

Tree species impact the terrestrial cycle of silicon through various uptakes

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Received: 24 December 2008 / Accepted: 15 August 2009 / Published online: 1 September 2009
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Abstract The quantification of silicon (Si) uptake by tree species is a mandatory step to study the role of forest vegetations in the global cycle of Si. Forest tree species can impact the hydrological output of dissolved Si (DSi) through root induced weathering of silicates but also through Si uptake and restitution via litterfall. Here, monospecific stands of Douglas fir, Norway spruce, Black pine, European beech and oak established in identical soil and climate conditions were used to quantify Si uptake, immobilization and restitution. We measured the Si contents in various compartments of the soil–tree system and we further studied the impact of the recycling of Si by forest trees on the DSi pool. Si is mainly accumulated in leaves and needles in comparison with other tree compartments (branches, stem bark and stemwood). The immobilization of Si in tree biomass represents less than 15% of the total Si uptake. Annual Si uptake by oak and European beech stands is 18.5 and 23.3 kg ha⁻¹ year⁻¹, respectively. Black pine has a very low annual Si uptake (2.3 kg ha⁻¹ year⁻¹) in comparison with

Douglas fir (30.6 kg ha⁻¹ year⁻¹) and Norway spruce (43.5 kg ha⁻¹ year⁻¹). The recycling of Si by forest trees plays a major role in the continental Si cycle since tree species greatly influence the uptake and restitution of Si. Moreover, we remark that the annual tree uptake is negatively correlated with the annual DSi output at 60 cm depth. The land–ocean fluxes of DSi are certainly influenced by geochemical processes such as weathering of primary minerals and formation of secondary minerals but also by biological processes such as root uptake.

Keywords Phytolith · Silicon cycle · Temperate forest · Tree species

Introduction

Silicon (Si) is the second mass abundant element of the crustal Earth (28.8% wt) (Wedepohl 1995), and a major solute of river discharge into oceans (Gaillardet et al. 1999). It plays a crucial role in major global biogeochemical processes such as the nutrition of both marine and terrestrial biota (Smetacek 1999; Epstein 1999), and the regulation of atmospheric carbon dioxide (Volk 1987; Berner 1997; Sommer et al. 2006) through the buffering of proton fluxes during silicate dissolution (Rai and Kittrick 1989). Plants can exert a strong imprint on the Si continental cycle through the uptake and restitution of Si (Derry et al. 2005; Street-Perrott and Barker 2008). Plants

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greatly differ in their ability to accumulate Si, a non-essential but beneficial element (Richmond and Sussman 2003; Ma and Yamaji 2006; Liang et al. 2007). They can accumulate Si in a similar extent as some major macronutrients: 0.1–10% of dry weight (Epstein 1999). Most studies of Si uptake in the higher plants were focusing on monocots which are typical Si-accumulators (Ma and Takahashi 2002). Taken up as aqueous monosilicic acid (H_4SiO_4^0), Si is translocated to transpiration sites (Jones and Handreck 1965) where it polymerizes as amorphous biogenic opal called phytolith (BSi), which returns to the soil within organic residues (Smithson 1956). Thus, in terrestrial ecosystems, BSi is distributed between plant and soil. In forest ecosystems, the BSi recycling is one of the major processes to control the hydrological output of aqueous monosilicic acid (Bartoli 1983; Alexandre et al. 1997; Markewitz and Richter 1998; Meunier et al. 1999; Lucas 2001; Watteau and Villemin 2001; Farmer et al. 2005). The quantity of Si recycled within the soil–tree cycle may be species-dependent since angiosperms enhance the weathering to a greater degree than gymnosperms (Moulton et al. 2000; Johnson-Maynard et al. 2005). Relative to broadleaved species, conifers generally accumulate low amounts of Si in their shoots (Geis 1973; Bartoli and Souchier 1978; Klein and Geis 1978; Carnelli et al. 2001; Hodson et al. 2005). Within conifers, Si accumulation by pine is ten times below than spruce (Hodson and Sangster 1999). In tropical conditions, Si uptake by forest vegetations is significant in comparison with weathering Si input and hydrologic Si output (Lucas et al. 1993; Alexandre et al. 1997; Conley 2002; Derry et al. 2005; Ziegler et al. 2005). In temperate forests, Bartoli (1983) has estimated that 80% of dissolved Si (DSi) derives from the BSi pool in deciduous stands against 20% in coniferous ones. Yet, the impact of tree

species on Si uptake and Si output to the hydrosphere is poorly known because studies in identical soil and climate conditions are lacking. The influence of soil type is, indeed, crucial, as the accumulation of BSi in the soil–plant system is directly governed by soil mineralogical compositions (Henriet et al. 2008a, b). The climate also impacts the BSi accumulation through plant transpiration (Raven 1983).

Here, we study, on a quantitative basis, the recycling of Si by various monospecific forest stands established in the same soil and climate conditions. We compare three coniferous and two broadleaved forest stands. Our study aims at answering two questions: (1) Is the tree uptake of Si impacted by tree species? (2) If it does, how large does the species effect impact the pool of dissolved Si?

Materials and methods

Experimental site

The experimental site is located at Breuil-Chenue (Nièvre-Morvan, France, latitude 47°18'10" N; longitude 4°4'44" E), on a plateau at 638 m a.s.l. Over the period 2001–2006, the mean annual rainfall and temperature are 1,212 mm and 9°C, respectively. According to the Köpper-Geiger climate map of Europe, the climate is Cfb, i.e. a temperate climate without dry season and with a warm summer (Peel et al. 2007). Table 1 presents the major soil characteristics at the experimental site. It is an acid brown soil, classified as an Alumnice Cambisol (IUSS Working Group WRB 2006), developed from granite very poor in major cations (0.5% MgO, 0.6% CaO and 4.4% K_2O). The native forest mixes trees dominated by European beech (*Fagus sylvatica* L.) and oak (*Quercus sessiliflora* Smith.). It was cleared

Table 1 Average value of major characteristics of the acid brown soil at the experimental site, as measured in eight soil profiles before plantation of experimental stands in 1976

Depth (cm)	C (%)	pH (H_2O)	pH (KCl)	Clay (%)	Silt (%)	Sand (%)
0–5	7.7 (1.0)	3.8 (0.1)	3.3 (0.1)	20 (3)	23 (4)	41 (9)
20–30	1.4 (0.2)	4.7 (0.2)	4.2 (0.1)	16 (4)	27 (3)	53 (6)
40–50	0.8 (0.2)	4.7 (0.1)	4.1 (0.0)	17 (3)	26 (4)	54 (6)
70–80	0.4 (0.1)	4.8 (0.2)	4.0 (0.1)	17 (3)	27 (5)	54 (8)

(Bonneau et al. 1977); the error associated with the mean ($n = 8$) is given in parentheses (standard error)

in 1976 and replaced by six monospecific plantations. Out of these, we selected five forest stands: Douglas fir (*Pseudotsuga menziesii* Franco), Norway spruce (*Picea abies* Karsten), Black pine (*Pinus nigra* Arn. *Ssp laricio* Poirét var *corsicana*.), European beech (*Fagus sylvatica* L.) and oak (*Quercus sessiliflora* Smith.).

Since surface runoff is negligible at the site (Ranger et al. 2004) and tree species have no effect on the available water capacity of soil below 10 cm depth (Levrel and Ranger 2006), the mean annual drainage over the period 2001–2006 (Table 2) was calculated by the following mass balance model:

$$\text{Drainage (mm year}^{-1}\text{)} = P - \text{In} - T - E_u \quad (1)$$

where P is the mean annual rainfall, In the mean annual rainfall interception, T the mean annual tree transpiration, E_u the mean annual evaporation from understorey vegetation and soil.

P and In were measured in the experimental site between 2001 and 2006. T was estimated from the relation between leaf area index (LAI) and the ratio of stand transpiration to the potential evapotranspiration (PET) (Granier et al. 1999). LAI was estimated from Breda et al. (2002). PET was measured in the experimental site between 2001 and 2006. E_u is proportional to the available energy below trees and it is calculated from the Beer–Lambert function and a light coefficient of extinction (0.5) (Granier et al. 1999).

Materials

Tree compartments

Ten trees were harvested in each stand in 2001 to collect branches, stemwood and stembark samples.

Leaves and needles were collected between 2001 and 2006 from five litter-traps per stand to estimate the mean annual Si restitution in solid form on topsoil. Needles were also collected from coniferous trees to evaluate the mean accumulation of Si.

Forest floor horizons

We define the forest floor by the whole set of organic horizons (Oln, Olv, Of and Oh) above the organo-mineral horizon (Ah). Under each forest stand, three replicates of organic horizons were sampled in November 2006 according to the forest humus classification (Brethes et al. 1995): Oln (plant remains), Olv (poorly fragmented), Of (fragmented) and Oh (dark humified organic matter).

Soil organo-mineral and mineral layers

Under each forest stand, 16 soil profiles were sampled in May 2001 at the following systematic depths (cm), which do not correspond to specific horizons: 0–5; 5–10; 10–15; 15–25; 25–40; 40–55 and 55–70.

Solutions

In each forest stand, we collected the solutions under the forest floor by using two replicates of sets of nine zero tension plate lysimeters made of polypropylene (Jaffrain et al. 2007). At 15, 30 and 60 cm depth, ceramic cup lysimeters were introduced into the soil profile (five replicates per forest stand). The ceramic cup lysimeters were connected to a vacuum pump which maintained a constant suction of -400 hPa. Rainfall was collected outside the forest stand by a daily collector system. Throughfall was collected

Table 2 Mean annual drainage (mm year $^{-1}$) estimated for each forest stand at the experimental site (Eq. 1)

Flux (mm year $^{-1}$)	Douglas fir	Norway spruce	Black pine	European beech	Oak
P	1212	1212	1212	1212	1212
In	545	557	327	351	351
T	567	567	283	432	432
E_u	41	41	181	67	67
Drainage	59 (73)	47 (72)	421 (81)	362 (81)	362 (81)

The mean annual rainfall (P), the mean annual rainfall interception (In), the mean annual tree transpiration (T) and mean annual evaporation from understorey vegetation and soil (E_u) were calculated over the period 2001–2006. The standard deviation, calculated by the method of the propagation of uncertainty, is given in parentheses and corresponds to inter-annual variations

every month by double gutters (three replicates per forest stand).

Biomass evaluation

The evaluation of tree biomass was done according to procedures described by Ranger et al. (1995) and Saint-André et al. (2005). It involved four steps. (i) The circumference of all trees was measured at 1.30 m height, $C_{1.30}$. (ii) Ten trees, representing the whole range of $C_{1.30}$ values, were selected to sample branches, stemwood and stembark. (iii) The weighed allometric relationships fitted for each individual compartment were calculated according to Sicard et al. (2005) for coniferous species and Ranger et al. (2004) for broadleaved species. (iv) Tree biomass (branches, stemwood and stembark) was quantified per hectare by applying fitted equations to the stand inventory. The uncertainty for tree biomass values varied between 3 and 10% (Sicard et al. 2005).

Analytical methods

Si contents in tree compartments

The total Si contents in tree compartments were determined after calcination at 450°C followed by borate fusion (Chao and Sanzalone 1992). Briefly, a crushed sample of 150 mg of the ignition residue was melted at 1,000°C for 5 min in a graphite crucible in the presence of 0.4 g Li-tetraborate and 1.6 g Li-metaborate. After dissolution of fusion beads in 10% HNO_3 , Si content was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The concentrations of the major elements were previously measured (Ranger et al. 2004). In this study, we express Si concentrations of tree compartments as SiO_2 percent.

For the extraction of phytoliths, i.e. biogenic silica (BSi), leaves and needles were washed successively with deionized water, HCl 1 M, 70% ethanol and rinsed again with deionized water in order to avoid aeolian contamination (Kelly 1990). About 5–10 g of dry matter was grinded and digested at 120°C in a concentrated HNO_3 (70%)/ H_2O_2 (30%) mixture until the reaction ceased (~ 10 days). BSi was filtered through a preweighed 0.2 μm filter and rinsed with deionized water. BSi concentrations were measured

gravimetrically (Kelly 1990; Carnelli et al. 2001). Here, we express BSi concentrations as SiO_2 percent.

Si contents in organic horizons

The total Si contents in forest floor horizons were determined after calcination at 450°C (Oln and Olv) and 950°C (Of and Oh) followed by borate fusion, as described here above.

The extraction of amorphous silica (ASi) was carried out following the heavy liquid method adapted from Kelly (1990). This method includes silt and sand-sized particles having a density below 2.3 g cm^{-3} , thereby involving silt- and sand-sized particles of BSi (2–2,000 μm), other poorly crystallized aluminosilicates and some crystallized minerals as revealed by X-ray diffraction, but excluding clay-sized particles ($<2 \mu\text{m}$). First, clay, silt and sand fractions were separated from fragmented (Of) and humified (Oh) organic horizons by dispersion with Na^+ resins (Rouiller et al. 1972; Bartoli et al. 1991). Silt and sand fractions were then treated by H_2O_2 5% (pH fixed at 5.5) at 70°C until full oxidation of organic matter, and subsequently by DCB to extract free iron compounds (Mehra and Jackson 1960). Finally, a second dispersion with sodium hexametaphosphate (Na-HMP) was necessary to eliminate the clay contamination.

To recover ASi by densimetric separation, 0.5–2 g of either sand or silt fraction were mixed with 20 cm^3 of zinc bromide solution (ZnBr_2 , density = 2.3 g cm^{-3}) and centrifuged at 4,000 rpm for 10 min. The supernatant containing the floating ASi was carefully removed with a pipette and filtered through a preweighed 2.0 μm teflon filter (PTFE) soaked with ethanol and rinsed with HCl 1 M and deionized water. The operation was repeated four times to remove most of the ASi from the sample (Kelly 1990; Herbauts et al. 1994; Carnelli et al. 2001). The filter was dried at 105°C for gravimetric quantification. Here, we express ASi concentrations as SiO_2 percent.

Si content in organo-mineral and mineral layers

The total Si contents in organo-mineral and mineral layers were determined after calcination at 950°C followed by borate fusion, as described here above.

Briefly, sand fraction ($>50\ \mu\text{m}$) was separated from fine earth ($<2\ \text{mm}$) by ultrasonic dispersion and wet sieving. Clay ($0\text{--}2\ \mu\text{m}$) and silt ($2\text{--}50\ \mu\text{m}$) fractions were then collected by gravimetric sedimentation. We used the same methodology described here above to recover ASi from the silt and sand fractions. For the 16 soil profiles sampled under each tree-species, we extracted ASi from 4 samples of the first soil layer ($0\text{--}5\ \text{cm}$) to study the variability of the ASi distribution.

Si content in solutions

Solutions of forest floor, soil, rainfall, stemflow and throughfall were filtered at $0.45\ \mu\text{m}$, maintained at 4°C and analysed. The Si contents in the solutions were measured by ICP-AES.

Microscopic analysis

Morphological features and chemical content of BSi and ASi particles were respectively examined by scanning electron microscopy (SEM: Leica Stereoscan 260) and energy dispersive X-ray analysis (EDX: EDAX system).

Determination of Al and Ti contents in selected samples

After calcination and borate fusion, the total Al and Ti contents were measured by ICP-AES (Al in leaves, needles, branches, throughfall, stemflow and forest floor solutions; Ti in leaves, needles, forest floor horizons, $0\text{--}5\ \text{cm}$ and $55\text{--}70\ \text{cm}$ layers).

Statistical analyses

Statistical analyses consisted in comparisons of means. They were performed with the SAS System (version 9.1, SAS Institute, Cary, NC, USA). Means were compared based on least significant differences (LSD Fisher). Means with various letters are significantly different at the 95% level of confidence.

Results

Si contents in the various compartments of the soil–tree system

Tree parts

As shown in Table 3, the mean content of SiO_2 in leaves and needles significantly decreased in the sequence European beech (1.59%) $>$ oak (1.17%) $>$ Douglas fir (1.13%) $>$ Norway spruce (0.97%) $>$ Black pine (0.05%). The concentrations of SiO_2 in old needles, as collected in litter traps (Norway spruce = 2.55%, Douglas fir = 2.05% and Black pine = 0.13%) (not shown), were higher than the ones of old and young needles collected from trees. In each specific stand, the SiO_2 concentrations were larger in leaves and needles than in other compartments (branches, stembark and stemwood).

Organic horizons and soil layers

The BSi concentrations of leaves and needles ranged from 0.02% (Black pine) to 1.93% (European beech) (Table 4). In leaves and needles, the total SiO_2

Table 3 Mean SiO_2 concentration in tree compartments (data expressed as percent of dry matter); when considering tree species, means with various letters are significantly different at

the 95% level of confidence; the error associated with the mean ($n = 3$) is given in parentheses (standard error)

	Total SiO_2 content (% wt)				
	Douglas fir	Norway spruce	Black pine	European beech	Oak
Leaves/needles ^a	1.13c (2E-2)	0.97d (1E-2)	0.05e (6E-4)	1.59a (1E-2)	1.17b (4E-3)
Branches	0.04c (4E-4)	0.06b (2E-4)	0.03c (1E-3)	0.07a (4E-3)	0.01d (4E-4)
Stem bark	0.04b (1E-3)	0.04b (2E-4)	0.02c (2E-3)	0.32a (2E-3)	0.02c (2E-3)
Stem wood	0.01ab (6E-5)	0.01a (4E-3)	0.01ab (2E-3)	0.004b (6E-5)	0.004b (6E-4)

^a Concentration of Si in the leaves collected in litter-traps and in the old and young needles collected from coniferous trees (November 2006)

Table 4 Mean total SiO₂ content ($n = 3$), biogenic SiO₂ content (BSi) and amorphous SiO₂ content (ASi) in leaves/needles, forest floor and soil layers

	Total SiO ₂ (% wt)					[BSi + ASi] (SiO ₂ % wt)				
	Douglas fir	Norway spruce	Black pine	European beech	Oak	Douglas fir	Norway spruce	Black pine	European beech	Oak
<i>Organic horizons</i>										
Leaf/needle	1.13	0.97	0.05	1.59	1.17	0.96	0.54	0.02	1.93	1.13
Oln	0.99	0.77	0.05	1.54	1.30	nd	nd	nd	nd	nd
Olv	2.30	2.07	0.35	2.97	1.46	nd	nd	nd	nd	nd
Of	6.44	4.38	11.40	13.51	5.71	1.22	1.10	0.08	0.21	0.49
Oh	20.88	12.06	38.06	39.43	44.01	0.43	0.45	0.11	0.12	0.39
<i>Soil layers (cm)</i>										
0–5	61.94	68.49	64.08	61.12	63.17	2.63	2.43	3.16	1.53	0.42
5–10	66.35	68.38	68.87	64.51	67.84	2.65	2.42	1.33	3.70	2.17
10–15	66.45	70.55	71.05	65.78	71.32	2.84	0.79	1.14	1.70	4.77
15–25	66.50	70.94	70.84	64.71	65.89	0.58	0.57	nd	1.31	1.14
25–40	67.65	72.27	73.02	65.55	69.42	0.63	0.61	nd	0.76	0.90

nd no data

concentration did not exactly correspond to the BSi concentration as measured gravimetrically. However, the former was correlated with the total SiO₂ content in falling litter Oln ($r = 0.97$) but not with that in the humified organic horizon Oh ($r = 0.1$).

In the Oh horizon, the relative proportion of [BSi + ASi] on the total SiO₂ content ranged between 0.3 and 3% depending on tree species. The relative standard deviation (RSD) (not shown) exhibited a large variability of the [BSi + ASi] distribution in the first soil layer (0–5 cm), as it ranged between 40 and 61% according to tree species. The concentrations of [BSi + ASi] in soil layers varied between 0.42 and 4.77% and were the largest at soil depth between 0 and 15 cm, and decreased from 15 to 40 cm in each stand (Table 4). The concentrations of [BSi + ASi] determined by heavy liquid method were similar to the ones calculated by Saccone et al. (2007) in forest soils with alkaline methods (on average 1.2–2%). Assuming 10% water content in [ASi + BSi] and 5% content of others elements than Si (Bartoli and Wilding 1980; Drees et al. 1989), the relative proportion of [BSi + ASi] on the total SiO₂ concentration in soil ranged between 0.5 and 5% depending on tree species. These values were very similar to the ones (1–3%) calculated by Blecker et al. (2006) in grasslands.

Solutions

The mean concentrations of DSi and DAL, as measured between April 2006 and April 2007 in throughfall and stemflow, forest floor and soil solutions, are presented in Table 5. They both increased in the sequence: throughfall ~ stemflow < forest floor leachate. They ranged from 0.86 to 1.81 mg l⁻¹ for DSi and from 0.54 to 1.74 mg l⁻¹ for DAL in forest floor leachates. The DSi content was the largest in the soil solution collected at 15 cm depth, and tended to decrease beneath in all forest stands.

BSi and ASi particles morphologies

From Fig. 1, BSi particles from the various tree species could be identified. We observed other siliceous amorphous substances (ASi) and other shaped BSi particles like “bilobate short cell”, “cylindrical polylobate”, “globular” and “favose”, probably inherited from the herbaceous understorey vegetation. BSi from conifers and broad-leaved tree species were characterized by elongate and circular shape. The Phytoliths of *Picea abies* and *Pinus nigra* seemed very similar to the ones of *Picea rubens* and *Pinus strobes* (Klein and Geis 1978) and *Pinus mugo* (Carnelli et al. 2001). The surface of *Pseudotsuga*

Table 5 Mean dissolved Si and Al contents in various solutions as measured between April 2006 and April 2007 (unpublished data, INRA-Champenoux, Nancy); the errorassociated with the mean (n = number of replicates) is given in parentheses (standard error)

	Douglas fir	Norway spruce	Black pine	European beech	Oak
<i>Si content in solution (mg l⁻¹)</i>					
Rainfall ($n = 12$)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
Throughfall ($n = 3$)	0.05 (0.02)	0.03 (0.02)	0.01 (0.01)	0.07 (0.07)	0.05 (0.05)
Stemflow ($n = 3$)	0.07 (0.05)	0.01 (0.14)	0.06 (0.06)	0.08 (0.05)	0.13 (0.11)
Forest floor ($n = 2$)	1.54 (1.04)	1.50 (1.13)	0.86 (0.44)	0.97 (0.43)	1.81 (0.90)
–15 cm ($n = 5$)	3.53 (0.65)	3.10 (0.37)	3.22 (0.48)	1.80 (0.57)	2.40 (1.13)
–30 cm ($n = 5$)	2.67 (0.34)	1.73 (0.30)	2.16 (0.28)	1.79 (0.28)	2.34 (0.34)
–60 cm ($n = 5$)	2.02 (0.40)	1.71 (0.32)	2.27 (0.29)	1.69 (0.25)	1.88 (0.30)
<i>Al content in solution (mg l⁻¹)</i>					
Throughfall ($n = 3$)	0.04 (0.02)	0.03 (0.02)	0.02 (0.02)	0.01 (0.02)	0.02 (0.02)
Stemflow ($n = 3$)	0.11 (0.27)	0.07 (0.05)	0.13 (0.14)	0.01 (0.01)	0.04 (0.03)
Forest floor ($n = 2$)	0.54 (0.08)	0.60 (0.28)	1.74 (0.56)	0.74 (0.25)	1.07 (0.41)

menziesii phytolith was smooth. The *Fagus sylvatica* phytolith was furrowed. Most of the *Quercus sessiliflora* phytoliths were long and smooth. Following ICPN names (Madella et al. 2005), the phytoliths of *Picea abies* and *Pinus nigra* are called “cylindric lacunose”; the phytoliths of *Fagus sylvatica* are called “cylindric sulcate” or “lamine tracheid”; the phytoliths of *Quercus sessiliflora* and *Pseudotsuga menziesii* are called “elongate long cell”. Phytoliths extracted from humus and soil layers exhibited dissolution features, as compared to the ones from leaves and needles. EDX analysis revealed the large dominance of Si (98%) in BSi particles isolated from leaf/needle materials. As compared to the former, ASi particles extracted from forest floor horizons and soil layers exhibited a larger Al content, likely because of Al adsorption onto the surfaces of siliceous amorphous compounds (Bartoli and Wilding 1980; Bartoli 1985).

Total Al and Ti content in the selected samples

As shown in Table 6, the total Al content of leaves/needles (0.02–0.05%) was smaller than the total Si content in all tree species (0.45–0.74%); except in Black pine (0.02%). The total Al content in leaves/needles and branches was significantly larger in coniferous than in deciduous species. The total Ti content increased in the sequence $Olv \ll Of < Oh < 0\text{--}5\text{ cm} < 55\text{--}70\text{ cm}$.

Discussion

Si uptake by forest trees

The recycling of Si by forest trees can be described considering a steady state system. Thus, the current Si annual uptake ($\text{kg ha}^{-1} \text{ year}^{-1}$) is estimated as follows (Ranger and Bonneau 1984; Ranger et al. 1997; Markewitz and Richter 1998):

$$\text{Uptake} = \text{Immobilization} + \text{Restitution} \quad (2)$$

where the annual Si restitution ($\text{kg ha}^{-1} \text{ year}^{-1}$) into soil is computed from Eq. 3

$$\text{Restitution} = \text{Litterfall} + \text{Crown leaching} \quad (3)$$

The total Si concentration of the ligneous biomass (branches, stemwood and stembark) was multiplied by the current annual biomass increment (averaged between 2001 and 2006; Sicard et al. 2005; Ranger et al. 2004) to compute the current annual immobilization of Si. The total Si concentration in leaves/needles and branches collected in litter traps was multiplied by the mean annual litterfall mass (averaged between 2001 and 2006; unpublished data, INRA-Champenoux, Nancy) to compute the annual restitution of Si in solid form. The concentrations of Si in throughfall and rainfall (Table 5) were used to calculate the concentration of Si leached by rainfall from tree crown (throughfall–rainfall); that concentration was further multiplied by the computed

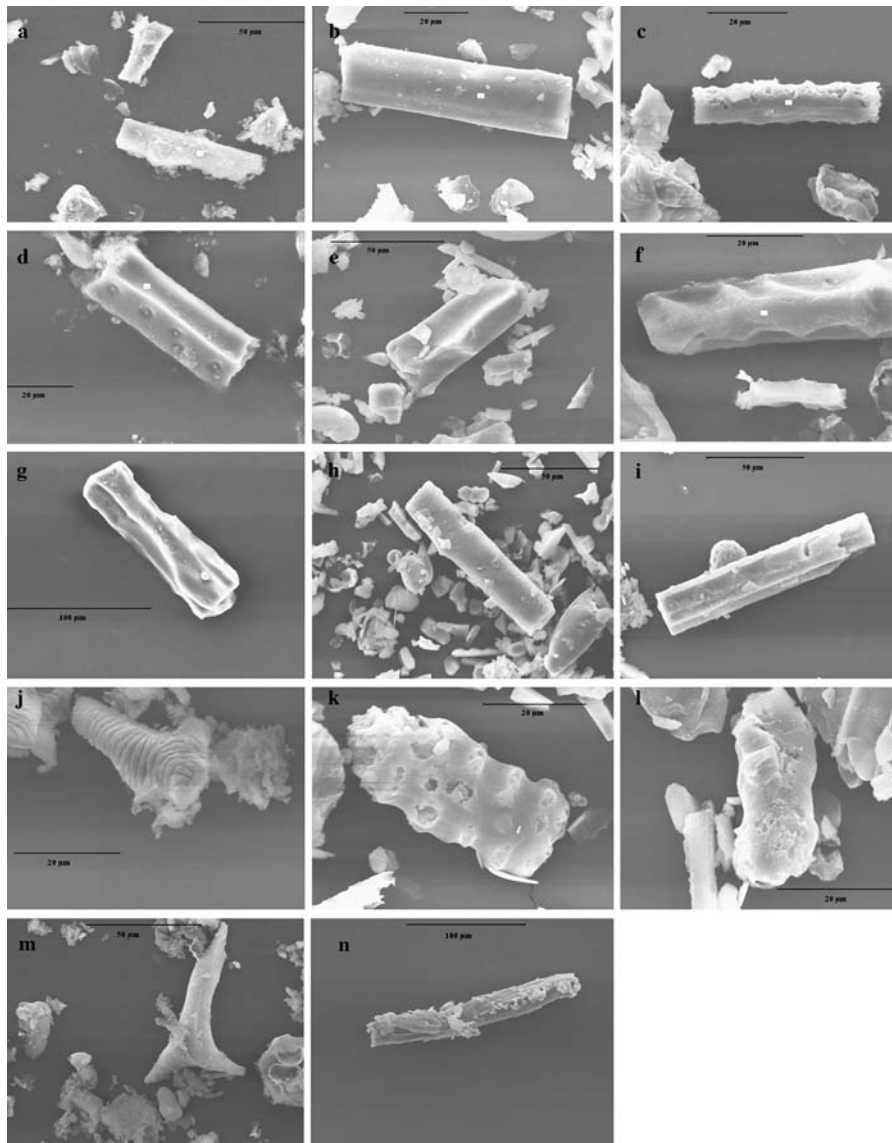


Fig. 1 Scanning electron micrographs of BSi (phytolith) from leaves/needles and ASi from humus and soil layers. **a** BSi isolates from *Pseudotsuga menziesii* needles. **b** ASi isolates from Oh under *Pseudotsuga menziesii*. **c** ASi isolates from soil (25–40 cm) under *Pseudotsuga menziesii*. **d** BSi isolates from *Picea abies* needles. **e** ASi isolates from Oh under *Picea abies*. **f** ASi isolates from soil (10–15 cm) under *Picea abies*. **g** BSi

isolates from *Pinus nigra* needles. **h** ASi isolates from Oh under *Pinus nigra*. **i** ASi isolates from soil (10–15 cm) under *Pinus nigra*. **j** BSi isolates from *Fagus sylvatica* leaves. **k** ASi isolates from Oh under *Fagus sylvatica*. **l** ASi isolates from soil (10–15 cm) under *Fagus sylvatica*. **m** BSi isolates from *Quercus sessiliflora* leaves. **n** ASi isolates from soil (25–40 cm) under *Quercus sessiliflora*

amount of crown leaching ($P - \text{In}$, Eq. 1). Here, only the contribution of the above-ground phytomass is considered, since the calculated Si-mass contained in tree-roots represents no more than 1% of the total uptake (Gérard et al. 2008).

From Table 7, the relative proportion of Si immobilization on Si uptake decreases as the

following sequence: European beech (15%) > Black pine (8.7%) > Douglas fir (4.5%) > Norway spruce (2.7%) > oak (2.1%). The maximum contribution of Si crown leaching to the total restitution of Si into soil is 2.5%. Our computations show that, at least, 83% of the Si uptake is annually recycled on topsoil throughout litterfall (Litterfall/Uptake: Table 7),

Table 6 Total Al and Ti contents in selected tree and soil compartments; when considering tree species, means with various letters are significantly different at the 95% level ofconfidence; the error associated with the mean ($n = 3$) is given in parentheses (standard error)

	Douglas fir	Norway spruce	Black pine	European beech	Oak
<i>Total Al content (% wt)</i>					
Leaves/needles	0.054a (1E-3)	0.050b (2E-3)	0.054a (1E-3)	0.020c (7E-4)	0.019c (2E-3)
Branches	0.018b (7E-4)	0.010c (7E-4)	0.022a (1E-3)	0.003d (8E-5)	0.002d (2E-4)
<i>Total Ti content (% wt)</i>					
Leaves/needles	0.001ab (5E-6)	0.002a (9E-4)	0.001b (3E-5)	0.001b (6E-5)	0.001b (6E-4)
Olv	0.003b (8E-5)	0.001d (5E-5)	0.002c (8E-5)	0.012a (2E-4)	0.002c (1E-4)
Of	0.018d (1E-3)	0.009e (4E-5)	0.049b (8E-4)	0.062a (8E-4)	0.024c (1E-3)
Oh	0.08c (5E-4)	0.04d (7E-4)	0.14b (4E-3)	0.16a (7E-3)	0.13b (8E-4)
0–5 cm soil layer	0.18a (1E-2)	0.20a (3E-2)	0.17a (1E-2)	0.19a (8E-3)	0.17a (1E-2)
55–70 cm soil layer	0.23a (2E-2)	0.21a (4E-3)	0.24a (4E-3)	0.21a (1E-2)	0.24a (2E-2)

Table 7 Mean annual values of Si immobilization, Si restitution through litterfall and crown leaching measured between 2001 and 2006; annual uptake of Si is deduced from Eq. 2; annual output of Si is deduced from Eq.1

	Si (kg ha ⁻¹ year ⁻¹)				
	Douglas fir	Norway spruce	Black pine	European beech	Oak
Immobilization	1.4 (0.2)	1.2 (0.3)	0.2 (0.1)	3.5 (1.5)	0.4 (0.1)
Litterfall	29.0 (8.0)	42.2 (14.1)	2.1 (0.8)	19.3 (6.4)	17.8 (5.3)
Crown leaching	0.2 (0.2)	0.1 (0.2)	0 (0.1)	0.5 (0.6)	0.3 (0.4)
Uptake	30.6 (8.0)	43.5 (14.1)	2.3 (0.9)	23.3 (6.5)	18.5 (5.3)
Si soil water output	1.1 (1.5)	0.7 (1.2)	9.4 (2.2)	6.0 (1.6)	6.7 (1.9)
Litterfall/uptake	0.95	0.97	0.91	0.83	0.96

The standard deviation, calculated by the method of the propagation of uncertainty, is given in parentheses and corresponds to inter-annual variations

whatever the species. These results accord with the fact that Si is deposited at the termini of the transpiration stream, mainly in the outer walls of the epidermal cells on both surfaces of the leaves (Marschner 1995).

As computed from Eq. 2, the mean annual Si uptake (Table 7) is clearly dependent on tree species, and decreases as the following sequence: Norway spruce (43.5 ± 14.1 kg ha⁻¹ year⁻¹) > Douglas fir (30.6 ± 8.0 kg ha⁻¹ year⁻¹) > European beech (23.3 ± 6.5 kg ha⁻¹ year⁻¹) > oak (18.5 ± 5.3 kg ha⁻¹ year⁻¹) \gg Black pine (2.3 ± 0.9 kg ha⁻¹ year⁻¹). The concentration of Si in plants is controlled by soil properties, climate and plant species (Jones and Handreck 1965; Raven 1983). Here, we isolate the impact of tree species on the uptake of Si since soil physical and

chemical properties were identical between trees plots when the experimental site was set up (Bonneau et al. 1977).

Our uptake values are very similar to the ones computed previously in temperate climate: 8–44 kg ha⁻¹ year⁻¹ in coniferous forests (Bartoli 1983; Markewitz and Richter 1998; Gérard et al. 2008), 10.8–32.3 kg ha⁻¹ year⁻¹ in mixed broadleaved-coniferous forests (Fulweiler and Nixon 2005; Garvin 2006) and 26 kg ha⁻¹ year⁻¹ in a broadleaved forest (Bartoli 1983). In humid tropical conditions, the recycling of Si by forest trees is evaluated up to 67 kg ha⁻¹ year⁻¹ in Congo rainforest (Alexandre et al. 1997).

The relatively low concentration of Si in branches, stembark and stemwood (Table 3) confirms the

relatively low transport of Si through the phloem to other plant parts (Raven 1983). As old needles accumulate more Si than young ones, needle age may influence Si accumulation (Bartoli and Souchier 1978). Considering the mean concentration of Si in young needles (Table 3), conifers accumulate less Si in comparison with the broad-leaved trees (Hodson et al. 2005).

DSi output

Most of the root uptake occurs within the first 50 cm of the soil (Drénou 2006). For instance, 93% of fine root length of Norway spruce is distributed between 0 and 50 cm depth in an acid brown soil (Puhe 2003). Based on literature data, Jackson et al. (1996) suggest that the rooting profile is shallower in temperate deciduous forest than in temperate coniferous forest, with respectively, 75 and 50% of roots in the uppermost 30 cm of the soil. In temperate and tropical forests, 78% of roots are distributed in the top 50 cm of the soil (Jackson et al. 1996). In our experimental site, the distribution of roots strongly decreases from 70 cm depth as suggested by field observations (Ranger et al. 2004). Thus, it is reasonable to expect that a major part of DSi is leached out from soil at 60 cm depth, and readily contributes to the hydrological output of Si.

The amount of DSi leached out from soil at 60 cm depth (Table 7) was computed by multiplying the mean annual drainage (Eq. 1, Table 2) and the average Si concentration in solution collected at 60 cm depth between April 2006 and April 2007 (Table 5). Since the two variables (drainage and concentration) are independent, we could calculate the standard deviation on the flux by method of the propagation of uncertainty. The mean DSi output ($\text{kg ha}^{-1} \text{ year}^{-1}$)

decreases as the following sequence: Black pine (9.4 ± 2.2) > oak (6.7 ± 1.9) > European beech (6.0 ± 1.6) > Douglas fir (1.1 ± 1.5) > Norway spruce (0.7 ± 1.2).

Origin of Si in organic horizons

The Si content is mostly controlled by biological recycling in the recent litter layer (Oln), and by bioturbation in the humified Oh horizon. Bioturbation mixes up silicate minerals from mineral horizons beneath through the action of living organisms (Giesler et al. 2000), and can be estimated through the fate of poorly mobile elements (Al, Ti).

Al is not essential, but toxic to plants. Rustad and Cronan (1995) observed that DAl leached from the O-horizons is much larger than the aboveground Al input (litterfall + throughfall + stemflow). It suggests a contribution of Al incorporated from the mineral layers beneath. From Table 8, the contribution of DAl released from weathering of soil minerals incorporated in the O-horizons is larger under Black pine ($8.9 \text{ kg ha}^{-1} \text{ year}^{-1}$), oak ($7.3 \text{ kg ha}^{-1} \text{ year}^{-1}$) and European beech ($5.1 \text{ kg ha}^{-1} \text{ year}^{-1}$) in comparison with Douglas fir ($0.7 \text{ kg ha}^{-1} \text{ year}^{-1}$) and Norway spruce ($1.1 \text{ kg ha}^{-1} \text{ year}^{-1}$).

Plants take up very small quantities of Ti, which is poorly mobile in soils (Fitzpatrick and Chittleborough 2002). The titanium ratio is defined as follows:

$$\text{Ti ratio} = \left[\frac{\text{Ti}_{\text{horizon}}}{\text{Ti}_{\text{reference}}} \right] \times 10^2 \quad (4)$$

where $\text{Ti}_{\text{horizon}}$ is Ti content in each specific individual horizon (Oln—0–5 cm soil layer), and $\text{Ti}_{\text{reference}}$ is Ti content in 55–70 cm soil layer.

From Table 9, Ti ratio increases from 0.38–0.56 in Oln to 70–89 in 0–5 cm soil layer, in parallel with the

Table 8 Aboveground Al inputs into forest floor, as computed from the concentration of Al in litterfall (Table 6), throughfall and stemflow (Table 5), mean annual litterfall mass and mean annual rainfall under canopy; amount of DAl released from the forest floor, as computed from the concentration of aqueous Al

	Douglas fir	Norway spruce	Black pine	European Beech	Oak
<i>Al ($\text{kg ha}^{-1} \text{ year}^{-1}$)</i>					
Al inputs in forest floor	2.7	2.5	3.3	0.8	1.2
Al output from forest floor	3.4	3.6	12.2	5.9	8.5
Al released from weathering	0.7	1.1	8.9	5.1	7.3

in forest floor solution (Table 5) and the estimation of drainage (Eq. 1, Table 2); Al released from weathering of silicate minerals admixed into forest floor is the difference between Al inputs and Al output (Rustad and Cronan 1995)

increase of mineral content. Under fir, Ti ratio increases from 7.7 in Of to 37 in Oh, and then abruptly to 78.3 in 0–5 cm soil layer (2.1-fold increase). Under spruce, Ti ratio increases from 4.4 in Of to 20.7 in Oh, and then abruptly to 86.5 in 0–5 cm soil layer (4.2-fold increase). Under the other forest stands (pine, beech and oak), Ti ratio increases from 10–29.8 in Of to 55–78.2 in Oh and slightly rises to 70.1–89.1 in 0–5 cm soil layer (1.1–1.3-fold increase). The increase of the Ti ratio is thus less abrupt in the latter tree stands, denoting less bioturbation in the two former ones.

Both Al and Ti bioturbation indexes show that the incorporation of soil minerals into organic horizons is less important under Douglas fir and Norway spruce than under Black pine, European beech and oak. This accords with the values of the concentration of SiO₂ inherited from soil minerals in Oh, which is lower in Norway spruce (11.6% wt) and Douglas fir (20.4% wt), in comparison with Black pine (37.9% wt), European beech (39.3% wt) and oak (43.6% wt) (Table 4). We can thus assume that the DSi concentrations in forest floor leachate result from a dynamic balance between (i) dissolution processes involving silicate minerals admixed into O-horizon as well as BSi particles returned to topsoil through litterfall, and (ii) neoformation of clay minerals, adsorption of Si onto iron and/or aluminium oxides as well as polymerization of BSi through the recycling of DSi by trees. Giesler et al. (2000) also suggested that DSi concentration in forest floor leachate might be controlled directly by the weathering of silicate minerals incorporated into forest floor (low pH and high concentration of low molecular organic acids) and indirectly by root uptake.

In this respect, phytolith solubility is partly influenced by the specific surface area of the particle

(Bartoli and Wilding 1980). As illustrated in Fig. 1, the morphology of BSi particles clearly differs within tree species. Thus, we can expect various dissolution rates of BSi particles in forest floor. Wilding and Drees (1974) have shown that phytoliths dissolution rates are a function of the phytoliths morphology: forest BSi is about 10–15 times more soluble than grass BSi, due to the higher specific surface area of the former.

Budget of Si in the soil–tree system

From Fig. 2, the annual Si uptake is negatively correlated with the annual DSi output at 60 cm depth. Under Norway spruce and Douglas fir, Si uptake is respectively 60 and 30 times larger than the amount of DSi leached out from soil. Under European beech and oak stands, Si uptake is about three times larger than the amount of DSi leached out from soil. In contrast, the uptake of Si by Black pine is about four times lower than the amount of DSi leached out from soil. Except for pine, Si uptake and restitution are largely significant in comparison with the annual leaching of Si. Using a numerical model, Gérard et al. (2008) suggest that the annual Si output (5.1 kg ha⁻¹ year⁻¹) is very small in comparison to Si uptake by Douglas fir (44.4 kg ha⁻¹ year⁻¹). In tropical conditions, the annual Si restitution into soil (41 kg ha⁻¹ year⁻¹) is also significant in comparison with annual Si leaching (11 kg ha⁻¹ year⁻¹) (Lucas et al. 1993). Under Black pine, the DSi output exceeds the Si uptake because DSi released by mineral dissolution does not readily contribute to the BSi pool of the vegetation. Considering all species, this reveals that the decrease of DSi in soil solution through clay formation is less important than the decrease of DSi in soil solution through root uptake, as argued by

Table 9 “Titanium ratio”, defined here as the Ti content in specific horizons (Oln—0–5 cm soil layer) divided by the Ti content in the mineral soil at 55–70 cm depth, considered as

reference horizon; when considering tree species, means with various letters are significantly different at the 95% level of confidence

	Douglas fir	Norway spruce	Black pine	European Beech	Oak
[Ti _{horizon} /Ti _{reference}] × 10 ²					
Leaves/needles	0.56a	0.43a	0.40a	0.48a	0.38a
Olv	1.56b	0.44d	0.88c	5.90a	0.87c
Of	7.74d	4.38e	20.44b	29.81a	10.12c
Oh	36.97c	20.72d	57.26b	78.20a	54.99b
0–5 cm soil layer	78.29bc	86.5a	73.26c	89.1ab	70.09c

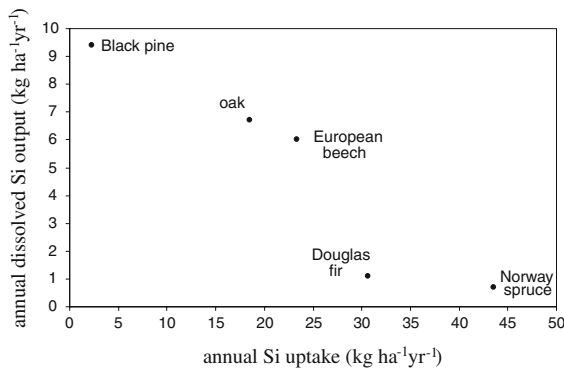


Fig. 2 Relationship between the annual uptake of Si by forest stands and the annual DSi output at 60 cm depth

Farmer et al. (2005). The fact that BSi pool of the vegetation acts as a sink for DSi is largely recognized in other studies of forest ecosystems (Bartoli and Souchier 1978; Bartoli 1983; Lucas et al. 1993; Alexandre et al. 1997; Giesler et al. 2000; Gérard et al. 2008). Consequently, the decrease of DSi content beneath 15 cm depth could be largely influenced by the active root uptake as suggested by Gérard et al. (2008). The Si cycling by plants can impact the clay mineral stability or formation. This phenomenon called “nutrient uplift” or “element translocation” can counteract the geochemical trend of Si leaching, and may account for the stability of clay mineral in upper soil horizons (Lucas et al. 1993; Lucas 2001; Kleber et al. 2007; Barré et al. 2009). If plants are rapidly cycling nutrients, the incorporation of BSi, that is more soluble than primary silicates, likely decreases the rate of primary silicates weathering (Kelly et al. 1998). On the other hand, Lucas (2001) suggests that Si uptake by plants directly impacts soil formation through the dissolution of primary minerals and/or the formation of secondary clays. The importance of biological uptake does not exclude the impact of geological processes on the decrease of DSi concentrations from 15 to 60 cm depth (Table 5). As suggested by Blecker et al. (2006), clay formation would deplete the concentration of DSi in soil solution. Besides, the reaction of silicic acid with aluminium to form hydroxyaluminosilicates (HAS) is also a Si sink which could influence DSi concentration through the weathering (Exley 1998). The increase of DSi concentration between 0 and 15 cm depth results from a combined effect of (i) the increase of mineral weathering driven

by organic ligands (Gérard et al. 2008), proton excretion and cations uptake by roots (Drever 1994; Kelly et al. 1998), and (ii) the dissolution of phytoliths returned on topsoil through litterfall (Lucas 2001). The DSi released by the dissolution of phytoliths could be immobilized through formation of clay minerals beneath (Lucas et al. 1993), and thus does not contribute to the leaching of DSi to the hydrosphere. Accordingly, our results can not provide direct evidence about the impact of various tree uptakes on the leaching of DSi from land to the ocean and can not prove the origin of DSi (geochemical or biological). However, since our data were performed in identical climate and soil conditions, we clearly demonstrate that tree species directly impact on Si uptake, immobilization and restitution and, consequently, on the DSi concentration in soil solution.

Implications

Plants largely contribute to the terrestrial Si reservoir since annual BSi production by plants ranges between 60 and 200 Tmol year⁻¹ (Conley 2002) and rivals that produced by diatoms in oceans (240 Tmol - year⁻¹) (Tréguer et al. 1995). The dissolution of BSi pool and release of DSi in the soil solution would strongly increase DSi output to oceans following deforestation (dissolution of terrestrial BSi pool and no Si uptake) (Conley et al. 2008). The leaching of aqueous Si from soil to rivers strongly impacts the oceanic biogeochemical cycle, as land–ocean flux contributes to more than 80% of the input of DSi to the oceans (Tréguer et al. 1995). The drainage losses of Si and the amount of Si recycled by forest trees are still poorly quantified. The results presented here show that forest tree species can strongly influence the cycling of Si. Thus, tree species must be taken into account in further studies concerning both mineral weathering and DSi fluxes to the hydrosphere. Forest ecosystems are usually considered as open systems, meaning that matter and energy are continually transferred across their boundaries. In this paper, we clearly demonstrate the impact of tree species on the retention of Si by the soil–tree system, as Si is conserved within the system through Si uptake by forest trees. Without considering Si retention by the soil–tree system, forest trees can enhance the release of DSi from soil mineral through weathering of silicate minerals. The recycling of Si

by forest trees generates a BSi pool in soil, more soluble than the silicate minerals (Frayse et al. 2006; Fraysse et al. 2009), and thus promotes the leaching of DSi to the hydrosphere. Considering Si retention by the soil–tree system, the hydrological output of Si is reduced when a large amount of Si is taken up by forest trees (terrestrial BSi pool). For calcium, Likens et al. (1977) also suggest that the quantities circulating within the ecosystem are much greater than those lost by leaching. The recycling of Si by forest trees is thus an important mechanism of Si conservation in the soil–tree system (Alexandre et al. 1997; Street-Perrott and Barker 2008). Indeed, during the growing season, Si released by mineral and [BSi + ASi] dissolution is largely taken up by forest vegetations and is concentrated in the BSi-plant pool before returning to soil. When plant uptake decreases during winter, DSi is much more leached from the soil profile (Gérard et al. 2002; Farmer et al. 2005). That increase of DSi output is mainly controlled by the decrease of Si uptake (Fulweiler and Nixon 2005), as weathering processes decline with a decrease of temperature (Farmer et al. 2005). Thus, on the basis of our data, we believe that the Si leaching from soil are liable to dominate over retention and recirculation of Si in the soil–tree system when root uptake is limited.

Conclusion

Our results provide clear answers to the questions raised in the Introduction section. (1) The tree species influence the uptake and restitution of Si to soil through litterfall. (2) Among other processes, the recycling of Si by tree species impacts the leaching of DSi from forest soils.

Si is mainly accumulated in leaves and needles. Consequently, Si becomes largely mobile in the soil–tree cycle through litterfall. The Si soil–tree cycle is clearly modulated by tree-species as shown by the distinct uptake, immobilization and restitution rates of Si. Moreover, our data show that the amount of DSi released from soil at 60 cm depth is negatively correlated with the uptake of Si by forest trees. As geochemical processes, tree species can also strongly impact on the content of DSi in the soil solution and, consequently, could influence the land–ocean fluxes of DSi.

It is now fundamental to quantify the respective contribution of the non biogenic and BSi mineral dissolution to the DSi pool. Ge:Si ratio (Derry et al. 2005) and stable Si isotopes (Ziegler et al. 2005; Opfergelt et al. 2008) seem to be relevant tools to investigate the origin of DSi, in order to clear up the biologic control on the Si export to the hydrosphere.

Acknowledgements We thank D. Gelhaye (INRA) and A. Lannoye (UCL) for field assistance, Prof. C. Vincke, Prof. M. Javaux, Dr. S. Opfergelt, A. Lambin (UCL) and P. Bonnaud (INRA) for technical support and pieces of advices, L. Ryelandt (UCL) for the SEM, B. Francq for the advices in statistic, as well as Dr. H. Titeux (UCL) for fruitful discussion. J.T. Cornelis is supported by the “Fonds pour la formation à la Recherche dans l’Industrie et dans l’Agriculture” (FRIA) of Belgium. This research was supported by the “Fonds Spécial de Recherche” (FSR) 2008 of the UCL. The Breuil-Chenue site belongs to the ORE network (long term observation of forest ecosystems) and received funds from the GIP ECOFOR for monitoring.

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