic accumulation processes (Alexandre et al., 1997; Blecker et al., 2006; Saccone et al., 2007; Cornelis et al., 2010). 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., 2011a). Although total PSi$_a$ pools were not different for the three human-affected land use types, there are significant differences in the vertical distribution of PSi$_a$. The PSi$_a$ peak at depth was absent under arable land and much less developed under pasture and grazed forest as compared to continuous forest. The absence

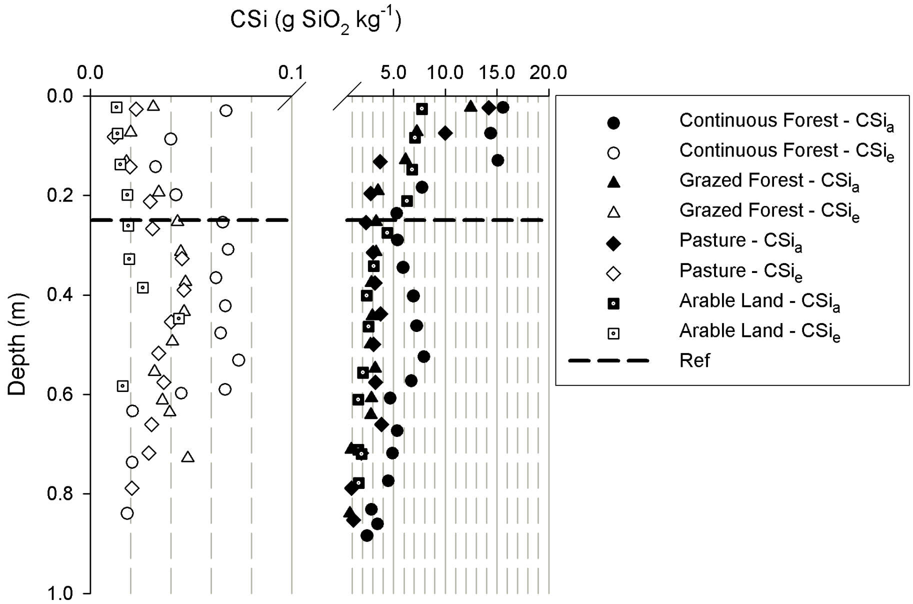

Fig. 4. Average distribution of alkaline extracted silica (CSi_a, solid black) and easily soluble silica (CSi_e, open) in g SiO_2 kg^{-1} dry soil in soils under various land uses in southern Sweden.

of a PSi_a peak at depth for arable land supports the hypothesis of insufficient ASi replenishment (Meunier et al., 2008). 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 of the Si that formerly accumulated here under forest.

PSi_a in the upper 0.25 m of the soil was higher under arable land than both under grazed forest and pasture. This is somewhat surprising, given the fact that harvesting is believed to limit PSi_a input (Vandevenne et al., 2011). 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 as compared to pasture and grazed forest may indicate that Si leaching under arable land is indeed more intense.

4.2 Amorphous silica and organic carbon

Plant-available Si is determined by the solubility of the different silica fractions present in the soil. Solubility is a function of temperature, particle size, pH, chemical composition (type of Al and Fe oxides), organic matter (OM) content and exposed surface area (Sommer et al., 2006; Höhn et al., 2008). In contrast to other factors like pH and clay, OC varied significantly between land use types (Table 1). Positive relationships between CSi_a and OC for grazed forest, pasture and arable land confirm that OC is often strongly related to ASi 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 input of roots with depth (Gill and Jackson, 2000), vertical translocation of phytoliths (Alexandre et al., 1997; Meunier et al., 1999), variations in silica solubility (Sommer et al., 2006) or (re-) precipitation of pedogenic silica (Cornelis et al., 2011b) with depth could all contribute to the observed ASi distribution. Our data do not allow to identify the relative contribution of each of these processes.

The percentage OC occluded in phytoliths is limited (Parr and Sullivan, 2005), no strict coupling between OC and CSi_a exists. Moreover most of the litter-Si in the phytoliths is not complexed with OM as dissolved organic carbon release rate is independent of silica release (Fraysse et al., 2010). OC could only be used as an indicator for CSi_a in topsoil layer, rather than a predictor as it only implies input of both OM and phytoliths. However, the difference in ASi and OC profiles observed under forest clearly indicate a differentiation in biological and pedogenic processes responsible for ASi and OC storage, and explains why OC cannot be used as an indicator along a profile.

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

Our data provide an opportunity to estimate historical changes in ASi storage in soils, and the magnitude of associated Si loss towards the aquatic system, assuming that a large part of ASi is converted to DSi and exported from

Table 2. Historical evolution (3000 BCE–2005 CE) 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 databank http://data.worldbank.org/, last acces: 22 February 2011.

Year	Continuous			Disturbed			Total Temperate		
	Area (Mha)	PSi_a (Tmol)	PSi_e (Tmol)	Area (Mha)	PSi_a (Tmol)	PSi_e (Tmol)	Area (Mha)	PSi_a (Tmol)	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)

the system. We neglect processes that can be responsible for ASi losses but do not result in increased Si delivery to rivers such as (re-)precipitation of dissolved ASi as secondary clays (e.g. koalinite and gibbsite) (Lucas et al., 1993), bio-mineralization (Van Cappellen, 2003), direct removal of ASi by annual crop harvest, timber logging and grazing (Vandevenne et al., 2011) and losses due to soil erosion (Triplett, 2008; Smis et al., 2011).

We also assume that our Swedish data are representative for the whole temperate region, which comprises 70 % of the Earth's land surface and varies strongly in climate, geology, pedology and vegetation. Clearly this implies that the obtained estimates can only be a first rough approximation. However, our up-scaling exercise is meant only to illustrate the possible importance of reduced amorphous Si-storage in terrestrial ecosystems and its potential impacts on the land-ocean flux. It is a best estimate which can be made based on current data, as research on the interactions between Si mobilisation and the processes above is still in a pioneer phase. Incorporating these processes will require a much more thorough study of all ecosystem soil processes affecting Si mobilisation. We hope our first estimate will encourage research on this topic.

The amount of ASi accumulated in soils depends upon the input, output and recycling of silica within the soil-vegetation continuum. Measurements of ASi pools in soils are rare, especially for temperate regions (Blecker et al., 2006; Saccone et al., 2007). Studies are constrained to specific vegetation types (forest or grassland), and data for arable land are lacking. Measured ASi pools typically range between 15 000 and 105 000 kg SiO_2 ha^{-1} (Struyf and Conley, 2011). We found that ASi pools in southern Sweden were larger in soils under continuous forest cover ($66\,900 \pm 22\,800$ kg SiO_2 ha^{-1}) and were lower under grazed forest, pasture and arable land (on average 26600 ± 6520 kg SiO_2 ha^{-1}). Our data fall within the range of total ASi pools that were previously observed. Our study found that PSi_a was reduced by $40\,300 \pm 23\,700$ kg SiO_2 ha^{-1}, and PSi_e by 634 ± 199 kg SiO_2 ha^{-1} due to anthropogenic disturbance of the ecosystem. The first official records from Råshult recording human disturbance date back to 1545 and the land use of that time has persisted until present. The length of the period of disturbance may therefore be estimated as 465 years, although there are traces of agriculture from medieval time. If we assume a constant annual loss between 1545 and 2010 this results in an average annual loss of 86.7 ± 51.0 kg SiO_2 ha^{-1} yr^{-1} from the PSi_a pool and 1.4 ± 0.4 kg SiO_2 ha^{-1} yr^{-1} from the PSi_e pool. This estimate is significantly higher than the increase in Si export that was observed after deforestation in Hubbard Brook Experimental Forest (on average 16 kg SiO_2 ha^{-1} yr^{-1}) (Conley et al., 2008), and it is also higher than the highest specific DSi fluxes for Swedish rivers reported (50 kg SiO_2 ha^{-1} yr^{-1}) (Humborg, 2008). We assumed the loss in PSi_a is converted in a net DSi delivery which is unlikely as discussed above (see earlier in this section). On top, these authors' measurements neither include all significant processes, such as physical ASi transport, responsible for net ASi and DSi delivery. Furthermore, the Si loss rates in both studies were based on riverine measurements which were possible influenced by different processes of Si sequestration.

Historical arable land and pasture distributions were reconstructed based on statistics combined with satellite information and specific allocation algorithms covering the period 10 000 BCE to 2000 CE (Klein Goldewijk et al., 2011). We assumed that the total area to be considered 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 after a conversion between both land use types. Based on these assumptions, total PSi_a (Fig. 5) and PSi_e (Fig. 6) pools were calculated at different moments in time in temperate regions (Table 2). According to our calculations, soils stored approximately 4010 ± 817 Tmol Si in 2005 CE, which represents a decrease of 400 Tmol Si since 3000 BCE. Recent

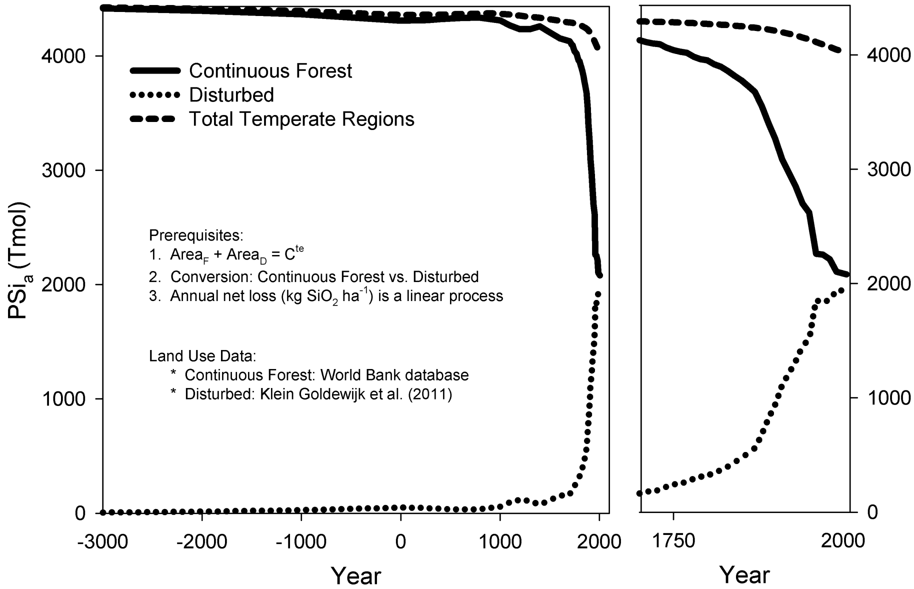

Fig. 5. Historical evolution (3000 BCE–2005 CE) of the amorphous silica pool (PSi_a, Tmol) for continuous, disturbed and total land area in temperate soils.

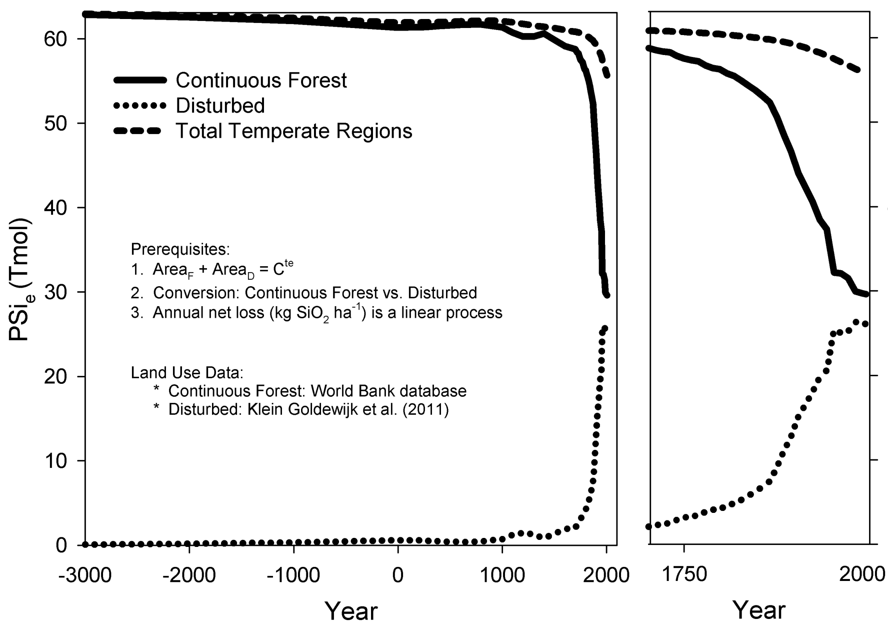

Fig. 6. Historical evolution (3000 BCE–2005 CE) of the easily soluble silica pool (PSi_e, Tmol) for continuous, disturbed and total land area in temperate soils.

land use conversion, after 1700 CE, has resulted in major depletion of PSi_a and PSi_e. In temperate regions from 3000 BCE onwards the PSi_a pool has decreased at a rate of 0.09 ± 0.06 Tmol Si yr^{-1} while recent agricultural expansion (after 1700 CE) is calculated to have resulted in an average decrease of 1.1 ± 0.8 Tmol Si yr^{-1} over the last 300 years. If all lost ASi would be delivered to the river system this would then correspond to 80 % increase of the temperate load (which is estimated 1.3 Tmol yr^{-1}) (Dürr et al., 2011) and a 20 % increase of the global land-ocean flux of DSi (which is estimated to be 5.6 Tmol Si yr^{-1}) (Tréguer et al., 1995). Clearly, the net contribution will be almost certainly lower than this estimate as not all lost ASi will be mobilised as DSi. Furthermore, Si retention within rivers and lakes is considerable: estimates range from 1.15 Tmol Si yr^{-1} to 2.4 Tmol Si yr^{-1} (Laruelle et al., 2009; Dürr et al., 2011) and it may be expected that a significant part of the surplus Si would also be retained. Despite all these uncertainties, our estimate shows that contemporary and historical land use changes may have a significant impact on Si delivery to freshwater systems and the oceans (Conley et al., 2008).

Uncertainties not only arise from the lack of information on the fate of the mobilised Si and the fact that our study area is probably not entirely representative for the entire temperate zone of the Earth. There are also uncertainties associated with historical land use data. 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, attention needs to be given in further studies to the effects of land use and land use history on ASi storage and mobilisation. Until now research has mainly focussed on natural ecosystems (Alexandre et al., 1997; Blecker et al., 2006; Saccone et al., 2007; Cornelis et al., 2011a) rather than systems affected by human impact (Kelly, 1998; Conley et al., 2008). Our study suggests that a correct assessment of human impact will be necessary to understand the Si cycle completely.

Our calculations suggest that total PSi_a pools have been reduced by ca. 10 % in temperate regions as a result of land use changes. Although a considerable amount is known about the factors controlling silicate weathering, to date there are very few studies that have considered the impact of changes in the terrestrial biosphere on Si fluxes (Conley, 2002; Street-Perrott and Barker, 2008). It should also be kept in mind that biological and geological processes may interact: removal of vegetation may affect mineral weathering rates (Kelly, 1998). Recent technological developments, based on the measurement of stable silicon isotopes and Ge/Si signatures may be of great use in furthering our understanding of the dynamics of terrestrial ecosystem pools (Derry et al., 2005; Ziegler et al., 2005; Blecker et al., 2006; Opfergelt et al., 2010; Cornelis et al., 2011b) as well as tracking the origin of Si in aquatic systems (Struyf and Conley, 2011). Ultimately a combined analysis of ASi pools under different land-uses and TSi (ASi + DSi) will be necessary to disentangle the effect of biological Si-cycling on land-ocean fluxes.

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 ASi inputs, affected key pedogenic processes and induced depletion of the ASi pool. 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 the larger easily soluble pools that were found under grazed forest and pasture indicate that arable fields have undergone a larger mobilisation/conversion of the labile ASi pool. Significant differences in the vertical PSi_a and PSi_e distributions result from the effect of deforestation on biogenic and pedogenic processes responsible for the Si distribution in our soils. Along the gradient, the disappearance of an ASi peak at intermediate depths implies that land use conversion limited biological cycling and intensified other processes responsible for the reduction of ASi (e.g. leaching and neoformation) at depth. Our data allowed us to make a first estimate of changes in ASi pools and its effect on the land-ocean Si flux. According to our calculations historical land use changes in temperate regions decrease ASi storage in soils by 10 % and could be responsible for up to ca. 20 % of the global land-ocean Si flux carried by rivers. Despite uncertainties, these estimates show the importance of contemporary and historical human perturbations on Si-cycling in soils and potential Si-delivery to the ocean. A new estimate will have to include a more spatially accurate database of ASi pools, a more thorough understanding of pedological soil processes affecting Si output over land use gradients, as well as the currently unknown contribution of ASi fluxes to total Si fluxes from the continents.

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