

Review Article

Silicon pools and fluxes in soils and landscapes—a review

Michael Sommer^{1,2*}, Danuta Kaczorek³, Yakov Kuzyakov⁴, and Jörn Breuer⁵

¹ Leibniz-Centre for Agricultural Landscape Research (ZALF) e.V., Institute of Soil Landscape Research, Eberswalder Strasse 84, D-15374 Müncheberg, Germany

² University of Potsdam, Institute for Geology, P. O. Box 601 553, D-14415 Potsdam, Germany

³ Agricultural University of Warsaw (SGGW), Department of Soil Environment Sciences, Division of Soil Science, Nowoursynowska 159, PL-02 776 Warsaw, Poland

⁴ Dep. of Agroecosystem Research, University of Bayreuth, D-95440 Bayreuth, Germany

⁵ University of Hohenheim, Landesanstalt für Landwirtschaftliche Chemie (710), Emil-Wolff-Straße 14, D-70593 Stuttgart, Germany

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Summary

Silicon (Si) is the second-most abundant element in the earth's crust. In the pedosphere, however, huge spans of Si contents occur mainly caused by Si redistribution in soil profiles and landscapes. Here, we summarize the current knowledge on the different pools and fluxes of Si in soils and terrestrial biogeosystems. Weathering and subsequent release of soluble Si may lead to (1) secondarily bound Si in newly formed Al silicates, (2) amorphous silica precipitation on surfaces of other minerals, (3) plant uptake, formation of phytogenic Si, and subsequent retranslocation to soils, (4) translocation within soil profiles and formation of new horizons, or (5) translocation out of soils (desilication). The research carried out hitherto focused on the participation of Si in weathering processes, especially in clay neof ormation, buffering mechanisms for acids in soils or chemical denudation of landscapes. There are, however, only few investigations on the

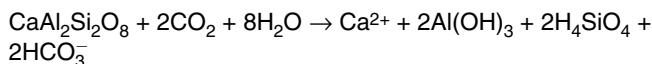
characteristics and controls of the low-crystalline, almost pure silica compounds formed during pedogenesis. Further, there is strong demand to improve the knowledge of (micro-)biological and rhizosphere processes contributing to Si mobilization, plant uptake, and formation of phytogenic Si in plants, and release due to microbial decomposition. The contribution of the biogenic Si sources to Si redistribution within soil profiles and desilication remains unknown concerning the pools, rates, processes, and driving forces. Comprehensive studies considering soil hydrological, chemical, and biological processes as well as their interactions at the scale of pedons and landscapes are necessary to make up and model the Si balance and to couple terrestrial processes with Si cycle of limnic, fluvial, or marine biogeosystems.

Key words: silicon / pedogenesis / biogenic Si / phytoliths / Si fluxes / biogeosystems

1 Silicon—the global context

Silicon (Si) is the second-most abundant element in the earth's crust with 28.8% (Wollast and McKenzie, 1983; Wedepohl, 1995). It occurs in more than 370 rock-forming minerals. Being an element of almost all parent materials, Si is one of the basic components in most soils. Soils show a huge span of Si contents ranging from <1 wt.-% Si in Histosols (e.g., Bennet et al., 1991; Komor, 1994; Steinmann and Shoty, 1997a, b) up to 45 wt.-% Si in very old Podzols developed in quartzitic sands (Skjemstad et al., 1992). Some secondary Si-enriched horizons are almost entirely built up by Si (SiO₂ > 95 wt.-%, Summerfield, 1983). Although a quantitatively important element in soils, Si has received relatively little attention by researchers compared to other elements.

On the other hand, Si plays a very important role in the global matter cycle, e.g., C cycle (Tréguer and Pondaven, 2000). Silicon distinctly influences the C cycle in two ways, namely through (1) weathering processes and (2) Si fluxes into the oceans. In weathering processes of primary silicates, CO₂ is consumed, e.g., by the following reaction:



At the end of a complex transport and process chain, HCO₃⁻ is stored as carbonates in marine biogeosystems. Thus, the processes of silicate weathering take part in the regulation of atmospheric CO₂ (Berner, 1995; Kump et al., 2000). The relationship between CO₂ and silicate weathering can be observed even at local scale within short periods of time. Andrews and Schlesinger (2001) reported an enhanced silicate weathering under conditions of experimentally elevated atmospheric CO₂ content (FACE).

In addition, the role of oceans for global C sequestration is coupled with the global cycle of Si (Tréguer et al., 1995; Ragueneau et al., 2000; Yool and Tyrrell, 2003). This is because diatoms—which need Si for their skeleton—comprise approx. 50% of the biomass in today's ocean (Tréguer and Pondaven, 2000). The larger the Si supply to oceans, the higher is the export flux of C to marine sediments (c.p.), the more C is finally removed from atmospheric CO₂ pool. In today's ocean approx. 5 Tmol Si y⁻¹ are supplied from the continents by rivers, which equals 80% of total annual fluxes into oceans (Tréguer et al., 1995; Conley, 2002); the remaining 20% are from dust and submarine hydrothermal sources.

* Correspondence: Prof. Dr. M. Sommer; e-mail: sommer@zalf.de

The ultimate source of the continental Si fluxes into the oceans are weathering processes in terrestrial biogeosystems. Herein, soils are the main reactors—mineral weathering is one of the major soil-forming process worldwide (Birke-land, 1999; van Breemen and Buurman, 2002). Nevertheless, Si dynamics in terrestrial biogeosystems cannot be understood solely by mineral weathering. This is due to the temporal development of terrestrial biogeosystems, especially soil formation. During pedogenesis, various pools (mineral, organo-mineral, biogenic) developed, which show contrasting solubilities in water as well as reaction rates with soil solutions. This is mainly caused by their different (reactive) surface areas and chemical/mineralogical composition. Consequently, fluxes in and from terrestrial to aquatic biogeosystems differ according to the relative portion of these pools, kinetics of Si dissolution from various pools, and directions and intensities of water fluxes.

To know the magnitudes, mechanisms, driving factors, and process dynamics of Si in soils helps to understand global issues of Si cycling. Here, we would like to summarize the existing knowledge on Si in soils at different spatial and temporal scales. In contrast to other reviews mainly concerning the mineralogy or chemistry of weathering, our special focus is on secondary Si pools in soils as well as Si fluxes in soils and terrestrial biogeosystems of humid climates.

2 Si pools in soils

Soils are the main reactor of terrestrial biogeosystems in which chemical processes interact with biological processes. Vertical and lateral translocation as well as temporary or permanent immobilization processes operate at various scales, which lead to very different Si pools in soils, first reviewed by McKeague and Cline (1963). Pools can be subdivided into mineral and biogenic pools according to their origin (Fig. 1).

2.1 Silicon in soils—the mineralogical perspective

Mineral Si pools in soils consist of three major phases, which are (1) primary minerals inherited from parent material, (2) secondary minerals (crystalline phases) developed through soil formation, mainly clay minerals, and (3) secondary microcrystalline (autigenic quartz, Opal CT, chalcedon) to poorly

ordered phases (Opal A, imogolite, allophane), which are also a result of soil formation (Chadwick et al., 1987b; Drees et al., 1989; Kanig, 1990; Matichenkov and Bocharnikova 2001; Monger and Kelly, 2002).

Among secondary Si minerals are clay minerals as well as “short-range-order minerals”, like imogolite and allophane (Wada, 1989; Harsh et al., 2002). These products of soil formation are poorly crystalline aluminosilicates with a high specific surface area and variable charge. Poorly ordered aluminosilicates are likely to occur in acid soils showing a molar Si : Al ratio of 0.5–1.0 (Farmer et al., 1980; Farmer and Fraser, 1982; Farmer 1984; Buurman and Van Reeuwijk, 1984). Imogolite and proto-imogolite are mostly reported from Podzols (Dahlgren and Ugolini, 1989; Gustafsson et al., 1995; Lundstroem et al., 2000; Mossin et al., 2002), whereas allophane occurs mainly in volcanic soils (Wada, 1989).

Silicates with low Al-content include crystobalite, secondary quartz, microcrystalline, as well as noncrystalline Si minerals (Flörke et al., 1991). Crystobalite is a dominant mineral of volcanic rocks and commonly occurs in soils developed from these rocks. Crystobalite has not been found in other soils (Drees et al., 1989). Only in diagenetic processes, opal A passes into crystobalite, which in turn is transformed into secondary quartz. Secondary quartz can also originate from opal (abiotic) in cemented soil profiles (i.e., duripan, “Ortstein”) or develops directly from siliceous gel (Drees et al., 1989; Monger and Kelly, 2002). Silicon may also be precipitated from soil solution as almost pure, amorphous silica phases on mineral surfaces (Drees et al., 1989).

Such factors like soil pH, temperature, presence of cations, and organic compounds in solution have influence on the formation of secondary Si-containing minerals in the soil environment (Monger and Kelly, 2002; Drees et al., 1989; Dove, 1995; Gerard et al., 2002). Acidification leads to disintegration of clay minerals, which become a source of Si. This phenomenon was observed in very acid soils, e.g., Podzols of temperate or boreal climates and acid topsoils of Luvisols (Veerhoff, 1992; Frank, 1993). Released silica might precipitate at mineral grain surfaces forming amorphous siliceous shells and covers, which have been observed by SEM-EDX (Fig. 2, Veerhoff and Brümmer, 1993). Silicon is also chemically adsorbed at surfaces of soil constituents, like carbo-

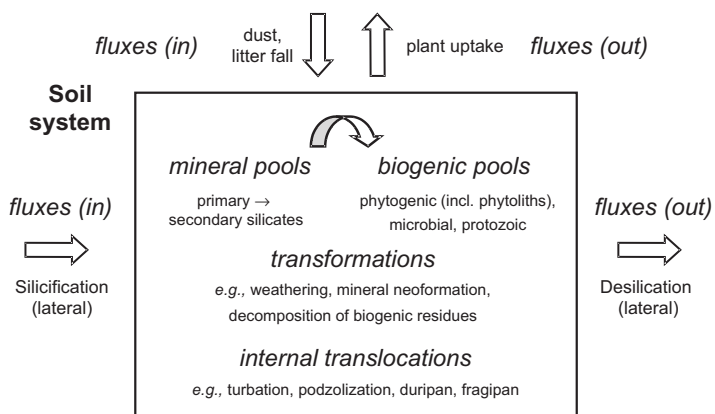


Figure 1: Pools, transformation, fluxes of Si in soils (without erosion/deposition).

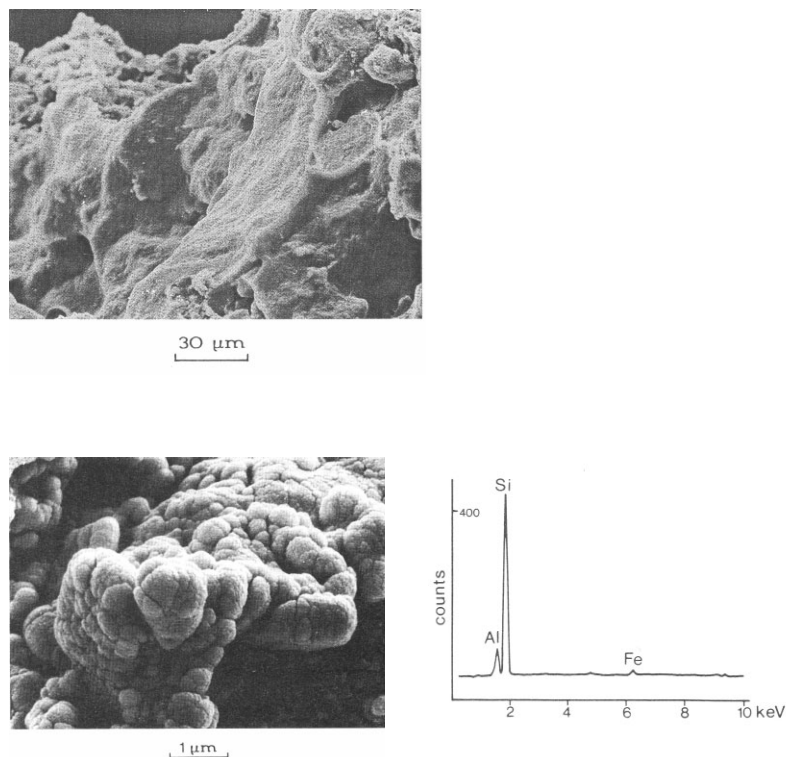


Figure 2: upper: SEM-micrograph of a silica coating on mineral surfaces (Btw horizon in a Luvisol from loess); lower, left: magnified surface from Fig. 2 (upper); lower, right: element-distribution surface by energy-dispersive X-ray spectrometry (EDX) (Veerhoff and Brümmer, 1993); by courtesy of G. Brümmer.

nates, Al hydroxides, and Fe oxides (Beckwith and Reeve, 1963; Iler, 1979; Glasauer, 1995; Dietzel, 2002; Pokrovski et al., 2003). For mixtures of different phases, e.g., soil horizons, indices of silica reactivity and silica saturation were developed from sorption isotherms (Gallez et al., 1977; Herbillon et al., 1977).

Iron hydroxides and especially Al hydroxides play a key role in the interaction between the solid and liquid Si phases in soils, which was known for longer time (Jones and Handreck, 1963; Beckwith and Reeve, 1964; Hingston and Raupach, 1967; Bruun Hansen et al., 1994; Farmer and Lumsdon, 1994). Sorption onto mineral surfaces is related to the amount, type, size, and crystallinity of Fe oxides and Al hydroxides. From formation as well as dissolution experiments of goethites and ferrihydrites Glasauer (1995) hypothesized Si inclusions or clusters near the Fe oxide surface with specific Si-O-Fe bonds. Morphological properties as well as crystallinity of goethites and ferrihydrites were related to the Si concentrations and pH of solutions. Glasauer (1995) explained the interactions between Fe oxides and Si by both, covalent and unspecific electrostatic bonds. At Fe oxide surfaces, polysilicic acid might be formed from orthosilicic acid (Glasauer, 1995; Dietzel, 2002), the latter of which is the dominant species in soil solutions with pH < 8.

Findings from the horizon and pedon scales, respectively, confirm the importance of redox processes for Si dynamics, when Fe oxides are present. Rückert (1992) observed an additional Si release during cyclic patterns of water-logging and drying in batch experiments, which were accompanied by variations of redox potential. This phenomenon is explained as a result of H⁺ production during oxidation of fer-

rous to ferric compounds and subsequent acid dissolution of clay minerals—a pedogenic process called “ferrolysis” (Brinkman, 1970, 1979). Although there is a long debate about the existence and significance of this process in soils (Eaqub and Blume, 1982; Rückert, 1992; reviewed in van Ranst and DeConinck, 2002), experimental results confirm an enhanced release of silicic acid following the oxidation of ferrous-silicate surface coatings, even in Fe-quartz systems (Morris and Fletcher, 1987). The Fe-Si-gels synthesized in reductive environments were unstable under oxic conditions due to Fe oxidation (Fe²⁺ → Fe³⁺) and subsequent Fe oxide crystallization. Nevertheless, a comprehensive analysis of the phenomena observed, e.g., along catenary redox gradients, is still missing.

2.2 Silicon in soil solutions

Silicon fluxes in soils and terrestrial biogeosystems are mainly mediated through water. Silicic acid (H₄SiO₄) is the main component of soil solutions, mostly as monomeric silicic acid (Iler, 1979; Drees et al., 1989; Dove, 1995). Monomeric silicic acid can be transformed into polymeric silicic acid under strongly alkaline conditions (Dietzel, 2000, 2002). Polymeric silicic acid is composed of two or more Si atoms and may occur in different forms, e.g., chains, branching forms, or spherical clusters (Dietzel, 2002). Riise et al. (2000) separated soil solutions of a Podzol with ultramembrane-filtration techniques. They showed more than 90% of Si to be in the smallest-size fraction (<1 kDa). Dissolution experiments with various minerals at pH 3 showed solutions to contain both monomeric and polymeric species (Dietzel, 2000), but polymeric Si decomposing into monomeric Si over time. Polymerization has also been observed at Fe oxide surfaces (Drees

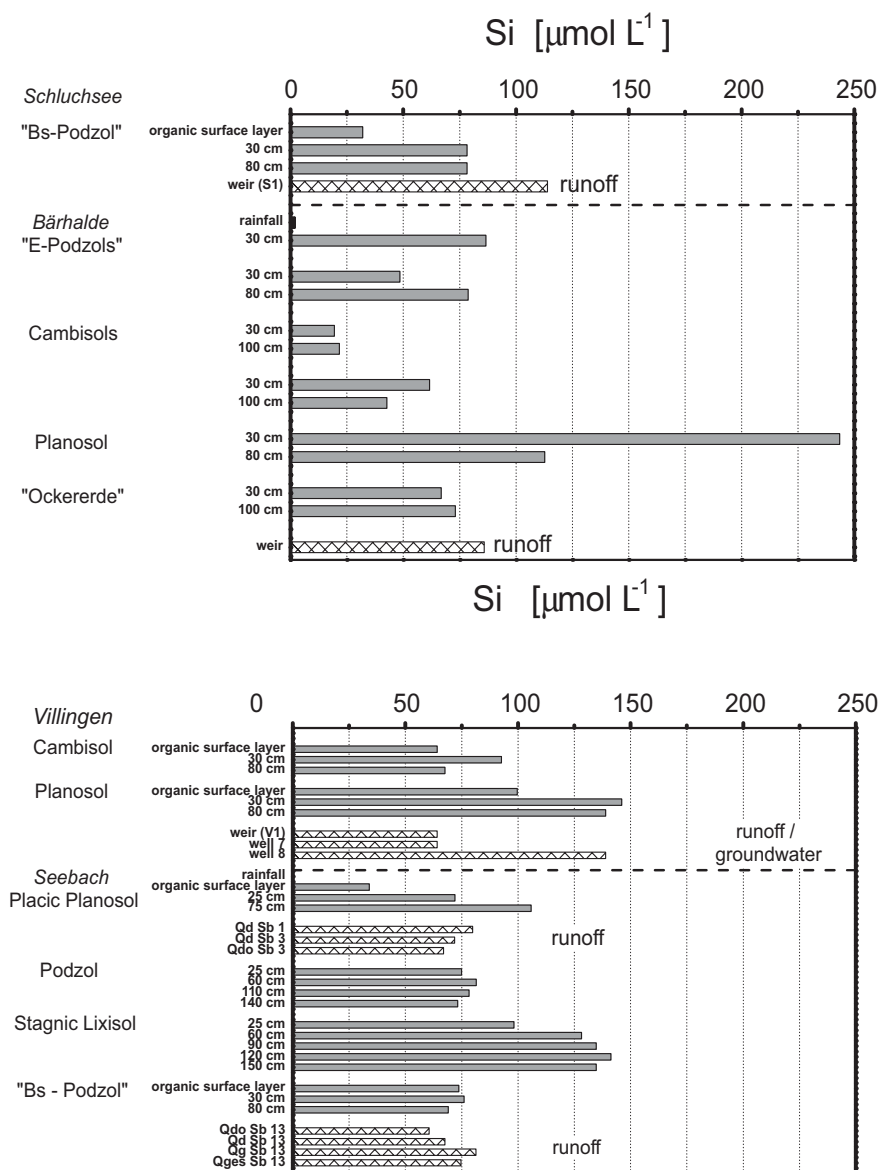


Figure 3: Silicon concentrations in soil solutions of a granite (upper) and sandstone catchment (lower) (Sommer, 2002; data compiled from Heyn, 1989; Meesenburg and Müller, 1992; Hinderer, 1995; Armbruster, 1998); soils arranged along toposequences, where adequate. Q = discharge, indices according to hydrograph separation: “d” = surficial layers (“Deckschichten”), “do” = upper surficial layers (“obere Deckschichten”), “g” = fractured aquifer “Kluftaquifer”, “ges” = total; “Ockererde” is an accumulation soil for Fe, Al, DOC (Fiedler and Jahn, 2005), “E-Podzol” and “Bs-Podzol” are Podzols dominated by E or Bs horizons (indicators for lateral podzolization, cf., Sommer et al., 2000, 2001).

et al. 1989; Dietzel, 2002)—a process which is confined to acidic solutions (pH < 6 according to Dietzel, 2002). Under soil conditions, Al seems to stabilize polymeric silicic acids against depolymerization (Dietzel, 2002). Complex bonds between silicic acid and the organic compounds of soil solutions are known, too (Matichenkov and Snyder, 1996).

The concentration of Si in soil solution depends on the solubility of primary and secondary Si compounds in soils. Solubility is a function of temperature, particle size, chemical composition (accessory elements), and the presence of disrupted surface layers (Drees et al., 1989). Quartz has a solubility of 36–250 μmol L⁻¹ in water depending on particle size and tem-

perature (Iler, 1979; Bartoli and Wilding, 1980; Dove, 1995). Due to surface coatings on quartz grains (Fe oxides, organic matter), the lower value is more realistic for quartz in soils. Somewhat higher solubilities can be observed for biogenic opal (20–360 μmol L⁻¹; Bartoli and Wilding, 1980; Bartoli, 1985). Synthetic amorphous silica shows a much higher solubility (1800–2100 μmol L⁻¹; Drees et al., 1989). The solubility of amorphous silica and crystalline SiO₂ is also influenced by soil pH, but essentially constant between pH 2.5 and 8.5 (c.p., Dove, 1995). Most soils are in this range of pH values. Only extremely acid topsoils of Podzols and acid sulfate soils have pH values <2.5. Strongly alkaline soils, like Solonetz, reveal pH values >8.5—in both cases higher Si concentra-

tions are to be expected due to pH effects, but not reported right now.

In-situ measured Si concentrations of soil solutions range from 0.4 to 2000 $\mu\text{mol L}^{-1}$, *i.e.*, there is a span over four orders of magnitude (Schwer, 1994; Riise et al., 2000; Gerard et al. 2002; Sommer 2002). However, most values lie between 100 and 500 $\mu\text{mol L}^{-1}$, which is somewhat higher compared to groundwater or surface waters (150–180 $\mu\text{mol L}^{-1}$; Gaillardet et al., 1999; Einsele, 2000) and oceans (approx. 70 $\mu\text{mol L}^{-1}$) (Treguer et al., 1995). Most important factors for Si concentrations in soil solutions seem to be parent material (notably content of weatherable minerals), stage of soil development, temperature (seasonal effects), and residence time of pore water. Gerard et al. (2002, 2003) showed capillary water (600 hPa) of a Cambisol from volcanic tuff to be higher in silicic acid concentration compared to free percolating soil water. Both showed a distinct seasonal dynamic with maximum values (185–240 $\mu\text{mol L}^{-1}$) in capillary water during summer and minimum values during winter time (150–200 $\mu\text{mol L}^{-1}$). Free percolating water behaved just in the opposite way. The differences were higher in topsoils compared to subsoil horizons. Gerard et al. (2002, 2003) also stated a correlation to soil temperature ($r^2 = 0.4$). Richards and Kump (2003) showed an increase in silicate dissolution with higher temperature (for catchment scale, *cf.*, Uhlenbrook et al., 2002, Fig. 6). This effect was counteracted by a lowered viscosity of water and subsequent lower residence time of pore waters in soils. Sommer (2002) compiled data from various studies on acid soils in base-poor catchments of the Black Forest (SW Germany). Here, *in-situ* measured Si concentrations of soil solutions in and near Fe-rich redoximorphic soils and horizons were higher compared to nonredoximorphic ones (Fig. 3, Sommer 2002). These data confirm the importance of redox reactions involving Fe oxides for Si concentrations in soil solutions.

Surprisingly high Si concentrations were measured in Histosols of fens or bogs. Komor (1994) observed Si concentrations of 310–530 $\mu\text{mol L}^{-1}$ in a calcareous fen without any trend in depth function. Bennett et al. (1991) reported 140–722 $\mu\text{mol Si L}^{-1}$ in soil solutions of two Histosols (fen, bog). The fen showed no trend in depth function, whereas an increase with depth by factor 5 was observed in the bog. Analyses on mineral phases showed an etching of silicate grain surfaces, incl. quartz. Together with the absence of any diatom shells, the authors concluded that organic acids dissolved the solid silicates. These findings are in contrast to the study of Steinmann and Shoty (1997a, b) who found an increase in Si concentrations of two Histosols with depth (18 → 82, 30 → 72 $\mu\text{mol Si L}^{-1}$, *Sphagnum* peat bogs), but analyzed Si enrichments in the upper 40 cm of the Histosols (*cf.*, Weiss et al., 2002).

2.3 Silicon in soils—the biological perspective

Biogenic Si pools in soils can be subdivided into phytogenic (including phytoliths), microbial, and protozoic Si (Fig. 4). In general, knowledge about size, properties, and transformation of these pools is very scarce for almost all soils. For bacterial and protozoic Si, we have only qualitative evidence that

these pools exist in soils (Clarke, 2003; *cf.*, Fig. 5). Microorganisms influence Si transformations in soils by (1) decomposition of plant litter, which releases Si from tissues, roots, *etc.*, and (2) active mineral dissolution, *e.g.*, by fungi hyphae (van Breemen et al., 2000; Hoffland et al., 2002; van Hees et al., 2004; Smits et al., 2005). Cell membranes of microorganisms might also function as seed crystals for Si precipitation (“biomineralization”, *cf.*, Lauwers and Heinen, 1974; Simkiss and Wilbur, 1989; Konhauser and Urrutia, 1999; Lierman et al., 2000; Kawano and Tomita, 2001), which is well known from biogeosystems with Si supersaturation, *e.g.*, geothermal springs (Renaut et al., 1998; Jones et al., 1999, 2001; Inagaki et al., 2003).

Most information has been gained for phytogenic Si, here defined as Si precipitated in roots, stems, branches, leaves, or needles of plants. Silicon is taken up by plants from soil solution either passively with the mass flow of water or actively, *e.g.*, by rice plants (Ma et al., 2001, 2006). Plants show Si contents ranging from 0.1 to 16 wt.-% d.m. (Raven, 1983; Sangster and Hodson, 1986; Epstein, 1994; Marschner, 1995; Datnoff et al., 2001). Takahashi and Miyake (1976) surveyed 175 plant species grown on the same soil. They distinguished between Si accumulators (Si uptake \gg water uptake) and nonaccumulators (Si uptake similar as or less than water uptake). Marschner (1995) divided higher plants in three groups according to their Si content (wt.-% of shoot

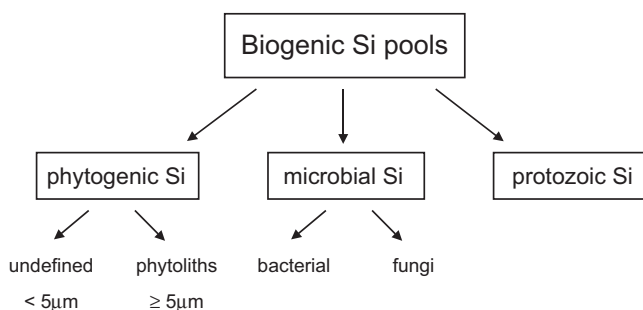


Figure 4: Biogenic Si pools in soils.

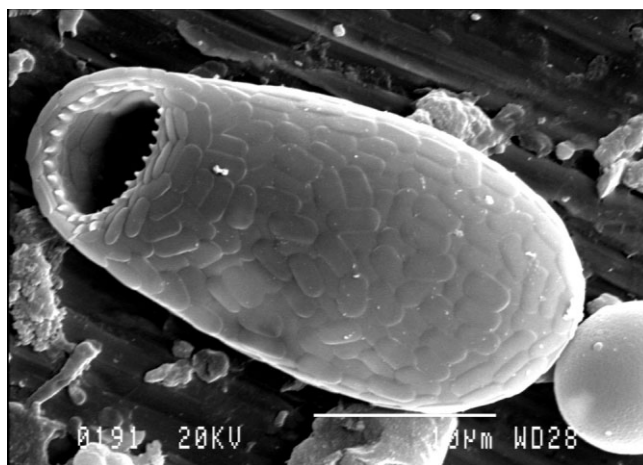


Figure 5: Example of a protozoic organism (Si shell) in soils: SEM of amoebae *Corythion dubium* living in drier parts of acid Histosols (*Sphagnum* peat). Scale bar = 10 μm ; photo by courtesy of Mariusz Lamentowicz, University of Poznan, Poland.

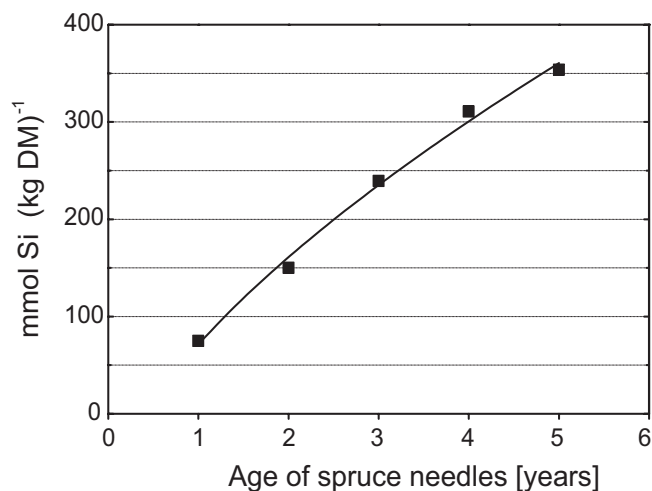


Figure 6: Contents of Si in spruce needles as a function of age (data from Ellenberg et al., 1986).

d.m.): (1) *Cyperaceae*, like horsetails, and wetland species of *Gramineae*, e.g., rice, with 10%–15% SiO₂, (2) dryland species of *Gramineae*, like wheat and sugarcane, with 1%–3% SiO₂, and (3) most dicotyledons with <0.5% SiO₂. Plants which accumulate Si, e.g., rice or horsetails, consequently supply more Si to soils during decay.

Analyses of leaves and needles in forests on Dystric Cambisols from loess-covered sandstones in the Solling (N Germany) have shown Si contents of 85–106 mmol (kg d.m.)⁻¹ in beech leaves and 226–286 mmol (kg d.m.)⁻¹ in spruce needles (Pavlov, 1972; Ellenberg et al., 1986). A clear, nearly linear relationship between the Si content and age of the needles was detected (Fig. 6). Holzapfel (1980) and Heyn (1989) analyzed much lower Si contents in litterfall of spruce stands on various granite soils in the Black Forest (SW Germany). Silicon contents in fine litter clearly separates stands on Dystric Cambisols and Podzols (≈ 12 mmol Si (kg d.m.)⁻¹) from redoximorphic Dystric Planosol and “Ockererde” (31 mmol Si (kg d.m.)⁻¹).

Silicic acid which has been taken up from soil solution (actively or passively) is precipitated primarily as amorphous silica (Opal A; SiO₂ · nH₂O) at cell walls, lumens, and in the intercellular voids (Jones and Handreck, 1967; Piperno, 1988; Watteau and Villemain, 2001; Ma et al., 2001; Neumann, 2003). Silica precipitation takes place when and where water evaporates from the plants, because then Si concentrations may exceed solubility limit. As a consequence, distinct higher Si concentrations can be observed around stomata (Fig. 7). Although most knowledge on biochemical mechanisms of silicification stem from diatom research (Müller, 2003), knowledge on Si compounds in plants has improved recently (Datnoff et al., 2001; Ma, 2003; Müller, 2003). Ca, Sn, or Zn silicates, which are built in border regions of the plants, e.g., cell walls, are converted into SiO₂ spontaneously (Neumann, 2003). Analysis by HRTEM shows that phytogenic Si is composed of a network of SiO₄ units connected by Si-O-Si covalent bonds (Mann and Perry, 1986; Perry, 1989). No Si-O-C or Si-C bonds have been observed so far (Exley, 1998).

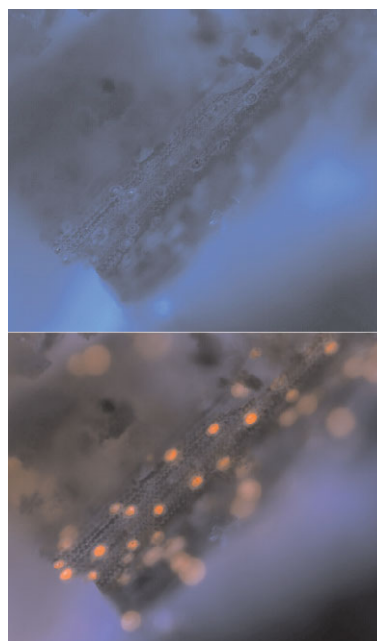


Figure 7: Concentrations of Si around stomata as detected by UV fluorescence. Upper: *Phragmites* stem; lower: overlain with photo obtained with laserscanning microscopy; photo by courtesy of J. Rühlmann, IGZ, Großbeeren, Germany.

The size of Si precipitates in plants ranges from 100 nm (Watteau and Villemain, 2001) to 200 μm (Piperno, 1988), i.e., six orders of magnitude (compare Fig. 8, 9). Therefore, we propose a separation of phytogenic Si into phytoliths (*sensu stricto*), i.e., Si precipitates > 5 μm Ø with a defined shape of plant organs (Fig. 4, 8), and undefined phytogenic Si < 5 μm Ø (Fig. 4, 9). Herewith we intend to separate classical phytoliths from phytogenic Si of high reactivity (surface : volume ratio) and ability for vertical and lateral transport within soils (with clay and fine silt fraction) (*cf.*, Wilding and Drees, 1974).

On basis of the existing limited data, phytoliths are regarded as the major component of the biogenic silica pool in soils followed by diatoms and sponge spicules (Meunier and Colin, 2001; Clarke, 2003). Phytolith content in soils ranges from 0.01 wt.-% up to 50 wt.-% of fine earth (<2 mm) (Jones and Beavers, 1964; Alexandre et al., 1997; Clarke, 2003). However, most soil horizons show phytolith contents in the range between 0.1 wt.-% and 3 wt.-%. Total phytogenic Si in soils must be even higher, because phytolith analysis normally is restricted to silt-sized particles and discards the fraction <5 μm during separation procedure. The few studies quantifying the relative portion of clay-size phytogenic Si (<2 μm) came up with 18%–65% of total phytogenic Si, depending on the plant species (Wilding and Drees, 1971, 1974; Bartoli and Wilding, 1980).

The depth distribution of phytoliths in soils is rather variable (Clarke, 2003). Although highest contents in undisturbed soils should be in surface horizons (Gol'eva, 1996, 1999, 2001), (1) vertical translocation into deeper soil horizons, (2)urbation processes (e.g., mixing by burrowing animals), and (3) erosion/deposition events modify a normative depth profile.

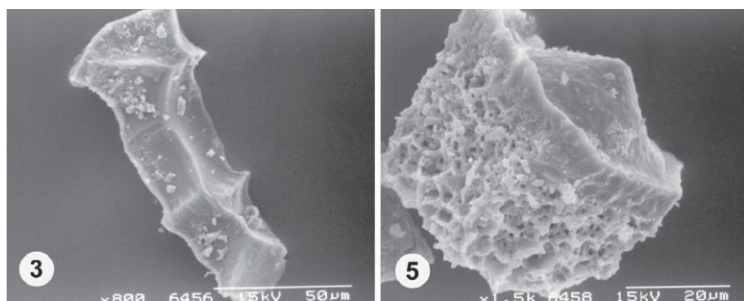


Figure 8: Upper: light-microscopic photographs of phytoliths isolated from soils; reprinted from *Runge* (1999), with permission from Elsevier. Lower: phytoliths (red arrows) in a thin section of a soil horizon; reprinted from *Stoops* (2003), with permission from Soil Science Society of America.

Single sedimentary soil layers (in colluvial soils) may show up to 90 wt.-% SiO_2 of fine earth, almost exclusively derived from phytoliths (*Meunier et al.*, 1999). Poorly drained, redoximorphic soils seem to contain more phytoliths compared to nonredoximorphic soils (*Jones and Beavers*, 1964; *Clarke*, 2003). However, no systematic survey on the occurrence of phytogenic silica as a function of vegetation, soils, and landscape position exists.

Studies on the chemical properties of phytogenic Si and its solubility under different environmental conditions are restricted to phytoliths (*Jones and Beavers*, 1963; *Wilding et al.*, 1979; *Bartoli and Wilding*, 1980). Accessory elements (Al, Fe, Ti, C, etc.) were found to comprise up to 6 wt.-% of phytolith mass. Experimental studies on phytolith dissolution in distilled water showed silicic acid equilibrium concentrations of 100–360 $\mu\text{mol Si L}^{-1}$ (*Bartoli and Wilding*, 1980), which was between those of quartz (36 $\mu\text{mol Si L}^{-1}$) and synthesized pure silica gels (2000 $\mu\text{mol Si L}^{-1}$). Clear differences between plant species were observed (*Bartoli*, 1985). Phytoliths from pine needles showed lower silicic acid equilibrium concentrations (100 $\mu\text{mol Si L}^{-1}$) than those from beech leaves (300 $\mu\text{mol Si L}^{-1}$). This may correspond to a higher Al content in the phytoliths of pine needles compared to beech leaves. Results of experiments, in which increasing Al substitution in silica gels leads to a reduced solubility in water, support this causal relationship. Finally, *Bartoli* (1985) concluded that a higher Al substitution at surfaces of phytoliths (Si : Al ratio between 1.5 and 8) is responsible for the reduction in solubility. In addition, a higher degree of crystallization of phytoliths in pine needles may explain a higher Si equilibrium concentra-

tion in beech leaves. *Wüst and Bustin* (2003) interpreted Al-Si phytolith development as detoxification of Al in soil solution of Histosols in Malaysia. The evidence of structural association of Al with Si was proved by NMR spectroscopy of diatom frustules at least (*Gehlen et al.*, 2002).

Early studies from the 1960s showed C_{org} to be occluded in silt-sized biogenic Si with C_{org} ranging from 0.2 to 4.7 wt.-% of biogenic Si, especially in the light fractions of phytoliths (*Jones and Beavers*, 1963; *Wilding et al.*, 1967). Further radiocarbon dating yielded 13,300 y b.p. (*Wilding*, 1967) from which the author concluded a long-term stability of biogenic Si. *Vice versa*, a recent study demonstrated the capability of occluded C in phytoliths for C sequestration of volcanic soils (*Parr and Sullivan*, 2005). The authors calculated recent C-sequestration rates of 18 $\text{g C m}^{-2} \text{y}^{-1}$ with phytoliths of sugarcane. From the stability of occluded C, they postulated phytolith C pools as important for global C sequestration in soils: 15%–37% of global long-term C accumulation in soils should be related to C sequestration in phytoliths. However, their extrapolation is based on a (too) small data set.

The morphology of phytoliths is regarded as a stable property and can be related to taxonomic units (*Piperno*, 1988; *Gol'eva*, 1999). Despite complex processes that may affect the phytoliths in soils (translocation, dissolution, erosion, and colluviation), *Alexandre et al.* (1999) have shown that soil phytoliths may be good tracers of vegetation changes. The study of phytolith assemblages of soils has also been used to trace Holocene grassland dynamics and forest-grassland shifts (*Piperno*, 1988; *Delhon et al.*, 2003). Some studies

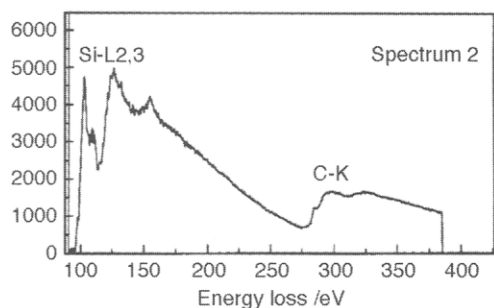
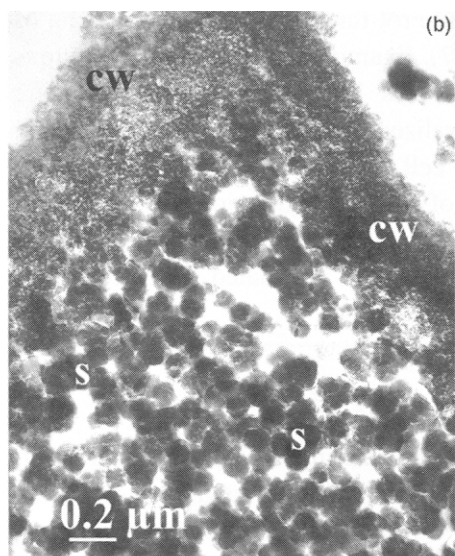


Figure 9: TEM micrographs and electron–energy loss (EEL) microanalyses of SiO₂ precipitates (s) between cellwalls (cw); precipitates match our definition of “undefined phytogenic Si” (<5 μm); photo reprinted from *Watteau and Villemain* (2001), with permission from Blackwell Publishing.

took O– (*Webb and Longstaffe, 2002*) and C–isotopic composition of phytoliths (*Kelly et al., 1998b*) for paleo-environmental reconstructions. However, the dissolution and recycling of phytolith Si in soils influences its use for reconstruction of paleo-environments—a problem comparable to diatom burial in marine biogeosystems (*Bidle and Azam, 1999; Ragueneau et al., 2000; Ridgwell et al., 2002*). The critical point in the use of phytoliths as paleoproxies is their conservation under various soil conditions, which is assumed in paleo-ecological studies, but not proved or studied explicitly.

2.4 Silicon in soils and landscapes—the pedogenic perspective

During soil development, Si can be leached out, redistributed, or accumulated in soils. Quantitative analysis on losses and gains of Si during soil development are scarce. For most soils of humid climates, Si losses are reported. This process of “desilication” is well known for (sub)tropical climates (*Lucas and Chauvel, 1992; Paquet and Clauer, 1997; Stonestrom et al., 1998*), but also takes place in younger soils (≤10,000 y) of temperate or boreal climates (Tab. 1). Here, the rate of Si losses range from 20 to 400 mmol Si m⁻² y⁻¹ which equals

Table 1: Mean annual Si losses from soils of temperate humid and boreal climates during soil development (based on mass-balance calculations).

Soil type (WRB, 1998)	Annual Si losses [mmol Si m ⁻² y ⁻¹]	Source
Podzols (base poor rocks)	20–250	<i>Tevel dal et al., 1990; Egli et al., 2001; Jersak et al., 1995, Kirkwood and Nesbitt, 1991</i>
Cambisols, Luvisols (marly glacial tills)	30–90	<i>Muir and Logan, 1982; Schlichting and Blume, 1962</i>
Stagnic Luvisol (loess)	73	<i>Flehming et al., 1990</i>
Cambisols (greywacke)	380	<i>Anderson et al., 2002</i>

approx. 0.2–4 kmol Si m⁻² during Holocene pedogenesis. These numbers are much smaller compared to total desilication of older soils, e.g., 28–70 kmol Si m⁻² from Alf- and Ultisols (incl. saprolite) developed on phyllite, granitic gneiss, and diabas in subtropical climate (*Oh and Richter, 2005*), or 96 kmol m⁻² in a Ferralsol of an old craton (*Brimhall et al., 1991*). Although desilication rates might be comparable, different total amounts result from different duration of soil development.

Chronosequence studies coupled with mass balances confirm the general trend of Si losses in freely draining soils of humid climates, although data from studies cited below should be recalculated according to *Egli and Fitze (2001)*. *Langley-Turnbaugh and Bockheim (1998)* reported total Si losses of 2.3–15.4 kmol m⁻² during pedogenesis in their chronosequence of Inceptisols–Spodosols–Ultisols on marine terraces (Fig. 10). Similar total Si losses (0.3–19 kmol m⁻²) were observed by *Brimhall et al. (1991)* and *Merritts et al. (1992)* in their study of a Mollisols–Inceptisols–Alfisols chronosequence on marine terraces (Fig. 9). *Ziegler et al. (2005)* stated increased total Si losses with age (0.3–38 kmol m⁻², Fig. 10) in a chronosequence of Inceptisols–Andisols–Ultisols–Oxisols on Hawaiian basalts. Few soils of the chronosequences showed Si accumulations, which is interpreted as atmospheric inputs of dust (*Brimhall et al., 1991; Merritts et al., 1992*) or lateral Si influx (*Langley-Turnbaugh and Bockheim, 1998*). *Ziegler et al. (2005)* corrected the influence of aeolian-dust inputs in their mass-balance calculations (*cf., Kurtz et al., 2001*).

From existing data, one can conclude the magnitude of desilication to depend on the (1) stage/duration of soil development, (2) content of weatherable minerals in the parent material, and (3) amount of percolating water (assuming steady state of biogenic Si pools at short time scales).

Accumulations of Si in soil horizons, pedons, rocks, or landscapes can be viewed as a result of the pedogenic process of “silicification”. Generally, surplus Si might stem from (1) weathering of dust inputs, (2) upper soil horizons, (3) groundwater, or (4) from a lateral transport from higher parts in the

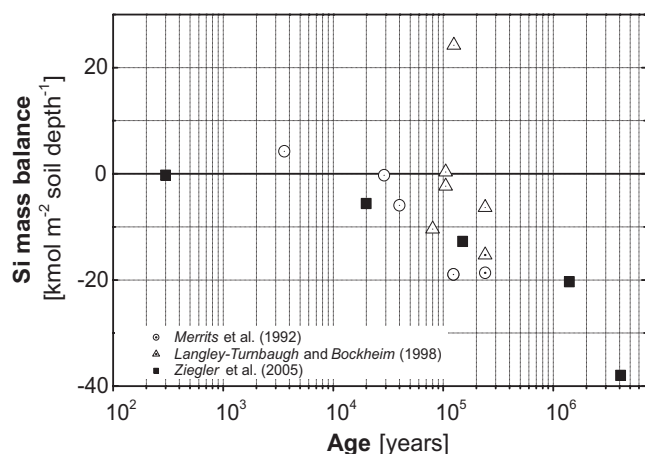


Figure 10: Si mass balance from chronosequence studies. Environmental settings: *Brimhall et al.* (1991), *Merritts et al.* (1992): marine terraces, 4–240 ka, arkosic sandstones, siltstones, shales, grassland, 1000 mm, 13°C; *Langley-Turnbaugh and Bockheim* (1998): marine terraces, 80–240 ka, loess over marine/eolian sands, forests, 1900 mm, 11.7°C; *Ziegler et al.* (2005): tholeiitic to alkalic basalts, forests, 0.3–4100 ka, 2500 mm, 16°C; calculation in *Ziegler et al.* (2005) without topsoil horizon.

landscape (Fig. 1). Most Si accumulations are reported from climates which show a distinct dry season (recent or relict). Here, Si infillings in subsoil horizons during wet seasons can be hardened by repeated desiccation in dry seasons. If this process continues for a longer time, duripan horizons will develop (*Torrent et al.*, 1980; *Chartres*, 1985; *Chadwick et al.*, 1987a, b; *Blank and Fosberg*, 1991; *Moody and Graham*, 1997; *Monger and Kelly*, 2002; *Kendrick and Graham*, 2004; *White et al.*, 2005). The cementation of grains in duripans is detectable by micromorphological analysis (*Brewer et al.*, 1972; *Flach et al.*, 1974; *Norton*, 1994). Surface encrustations in semiarid climates, so-called “hardsetting soils”, are also interpreted as a redistribution and subsequent precipitation of Si, either in a vertical (*Chartres et al.*, 1990) or lateral mode (*Breuer*, 1994; *Breuer and Schwertmann*, 1999). Pedogenesis on soft siliceous lacustrine sediments in a volcanic region of Mexico were studied by *Gutierrez-Castorena et al.* (2005, 2006). They proved an *in-situ* silicification of roots by micromorphological analysis coupled with X-ray diffraction and EDXRA.

Silica which is leached from soils in one part of a landscape might be (re-)precipitated in other parts. When Si influxes and desiccation continued over a longer time, thick hardened layers, so-called “silcretes”, develop in groundwater or slope-water soils (*Summerfield*, 1983; *Milnes et al.*, 1991; *Walther*, 1993; *Thiry*, 1997; *Thiry and Millot*, 1997; *Webb and Golding*, 1998). These Si-accumulation layers vary from 1 to 5 m in thickness and show SiO₂ contents >95 wt.-%. (*Summerfield*, 1983). Evidence for Si accumulations even in soils of humid climates was given by *Thiry et al.* (1988) for temperate and by *Pfisterer* (1991) for tropical climates (see also *Pfisterer et al.*, 1996). The latter proved Si accumulation in downslope soils of a catena from ultrabasites to be a recent phenomenon. *Langley-Turnbaugh and Bockheim* (1998) interpreted a positive Si mass balance in a stagnant-water soil (Epiaquod)

as silicification due to lateral Si inputs. Some of the silica mobilized in soils might also be transported into saturated zone and (re-)precipitated as SiO₂ in its rocks. This was proven by *Basile-Doelsch et al.* (2005) in a sandstone complex of S France using Si-isotope analysis (for chemistry *cf.*, *Harder and Flehming*, 1970).

In humid climates, Si accumulations are well-known from limnic biogeosystems, *e.g.*, from abundant diatom accumulation in lake sediments (diatomite, *Füchtbauer*, 1988). Some of these accumulations show SiO₂ contents of 50–70 wt.-% and were used as Si deposits (“Kieselgur”) (*Benda and Brandes*, 1974; *Benda and Mattiat*, 1977). The only source for these deposits can be weathering and subsequent leaching as well as translocation processes in the soil cover of the lake catchments (*Tessonow*, 1966). However, the dependency of recent limnic Si accumulation (amount, rates) from Si dynamics in neighboring soils has not been studied in a quantitative manner so far.

For global biogeochemical Si cycling, it is important to note that silicon of all these different accumulation forms does not leave the continents. However, the size and dynamics of these continental Si pools are poorly known up to now.

Besides desilication and silicification, Si is involved in some other pedogenic processes. Fragipan genesis has often been related to Si accumulations in subsoils (*Marsan and Torrent*, 1989; *Franzmeier et al.*, 1989; *Karathanasis*, 1989). Even the development and strength of plough pans in Mollisols derived from loess were interpreted as deposition of amorphous Si at particle surfaces (*Brown and Mahler*, 1987). Cementation of “Ortstein” horizons, a result of podzolization (*Kaczorek et al.*, 2004), is interpreted as infillings and coprecipitation of Si with Al by several authors (*McKeague and Kodama*, 1981; *Farmer et al.*, 1984, 1985; *Ross et al.*, 1989; *Stahr et al.*, 2003). In addition, there are some hints that even nonhardened spodic horizons might act as a sink for Si—either by an accumulation of phytoliths (*Farmer et al.*, 2005) or by sorption onto clay minerals and/or mineral neosynthesis, *e.g.*, imogolite (*Farmer et al.*, 1985; *Farmer*, 1986; *Su et al.*, 1995; *Zysset et al.*, 1999; *Giesler et al.*, 2000). Consequently, lateral podzolization which leads to “Bs-Podzols” at lower slopes (*cf.*, *Sommer et al.*, 2000, 2001) should also behave as Si sink at landscape scale—a sound hypothesis which has to be proven in future research.

There is no accepted method for analyzing pedogenic Si phases up to now, like DCB extraction for pedogenic Fe (reviewed in *Sauer et al.*, 2006). According to *Kendrick and Graham* (2004), Tiron-extractable Si (*Kodama and Ross*, 1991) might be suitable for quantification of secondary, pedogenic Si. In Alfisols and Mollisols along a mediterranean chronosequence on arkosic sediments (11,500–500,000 y), they proved Tiron-Si to increase with age from 0.9–3.3 wt.-% (depth-weighted profile averages), although a high variability at each terrace was observed.

3 Silicon fluxes in soils and landscapes

Silicon fluxes in terrestrial biogeosystems can be viewed at different spatial and temporal scales. Here, we would like to

focus on (1) recent external Si fluxes mediated by water flux, *i.e.*, the atmospheric inputs *via* rainfall and outputs *via* seepage from pedons and catchments, and (2) the recent internal Si fluxes through vegetation.

3.1 External Si fluxes

Except in semiarid and arid climates, where dust represents an important Si influx into soils, atmospheric Si fluxes into terrestrial biogeosystems are comparably small. Reported data from humid climates showed annual Si inputs through rainfall ranging from 0.1 to 20 mmol Si m⁻², with most values <5 mmol Si m⁻² y⁻¹ (Stednick, 1981; Bruijnzeel, 1982; Creasey et al., 1986; Dethier, 1986; Poels, 1987; Lelong et al., 1990; Pfisterer, 1991; Cornu et al., 1998; Markewitz and Richter, 1998; Bouchard and Jolicoeur, 2000; Sommer, 2002). However, one has to keep in mind that data on wet deposition are based on water analysis performed after filtering (0.20–0.45 µm) of rainwater. This pretreatment as well as the exclusion of dry deposition leads to an underestimation of total Si influx of unknown magnitude. Nevertheless, in most studies on Si budgets (input *minus* output), inputs are neglected due to their low values; Si outputs were used for interpretation instead.

Recent Si leaching from soils, *i.e.*, recent desilication, can be found in all climatic zones of the earth, where enough water is available. In poorly developed soils of the subarctic climate, the Si flux out of soils might be in the same order of magnitude (50–120 mmol Si m⁻² y⁻¹, Anderson et al., 1997, 2000) as in strongly developed soils of tropical climate (70 mmol Si m⁻² y⁻¹, Oliva et al., 1999). Very early pedogenesis (4 y) on dacitic tephra of Mount St. Helens (5.5°C, 2300 mm annual rainfall) already showed desilication rates (15 cm depth) of 273 → 119 mmol Si m⁻² y⁻¹ decreasing with age (Dahlgren et al., 1999).

The annual leaching of Si from soils in temperate humid climate is almost as high as in soils of other climates. Baker and Scrivner (1985) simulated Si leaching from a Luvisol developed in loess on basis of repeated wetting and drying of soil samples. They came up with an annual Si loss of 193 mmol Si m⁻². *In-situ* measurements showed redoximorphic soils, *e.g.*, Dystric Planosols, to have higher values (95–167 mmol Si m⁻² y⁻¹) compared to Podzols (88–109 mmol Si m⁻² y⁻¹) and Dystric Cambisols (32–59 mmol Si m⁻² y⁻¹; Heyn 1989; Meesenburg and Müller, 1992; Armbruster, 1998). Highest recent desilication can be expected from young soils on ultrabasic rocks in tropical humid climates. This is confirmed by studies from Bruijnzeel (1982) and White et al. (1998) showing actual desilication rates of ≈900 mmol Si m⁻² y⁻¹.

Although in most case studies soil water movement is modeled with simple capacity approaches, the results show desilication to be a contemporary process in all humid climates of the world. Recent rates as well as absolute losses over time of soil development vary according to parent material, hydrological conditions, and stage of soil development (White 1995; Anderson et al., 2000). However, there are too few systematic studies on recent Si leaching along gradients of driving factors. Consequently, a comprehensive model of magnitude and intensity of desilication is missing up to now.

Numerous studies have been published on Si fluxes from watersheds, mostly in the context of chemical denudation. At catchment scale, annual Si outputs from 0.1 to 8 kmol ha⁻¹ y⁻¹ were reported (Stednick, 1981; Creasey et al., 1986; Dethier, 1986; Berggaut and Verba, 1987; White and Blum, 1995b; White et al., 1998; Hyman et al., 1998; Oliva et al., 1999, 2003; Freyssinet and Farah, 2000; Bouchard and Jolicoeur, 2000; Sommer, 2002; Turner et al., 2003). Most influence on Si fluxes was attributed to watershed lithology and runoff. Bluth and Kump (1994) found very high dependency of Si outputs from runoff (log-log model, r² from 0.8 to 0.9, data from catchments in USA) only after grouping rivers in respect to dominant lithology. At high discharge (>1000 mm y⁻¹), rivers draining areas with carbonatic rocks showed surprisingly higher Si fluxes than silicate rocks, which was attributed by Bluth and Kump (1994) to rapid solution of biogenic Si of the carbonatic rocks (either disseminated or interbedded). However, methodology of Bluth and Kump (1994) tend to overestimate Si fluxes and may not be suitable for regional scale according to Fulweiler and Nixon (2005).

To reduce lithological effects, White and Blum (1995a) studied 68 granitic catchments along a broad climatic range, mostly from northern hemisphere. They found Si fluxes from watersheds to be correlated with temperature, which influences silicate-weathering rates (Arrhenius model, r² = 0.51), as well as runoff (linear model, r² = 0.41). Drever and Zobrist (1992) analyzed chemistry of surface waters from small catchments along an altitudinal gradient in the Swiss Alps (360–2400 m a.s.l.; base-flow sampling). The exponential decrease in Si concentrations (252 → 14 µmol L⁻¹) with increasing elevation might be related to temperature, although a lack of dependence of weathering stoichiometry on elevation had to be stated by the authors. For large world rivers, Turner et al. (2003) found a relationship between Si fluxes and runoff as did Anderson et al. (1997) for watersheds in glacial environments and Fulweiler and Nixon (2005) for a coastal river in temperate humid climate. However, Oliva et al. (2003) in their global review on granitic watersheds found a dependency of Si fluxes from watersheds only from temperature, but no relationship to runoff. The authors stated additional factors to be important, especially the presence and depth of soil cover.

Sommer (2002) compiled existing data from granite and sandstone catchments in the cool-humid Black Forest (SW Germany). Except the atmogenic element C, Si was found to be the most abundant element in solutional outputs (Fig. 11) and, therefore, most be important for chemical denudation of these landscapes built-up by base-poor rocks. By separating sandstone from granite catchments, a very close relationship between Si fluxes and discharge heights was observed (linear model, r² = 0.85, Fig. 12a)—despite very different processors, study periods, instrumentations, equipments, *etc.* The combined effect of runoff and parent material can be observed in Fig. 12b, where Si fluxes of single years are plotted. Silicon fluxes from the granite catchments (higher in feldspars and micas) were always higher than those from quartzitic sandstone catchments, irrespective of discharge.

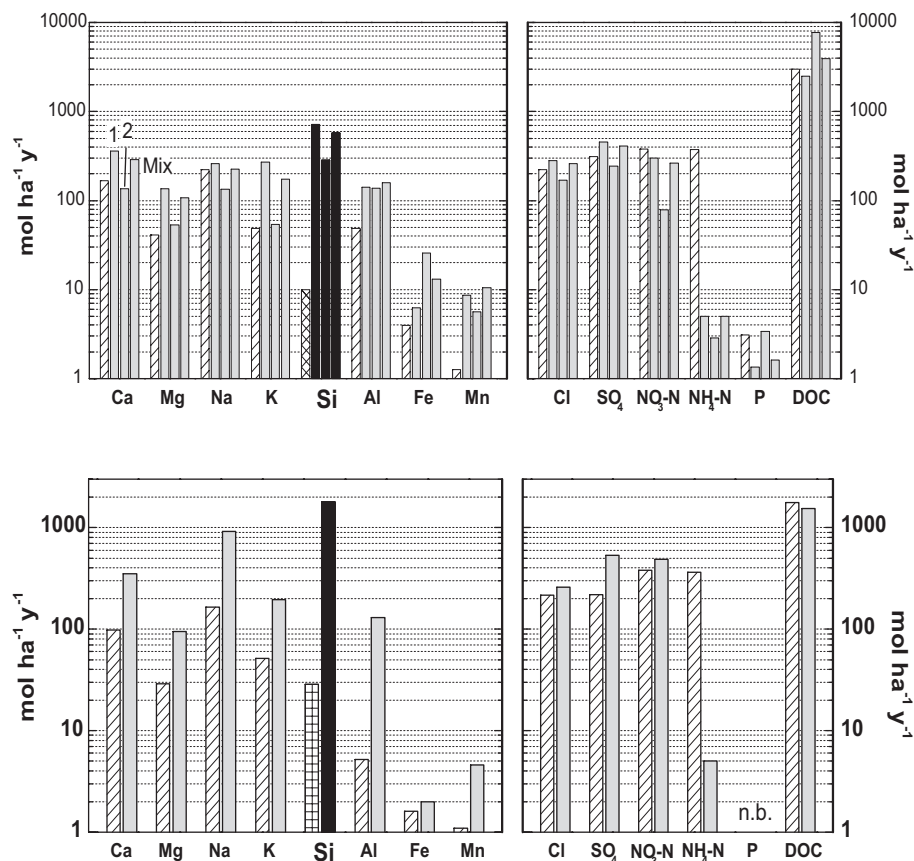


Figure 11: Element fluxes in catchments of the Black Forest, SW Germany (hatched bars = input, grey bars = output, Si outputs in black). Upper: “Huzenbacher See” (three subcatchments, siliceous sandstones) according to *Thies* (1994); lower: “Schluchsee” (S1, granite) according to *Armbruster* (1998).

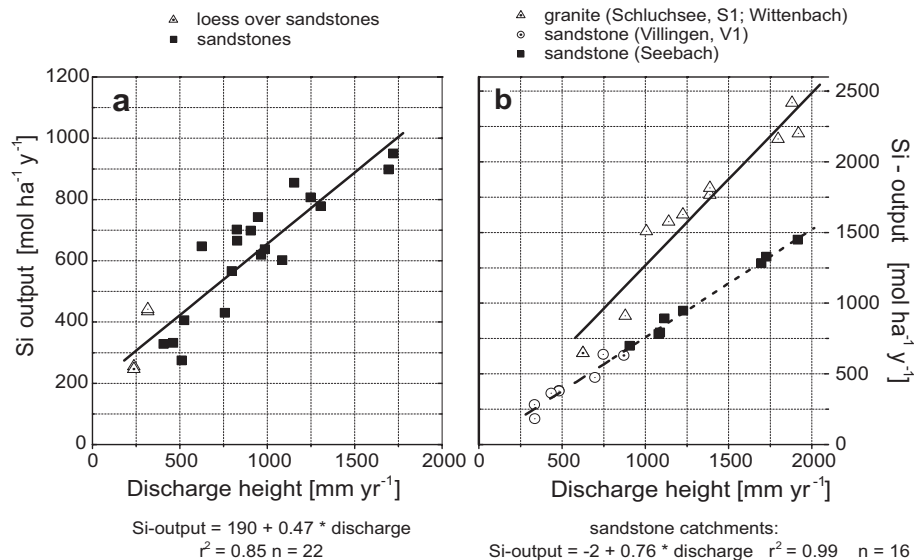


Figure 12: Outputs of Si related to runoff (discharge heights). (a) Mean values for ≥ 2 y of measurement; sandstone catchments of the Black Forest, SW Germany (different sources, compiled in *Sommer*, 2002); (b) annual values for granite catchments “Schluchsee” (S1, 1988–1996; *Armbruster*, 1998), “Wittenbach” (1988; *Bauer*, 1993), and sandstone catchments “Villingen” (V1, 1988–1995; *Armbruster*, 1998), *Seebach* (Sb13, 1985–1992; *Hinderer*, 1995).

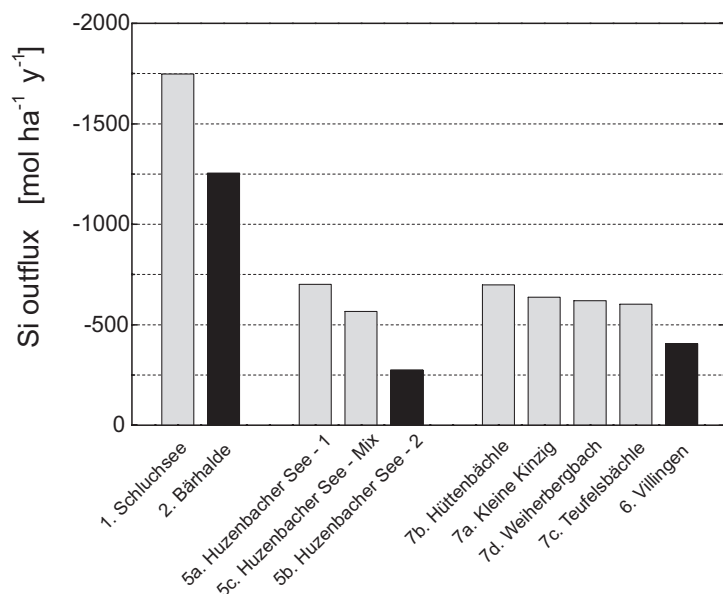


Figure 13: Influence of soil pattern on mean annual Si outputs (two granite catchments “Schluchsee”, “Bärhalde”, eight sandstone catchments). Grey bars = catchments without redoximorphic (Dystric Planosols) or organic soils (Histosol) along brooks; black bars = catchments with redoximorphic (Dystric Planosols) or organic soils (Histosol) along brooks (Sommer, 2002; data compiled from Thies, 1994; Hinderer, 1995; Armbruster, 1998; Höhn et al., 1998).

Very surprising is the almost functional relationship between discharge and Si flux of the two sandstone catchments “Villingen” and “Seebach”. Although being km apart and studied by different people in different periods of time with different equipment, individual relationships showed the same slope in the regression equation (linear model, $r^2 = 0.99$). Both catchments not only reveal very similar lithological conditions, but also soil pattern, especially similar soils next to the streams. Here, redoximorphic, acid stagnant-water soils (Dystric Planosols) developed during pedogenesis in both areas. The only factor being different between both catchments is discharge, which is strongly correlated to rainfall at regional scale (curvilinear regression, $r^2 = 0.97$ for 52 catchments of SW Germany; mean annual values: 1328 mm at “Villingen”, 1935 mm at “Seebach”). The influence of spatial soil distribution on Si fluxes from watersheds is demonstrated in Fig. 13. If Dystric Planosols or Histosols developed near brooks, Si fluxes are lower compared to situations where these soils were not developed (*c.p.*). The phenomenon observed adds another driver to Si cycle in watersheds, *i.e.*, soil pattern, although the mechanism is still unclear (dynamic building-up of biogenic Si pools?). It is important to note that this influence is not a question of a percentage of a certain soil in a catchment, but of its spatial location relative to a brook or stream (*cf.*, concept of “sensitive areas” in Sommer, 2006).

Several other studies addressed soils—here perceived as stage of soil development and soil pattern—to be important for Si fluxes from catchments: Anderson et al. (2000) for meta-greywackes/meta-pelites in a proglacial environment, Berggaut and Verba (1987) for glacial tills in Taiga, Farley and Werrity (1989) for glacial tills in per-humid Scotland, Bluth and Kump (1994) for basaltic watersheds in tropical Hawaii, and Braun et al. (2005) for granitoid catchments in the Congo basin. Especially the latter came to the same results like Sommer (2002) in that soils developed nearby the streams were most influential on Si exports from catchments.

In summary, a hierarchy of driving variables can be established for Si fluxes from catchments: At global scale, runoff and, inferior, temperature are the main drivers of Si fluxes. However, at regional scale, Si fluxes are a function of (1) catchment lithologies first, *i.e.*, the content of weatherable minerals in the parent materials of the soils, (2) second the hydrological conditions, *i.e.*, discharge, and (3) finally the soil pattern developed in the catchments. Silicon fluxes from terrestrial biogeosystems of humid climates seem to be transport-limited. The close—in some cases almost functional—relationships between Si outputs and runoff require highly reactive pools along the flowpaths of water along which infiltrated water and soils’ solid phases equilibrate in a very fast manner. Actually drivers are identified, but not the reactive pools (mineral or biogenic?).

3.2 Internal Si cycling—the influence of vegetation

Silicon is included in the internal element cycling of a given terrestrial biogeosystem by plant uptake from soil solution. Plants enhance weathering of silicates by rising CO_2 partial pressure in soil solution and exudation of organic acids, which leads to an increased Si release into soil solutions (Kelly et al., 1998a; Moulton et al., 2000; Hinsinger et al., 2001; Lucas, 2001). Silicon fluxes back to soil occur *via* throughfall, stem flow, and litterfall. For temperate humid climate, Si fluxes of 2–240 $\text{mmol m}^{-2} \text{y}^{-1}$ by litterfall were reported: Prusinkiewicz et al. (1974) analyzed Si fluxes from 140 (mixed forest) to 240 $\text{mmol m}^{-2} \text{y}^{-1}$ (deciduous forest) by litterfall on Podzols of glaciofluvial sands. Holzapfel (1980) and Heyn (1989) published much lower values for litterfall (2–11 $\text{mmol Si m}^{-2} \text{y}^{-1}$) and throughfall (3–10 $\text{mmol Si m}^{-2} \text{y}^{-1}$) in their study on Podzols, Dystric Cambisols, and Dystric Planosols from granite. Ellenberg et al. (1986) measured annual Si fluxes by litterfall of 76 $\text{mmol m}^{-2} \text{y}^{-1}$ (beech) and 190 $\text{mmol m}^{-2} \text{y}^{-1}$ (spruce) on Dystric Cambisols from sand-

stone. *Bartoli and Souchier* (1978) and *Bartoli* (1983) studied Si cycling on Dystric Cambisols and Podzols developed from sandstone in temperate humid climate. They reported Si fluxes by litterfall of 18 mmol m⁻² y⁻¹ (pine), 75 and 81 mmol m⁻² y⁻¹ (fir, mixed beech-fir), and 127 and 167 mmol m⁻² y⁻¹ (beech).

Tobon et al. (2004) studied throughfall and stemflow in a toposequence of four undisturbed forests in Amazonia (plain, high and low terrace, floodplain). Whereas Si fluxes with throughfall were in the range of 12–19 mmol Si m⁻² y⁻¹, stemflow was about three orders of magnitude lower with 0.3–1 mmol Si m⁻² y⁻¹. *Markevitz and Richter* (1998) reported only 0.8 mmol Si m⁻² y⁻¹ by throughfall in subtropical Calhoun Experimental Forest, *Freyssinet and Farah* (2000) analyzed 4 mmol Si m⁻² y⁻¹ by throughfall in a rainforest of Amazonia. *Cornu et al.* (1998) compared Si fluxes from a high rainforest and scleromorphic forest (Campinarana) along a Ferralsol–Podzol toposequence of Amazonia. Similar Si fluxes with throughfall were observed, namely 5 mmol Si m⁻² y⁻¹ under Campinarana and 8 mmol Si m⁻² y⁻¹ under rainforest. Stemflow yielded similar Si fluxes in both forest types (<0.2 mmol Si m⁻² y⁻¹). However, fluxes with litterfall differed by almost one order of magnitude, *i.e.*, 18 mmol Si m⁻² y⁻¹ in Campinarana and 116 mmol Si m⁻² y⁻¹ in high rainforest (*cf.*, *Lucas et al.*, 1993). *Alexandre et al.* (1997) reported 207–271 mmol Si m⁻² y⁻¹ as litterfall from a rainforest in Congo (Ferralsol from schists and quartzites). So far, highest Si fluxes with litterfall were calculated for a soil from trachytic ash at Reunion Island with 3500–4900 mmol Si m⁻² y⁻¹ (*Meunier et al.*, 1999). Even higher values can be expected from grassland biogeosystems, because grasses will probably accumulate more Si per gram biomass compared to trees. However, systematic inventories on fluxes in these biogeosystems are still missing.

Reported values indicate litterfall to be the most important flux from vegetation to soil, followed by throughfall. *Farmer* (2005) stressed the importance of the adequate method to analyze Si in litter, especially to dissolve phytoliths. Although data are scarce, the Si flux with stemflow seems to be a negligible flux in internal Si cycling. No data were found in respect to Si fluxes through root decay.

At longer time scales, Si cycling through plants has consequences for soil development itself. In an excellent paper on the role of plants in weathering processes, *Lucas* (2001) developed a framework for feedback reactions between element cycling by plants and soil mineralogical properties. For example, he attributed the widespread phenomena of kaolinite stability in topsoils of strongly weathered Ferralsols to Si pumping from deeper horizons through vegetation, which leads to permanent higher Si concentrations in topsoils.

On the basis of current literature, the recent internal Si flux of terrestrial biogeosystems mediated by vegetation has been shown to be in the same order of magnitude as the Si outputs from soils or catchments. Consequently, Si cycling through vegetation plays an important role for recent Si cycling inputs and outputs from terrestrial biogeosystems (*cf.*, *Farmer et al.*, 2005; *Derry et al.*, 2005). External Si losses from soils (Fig. 1)

might be reduced whenever the (internal) rate of phytogetic Si production is higher than its dissolution rate, *i.e.*, when a biogenic Si sink develops in soils. The dynamics and controlling factors of building-up and dissolution of these phytogetic sinks is one of the most interesting topics for future research, especially from pedological perspective. However, Si fluxes should not only be viewed in quantity, but in quality as well. In addition to a systematic survey of bulk fluxes, plant-related Si fluxes should be differentiated in terms of particle size, chemical composition, solubility, *etc.* Special interest must be given to the fine-silt- and clay-size fraction (<5 µm) of phytogetic Si. Due to its high surface : volume ratio, this fraction most probably play a crucial role in Si fluxes from terrestrial biogeosystems.

4 Silicon in soils and landscapes—the open questions

Generally, the knowledge on pools and fluxes of Si in soils is scarce, especially when compared with minor elements, like Fe, Ca, N, *etc.* Therefore, the following questions are essential for future research from the pedological perspective:

1. How can we identify different secondary Si pools in soils (*e.g.*, by development of a sequential-extraction procedure)? How suitable are stable-isotopic techniques (³⁰Si/²⁸Si) or Ge : Si ratios for tracking Si through complex process chains in terrestrial biogeosystems? Can we quantitatively separate mineral and biogenic Si pools in soils? What are their relative proportions under which environmental conditions? How can we differentiate between different biogenic Si pools?
2. What is the magnitude, stability, and dynamic of phytogetic Si pools in various soils and vegetation types (especially phytoliths vs. undefined phytogetic Si)? How important are phytolith inclusions (Al, Fe, P, C_{org}, *etc.*) in terms of stability and functions?
3. How do microorganisms affect the internal Si cycling due to decomposition of organic litter in soils? Do microorganisms built-up an own (stable) Si pool? Are microorganisms significant drivers of mineral weathering and dissolution of secondary Si phases?
4. How dynamic is the biogenic Si pool in (1) short-term Si cycling and (2) long-term trend (building-up, degrading)? Which are the driving factors? How is the (internal) biological Si cycling related to annual Si losses?
5. Are the recent Si fluxes from soils related to Holocene mass balances on Si (desilication as contemporary process)? Are Si-accumulation zones developed in soils and soil covers of temperate humid climates? If yes, under which combinations of soil forming factors?
6. How do soils (properties, stage of development, pattern) influence Si fluxes from terrestrial to neighboring fluvial and limnic biogeosystems? Where are sensitive areas in respect to Si fluxes between neighboring biogeosystems?

Soil scientists should focus on these topics in a joint effort with botanists, mineralogists, geochemists, limnologists, and hydrologists. Only by this interdisciplinary approach, we will come to a comprehensive understanding of Si cycling in soils and terrestrial biogeosystems.

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