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Silica uptake and release in live and decaying biomass in a northern hardwood forest

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Abstract. In terrestrial ecosystems, a large portion (20–80%) of the dissolved Si (DSi) in soil solution has passed through vegetation. While the importance of this “terrestrial Si filter” is generally accepted, few data exist on the pools and fluxes of Si in forest vegetation and the rate of release of Si from decomposing plant tissues. We quantified the pools and fluxes of Si through vegetation and coarse woody debris (CWD) in a northern hardwood forest ecosystem (Watershed 6, W6) at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA. Previous work suggested that the decomposition of CWD may have significantly contributed to an excess of DSi reported in stream-waters following experimental deforestation of Watershed 2 (W2) at the HBEF. We found that woody biomass (wood + bark) and foliage account for approximately 65% and 31%, respectively, of the total Si in biomass at the HBEF. During the decay of American beech (*Fagus grandifolia*) boles, Si loss tracked the whole-bole mass loss, while yellow birch (*Betula alleghaniensis*) and sugar maple (*Acer saccharum*) decomposition resulted in a preferential Si retention of up to 30% after 16 yr. A power-law model for the changes in wood and bark Si concentrations during decomposition, in combination with an exponential model for whole-bole mass loss, successfully reproduced Si dynamics in decaying boles. Our data suggest that a minimum of 50% of the DSi annually produced in the soil of a biogeochemical reference watershed (W6) derives from biogenic Si (BSi) dissolution. The major source is fresh litter, whereas only ~2% comes from the decay of CWD. Decay of tree boles could only account for 9% of the excess DSi release observed following the experimental deforestation of W2. Therefore, elevated DSi concentrations after forest disturbance are largely derived from other sources (e.g., dissolution of BSi from forest floor soils and/or mineral weathering).

Key words: coarse woody debris; decomposition; deforestation; silica.

INTRODUCTION

In terrestrial ecosystems, vascular plants take up large quantities of Si from soil solutions in dissolved form (DSi) and return Si to the soil as micrometer-scale amorphous SiO₂ bodies termed phytoliths (more generally known as biogenic Si; BSi) (Bartoli 1983, Lucas 2001, Struyf and Conley 2012). This biological recycling is an important component of Si dynamics at soil-column to watershed scales (Alexandre et al. 1997, Meunier et al. 1999, Sommer et al. 2006, Gérard et al. 2008, Ronchi et al. 2015), because (1) accumulation of BSi in vegetation delays the export of Si via fluvial systems (Meunier et al. 1999, Struyf et al. 2009); (2) Si uptake alters pore-water chemistry and therefore the stability of other Si-bearing phases (Lucas et al. 1993, Velde and Barré 2009); and (3) the BSi that accumulates in organic soil horizons (i.e.,

the forest floor) represents a source of particularly soluble Si (Bartoli 1983, Sommer et al. 2006). Because 20–80% of DSi in soil solutions derives from dissolution of BSi (Bartoli 1983, Derry et al. 2005, Gérard et al. 2008, Lugolobi et al. 2010), cycling of Si by vegetation is known as “the terrestrial Si filter” (Struyf and Conley 2012).

In an ecosystem at steady-state with a stable vegetation community, the annual uptake of Si (as DSi) by plants should equal the return of Si (as BSi) to the topsoil. Dissolution of BSi in the soil and weathering of mineral-bound Si must then balance the uptake into plants and the loss of DSi in drainage waters. Conversely, a perturbation to the terrestrial Si filter is likely to result in changes in BSi storage and fluxes of DSi exported from the system (Street-Perrott and Barker 2008, Struyf et al. 2010, Clymans et al. 2011, Guntzer et al. 2011). This topic has received increased attention since changes in stream DSi concentrations relative to other nutrients can affect downstream phytoplankton community assemblages and water quality (Conley et al. 1993, 2008b, Colman and Bratton 2003). Several studies have shown that human

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activities can directly influence terrestrial ecosystem Si cycling (Engle et al. 2008, Clymans et al. 2011, Carey and Fulweiler 2012a, 2015, Keller et al. 2012). In a particularly drastic example, the deforestation of a whole watershed led to a persistent (>20 yr) increase in DSi fluxes at the Hubbard Brook Experimental Forest (HBEF), a temperate hardwood forest (Conley et al. 2008a). However, little attention has been paid to the period of ecosystem adjustment and timescales of recovery (Ranger et al. 2002, Song et al. 2014). At the HBEF, for example, even 20 yr of data do not allow us to predict whether original conditions will be re-established after forest disturbance or if a new, alternative steady state between Si inputs and losses will be attained.

The return of Si from vegetation to the forest floor is largely through fine litterfall—leaves, needles, fruits, and small branches. In addition, the physical fragmentation of large branches and the death of whole trees returns Si bound in wood and bark to the forest floor. This coarse woody debris (CWD) has long been recognized as an important ecological component of forests (Harmon et al. 1986). Although for most nutrients, the pool in CWD is small relative to soils or living biomass (Likens et al. 1994, 1998, Krankina et al. 1999, Laiho and Prescott 1999, Likens 2013), nutrient dynamics in CWD may be important for long-term forest sustainability (Kuehne et al. 2008, Shortle et al. 2012). Investigating the rate of Si release during the decomposition of CWD in different forests is essential to assess the impacts of silviculture or climate change (including pest outbreaks, ice and wind storms, and fire) on ecosystem Si dynamics. Conley et al. (2008a) suggested that decaying wood could contribute to the excess DSi (relative to a reference watershed) measured in stream water following experimental deforestation at the HBEF. This conclusion implies relatively rapid release of BSi stored in the woody debris. However, there are currently no estimates of Si release rates from decaying tree boles to test this hypothesis.

Our study had four key aims:

1. to determine the Si release rate from decaying wood and bark for the dominant tree species in the northern hardwood forest at Hubbard Brook;
2. to develop relationships that can be used to estimate Si losses from decaying CWD at the HBEF and other temperate forest ecosystems;
3. to construct a vegetation Si budget for a reference northern hardwood forest (watershed 6 at the HBEF) based on new and published data; and
4. to evaluate the hypothesis that decaying wood contributes significantly to excess stream DSi following deforestation, as observed in watershed 2 at the HBEF.

We measured Si concentrations in leaves and in fresh and decaying bole segments of the three co-dominant tree species in the northern hardwood forest at the HBEF. The leaf and bole data were combined with known amounts of living and dead standing biomass (Whittaker

et al. 1974, Battles et al. 2013) and tree mortality data (Siccama et al. 2007) to estimate pools and fluxes of Si through the terrestrial Si filter during a period of steady-state aboveground biomass (1992–2012). Data from the CWD decomposition study were used to assess the importance of CWD to ecosystem Si dynamics in undisturbed and deforested watersheds (i.e., watershed 6 and watershed 2, respectively), at Hubbard Brook.

MATERIALS AND METHODS

Hubbard brook experimental forest

This study was performed at the Hubbard Brook Experimental Forest (HBEF) in central New Hampshire, USA (43°56' N, 71°45' W). The experimental watersheds examined in this paper are dominated by sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.) and yellow birch (*Betula alleghaniensis* Britt.). Together, these three species accounted for 86% of the aboveground living tree biomass in 1991 (Siccama et al. 2007). The mean annual air temperature in the study area is 5.5°C, with average daily temperatures ranging between –8.3°C in January to 18.7°C in July (Bailey et al. 2003). Precipitation in the study watersheds averages 1434 mm and is spread throughout the year (Bailey et al. 2003). About 26% of the annual precipitation falls as winter precipitation, about half of which falls as snow (Federer et al. 1990, Bailey et al. 2003).

Since 1965, intensive monitoring of the hydrosphere, lithosphere, biosphere, and atmosphere of HBEF has provided a unique and invaluable long-term biogeochemical record (Likens 2013). Here we combine these published records with new experimental data from fresh and decaying boles from an in situ decomposition study, and from a leaf sampling campaign, to constrain Si dynamics in two south-facing watersheds. These comprise a reference watershed (W6, 13.2 ha) and a deforested watershed (W2, 15.6 ha). The reference watershed has been undisturbed since the start of monitoring in 1965. Here, inventories of living and dead biomass (above and below ground) were conducted in 1965, 1977 and every 5 yr thereafter (Whittaker et al. 1974, Battles et al. 2013). The whole-watershed deforestation experiment on W2 was conducted to quantify the importance of vegetation uptake, and the impact of disturbance, for watershed nutrient and hydrologic cycles. Briefly, all trees, shrubs and woody vegetation were cut with a chainsaw during the winter of 1965–1966 and left on the ground. Herbicides were applied for 3 yr following cutting to prevent regrowth, and vegetation was allowed to regrow thereafter (Likens et al. 1978). Streamwater chemistry has been monitored in both watersheds since 1965 (Likens 2016a, b).

Vegetation sampling

Mass and nutrient dynamics (C, N, P, K, Ca), not including Si, of fresh and decaying bole samples in the

Hubbard Brook valley have been reported by Johnson et al. (2014). They performed a 16-yr in situ incubation procedure on boles from which we analyzed archived bark and wood samples for Si content (Johnson et al. 2014, 2016). Similarly archived leaf samples of the dominant tree species for the period 1998–2010 were used to determine Si storage in the canopy of the northern hardwood forest at the HBEF.

Bole samples.—Details regarding sample preparation, field sampling, and estimation of mass loss can be found in Johnson et al. (2014, 2016). Briefly, in July 1990 and May 1991, 71 trees of the three co-dominant species were felled with a chainsaw in and around the south-facing experimental watersheds at the HBEF (Johnson et al. 2014). The trees were approximately 50–70 yr old. For each felled tree, two adjacent segments of the bole (1.0–1.5 m in length) were isolated using a chainsaw. Initial dimensions were measured on all segments; thereafter one of the two segments was placed on the forest floor under intact forest canopy. The incubated bole segments were placed on sloping ground, away from seeps and water-logged areas, with the long axis oriented perpendicular to contours. The second segment was taken to the lab for sampling, so each of our 71 samples incubated in situ was paired with a fresh sample from the same tree.

Incubated boles were collected from the field in April, 1993 (2 yr after felling); May–July, 2001 (10 yr); and July, 2007 (16 yr). Three boles of each species (nine total) were collected in 1993 and 2001. In 2007, three American beech, six sugar maple and six yellow birch boles were collected. Any surface litter on the bole was removed, the bole was gently rolled onto a sampling tarp, and loose material was collected in a bag. Once returned to the lab, the bole dimensions were remeasured and the bark removed. The incubated boles were subsampled and prepared for chemical analysis in the same manner as the fresh boles. Two samples originating from beech boles collected in 2001 (10 yr) had so little bark that it was not sampled and judged to be completely decomposed.

Leaf samples.—Leaf tissue was collected for the three dominant tree species (yellow birch, American beech and sugar maple) at the full-grown stage. Individual leaves were collected from manually cut branches throughout the canopies of trees at different elevations adjacent to, but representative of, W6. Fifteen trees (five per species in the low, middle and high elevation zones) were sampled each year from 1998 to 2010 (Conley et al. 2016). The leaf samples were composited by species, dried and ground before analysis.

Chemical analysis

Chemical measurements were made on 64 bark samples (33 fresh, 31 decomposed), 66 wood samples (33 fresh, 33 decomposed) and 155 leaf samples. The methods used to determine C, N, and major elements in wood and bark can be found in Johnson et al. (2014). For this study, we also analyzed the Si concentration in all bark, wood, and leaf

samples. A single-step alkaline digestion was performed on the bark and wood samples, in which 100 mg of dried and homogenized tissue was digested in 40 mL of 0.5 mol/L NaOH at 85°C for 4 h in a shaking bath. A 2-mL aliquot was retrieved at the end of the procedure and neutralized with 4 mL of 0.25 mol/L HCl. For leaf samples, a single-step alkaline digestion was performed, in which 30 mg of dry tissue was digested in 40 mL of 0.1 mol/L Na₂CO₃ at 85°C for 4 h in a shaking bath. A 1-mL aliquot of the digest solution was neutralized with 9 mL of 0.021 mol/L HCl. Direct comparison of leaf and bole Si data would be problematic if the stronger alkaline solution used for the boles (0.5 mol/L NaOH cf. 0.1 mol/L Na₂CO₃) yielded different Si concentrations than the solution used for the leaf digestions. However, we verified that the measured leaf Si concentration was independent of the strength of the alkaline solution (see Appendix S1: Fig. S1), indicating that the two datasets can be compared. All extracts were analyzed for DSi colorimetrically (SmartChem 200, AMS France, Frepillon, France) using the molybdate-blue method (Strickland and Parsons 1968). A total of 19 randomly selected samples of wood and bark, and all leaf samples, were analyzed in duplicate. This approach resulted in an average within-method uncertainty of 11% and 3%, respectively, for all tree species and sampling years.

Statistical analysis

The experimental design of the CWD incubation study favors the use of a paired ANOVA to test the significance of differences in chemical concentrations between fresh and decomposed wood and bark at each sampling (2, 10, and 16 yr). The Levene's test was used to check for homogeneity of variance ($P > 0.05$). The ANOVA function was used in the R software package (R Core Team, 2012). All tests were carried out with a significance level of 0.05.

Bole decay (i.e., the mass loss based on the change in mass experienced by the decayed log) was modeled as an exponential (first-order) decay process (Arthur et al. 1993, Johnson et al. 2014). Nutrient dynamics in decaying boles have previously been modeled using a combined power-exponential equation by Brais et al. (2006), who showed that a power-exponential model appears to be better in describing the nutrient release of decaying wood than simpler models. The combined model accounts for the possibility that the nutrient content in boles could feasibly remain unchanged (i.e., no loss of nutrient during bole decay), release nutrients more gradually with time (i.e., at a slower rate than bole decay), or even exhibit higher than initial quantities if external inputs are important. Following this previous work, we used a combined power-exponential equation to describe the change in the concentration of Si during decomposition of CWD:

$$Y_t = a \cdot (t + 1)^b \cdot e^{k_n \cdot t}, \quad (1)$$

where Y_t is the concentration of Si at time t (yr). Parameters a , b , and k_n were estimated by nonlinear

regression using the *NLS* function in R. Using $t + 1$ in the power term has the desirable property that $Y_t = a$ when $t = 0$. Thus, parameter a can be interpreted as the concentration of the nutrient in fresh wood or bark. The use of a combined power-exponential model allows for the deletion of a term (power or exponential) of Eq. 1 if the associated coefficient (here b or k_n) is not significantly different from zero (Brais et al. 2006). Our data analysis for Si concentrations revealed that estimates of k_n were not significantly different from zero, so Eq. 1 was simplified to a simple power model ($b < 1$):

$$Y_t = a \cdot (t+1)^b. \quad (2)$$

Vegetation Si pools and dynamics

Annual uptake and standing stocks of Si in living and dead biomass (above and below ground) were estimated by combining the measured Si concentrations with allometric estimates of wood, bark, branches, root, and leaf biomass for inventory years 1992 to 2012 in the reference watershed (W6; Battles et al. 2015a, b, c, 2016a, b). The biomass of living trees was calculated from site-specific allometric equations in which parabolic volume of the tree bole is used to estimate biomass (Whittaker et al. 1974). The original equations were refit using the most complete and correct dimensional analysis data (Falster et al. 2015). The biomass in standing dead trees was depreciated from live tree values based on estimates of fragmentation and decay following procedures outlined in Siccama et al. (2007). We only measured Si concentrations in wood and bark of boles and in leaves for the three dominant tree species in the study watersheds. These components make up about 85–95% of the aboveground living biomass, and 80–95% of the aboveground dead biomass, for all inventory years, and thus dominate the calculations of Si dynamics in vegetation. Nevertheless, to estimate the total Si pool in vegetation and Si fluxes associated with uptake at the watershed scale, we made the following assumptions:

1. Si concentrations in wood, bark and leaves of American beech, yellow birch and sugar maple can be used to calculate Si pools in white ash, white birch and red maple, respectively; and average Si concentrations for the three dominant species can be used for all other species (Siccama et al. 2007). This assumption introduces a relatively small uncertainty because (1) the contribution of these other species to total biomass is small (5–15%); (2) measured wood and bark Si concentrations compare well with other studies in temperate regions (including conifer species: Table 1); and (3) interannual variability of Si concentrations in leaves is larger than interspecies variability, suggesting that repeated sampling over time captures most of the potential uncertainty in leaf Si concentrations.
2. The wood-to-bark ratio is the same in roots, stems, and branches. The wood-to-bark ratio of stems was

therefore used to calculate the biomass of wood and bark in roots and branches.

3. The Si concentrations in wood and bark of the stem are applicable to wood and bark in the roots and branches. For branches this correspondence is supported by literature data (Table 1). Reports on the Si concentration of tree roots are rarely found in the literature, mainly because of the difficulty in cleaning roots from all sources of mineral contamination. The few data available (e.g., 240 mg SiO₂ per kg for spruce roots, reported in Gérard et al. 2008) suggest a similar concentration to bole biomass. Clearly, though, careful analysis of the Si content of tree roots would allow a more robust estimate of Si storage in belowground biomass.

RESULTS

Si concentrations and pools in fresh and decaying boles

For fresh logs of all tree species, BSi concentrations in the bark were higher than in wood (Table 2). American beech averages $6,634 \pm 1,870$ mg SiO₂ per kg (mean \pm SD) in its bark, an order of magnitude higher than bark of yellow birch (436 ± 138 mg SiO₂ per kg) and sugar maple (315 ± 45 mg SiO₂ per kg). The wood of yellow birch (309 ± 84 mg SiO₂ per kg) contains significantly greater ($P < 0.05$) BSi than both sugar maple (170 ± 24 mg SiO₂ per kg) and American beech (190 ± 47 mg SiO₂ per kg).

BSi concentrations increased with time of decomposition (2, 10, and 16 yr) for wood (except yellow birch) and bark (except American beech; Table 2). These two exceptions remained stable during the 16-yr decomposition period; no bole tissues exhibited significant decreases in Si concentration during decomposition. Significant ($P < 0.05$) enrichment of BSi in wood and bark was only observed after 10 or more yr of decomposition (Table 3). The magnitude of changes in BSi concentration was largest in bark tissues.

Relationships for the change in the concentration of Si over the course of decomposition were developed for wood and bark, respectively (Eq. 2, Fig. 1). Because of small sample sizes and high within-species variability, we combined data for all three species to develop the relationship for wood. The exceptionally high Si concentrations in the bark of American beech would dominate any modeling effort, and dwarf the significant increases in bark Si concentrations for the other tree species. Furthermore, our data indicated no significant change in the Si concentration of beech bark over 16 yr of decomposition. Therefore, we used the data for yellow birch and sugar maple bark to develop a relationship for bark Si concentrations for those species during decomposition (Fig. 1), while assuming that the Si concentration in beech bark remained constant during decomposition. The fitted models explained 29% and 56% of the variance for wood and bark, respectively.

TABLE 1. Overview of published literature reporting the BSi (mg SiO₂ per kg) for the wood, bark, and branches compartments of different tree species. The applied method is reported if available.

Reference	Sample	Species	Method	BSi (mg SiO ₂ per kg)
Amos 1952 in Scurfield et al. 1974	Wood	440 broad-leaved	n.d.	1,000–30,000
Torelli and Čufar 1995	Wood	43 Mexican tropical hardwood	n.d.	3,000–47,000
Meunier et al. 2008	Wood	Tropical wood	Borate fusion	25–900
Gérard et al. 2008	Wood	Douglas fir	Physical separation	900
	Bark	Douglas fir	Physical separation	4,440
	Branch	Douglas fir	Physical separation	3,300
Carnelli et al. 2001	Wood	Dicotyledons from alpine regions	Physical separation	100–2,100
	Wood	Conifers from alpine regions	Physical separation	200–5,300
Cornelis et al. 2010b	Wood	European beech/Oak	Borate fusion	40
	Bark			200 (Oak)–3,200 (Beech)
	Branches			100–700
	Wood	Douglas fir/Norway spruce and Black pine	Borate fusion	100
	Bark			200–400
	Branches			300–600
Sommer et al. 2013	Wood	European beech	Total digest (HNO ₃ and HF)	37
	Bark	European beech	Total digest (HNO ₃ and HF)	5,540
	Branches/twigs	Litter beech forest	Total digest (HNO ₃ and HF)	3,562
This study	Wood	American beech	Alkaline digestion	190 ± 47
		Sugar maple	Alkaline digestion	170 ± 24
		Yellow Birch	Alkaline digestion	309 ± 84
	Bark	American beech	Alkaline digestion	6,634 ± 1,870
		Sugar maple	Alkaline digestion	315 ± 45
		Yellow Birch	Alkaline digestion	436 ± 138
	Leaves	American beech	Alkaline digestion	14,700 ± 4,200
		Sugar maple	Alkaline digestion	12,400 ± 4,200
		Yellow Birch	Alkaline digestion	3,400 ± 1,300

Total nutrient contents in CWD can either remain unchanged or decrease more gradually than the bole loses mass. Both these scenarios would cause an apparent enrichment in the residual bole. In extreme cases, external nutrient inputs could create a situation in which the nutrient content of the boles increases during decomposition. A comparison of the relative amount of Si remaining during bole decay illustrates the dominant processes that control Si release or retention for specific tree species. Those fractional changes in the standing stocks of Si in decaying boles, together with the average mass decay curve for the studied boles (from Fig. 1 in Johnson et al. 2014), are shown in Fig. 2. A value greater than 1.0 would indicate a net increase in the amount of Si compared to the amount in the fresh bole, indicating an external source of Si. A value concomitant with the mass decay curve indicates Si release commensurate with bole decay, while values between the mass decay curve and 1.0 suggest preferential retention. Boles of American beech lose Si at a rate similar to the total mass loss from the boles, while sugar maple and yellow birch boles

release Si more slowly than total mass loss due to decomposition.

Si pools and fluxes in forest vegetation at HBEF

We used average Si concentrations for fresh leaves, wood and bark, together with estimates of tree biomass for the inventory years 1992 to 2012 (Battles et al. 2015a, b, c, 2016a, b) to calculate vegetation Si pools in the reference watershed, W6, at the HBEF. Mortality and CWD data from Siccama et al. (2007) and Fahey et al. (2005) were used with our Si release data to calculate Si pools in CWD and Si fluxes into and out of living and dead biomass pools (Fig. 3).

Si pools in living and dead biomass.—The BSi pools (mol Si per ha) for live and dead above- and belowground biomass, are reported in Table 4 for the inventory years 1992 to 2012. In the period 1992–2012, the total aboveground and belowground biomass BSi pool ranged between 2,095 and 2,178 mol/ha in living and dead stand-

TABLE 2. Evolution of mean BSi (mg SiO₂ per kg) in bark and wood of Beech, Sugar Maple, and Yellow Birch based on NaOH extracted concentrations (since 1991).

BSi (mg SiO ₂ per kg)		REF			2 years			10 years			16 years		
		<i>n</i>	Mean	Std	<i>n</i>	Mean	Std	<i>n</i>	Mean	Std	<i>n</i>	Mean	Std
Bark	Beech	9	6,634	1,870	3	6,897	252	1	6,900	NA	3	5,625	1,866
	Sugar Maple	12	315	45	3	397	53	2	1,038	276	6	1,323	815
	Yellow Birch	12	436	138	3	510	184	3	797	228	6	1,125	354
Wood	Beech	9	190	47	3	243	37	3	722	380	3	415	108
	Sugar Maple	12	170	24	3	229	38	2	273	90	6	448	163
	Yellow Birch	12	309	84	3	345	57	3	484	132	6	332	74

ing trees. About 31% of the BSi in vegetation is annually produced in leaves (ca. 653 ± 130 mol/ha), about 65% of the biomass BSi pool is stored in live biomass (excluding leaves; ca. $1,350 \pm 110$ mol/ha), mostly aboveground (ca. $1,110 \pm 104$ mol/ha). Dead above and belowground biomass contains approximately 4% (ca. 120 ± 13 mol/ha) of the standing BSi stock.

In addition to standing biomass, there is also a significant amount of CWD in the forest, consisting of fallen trees, fragmented branches and other large-diameter biomass components. The mass of CWD has been measured twice in HBEF, and equaled 10.6 Mg/ha and 9.4 Mg/ha for 1973 (Tritton 1980) and 1995 (Fahey et al. 2005), respectively. The Si pool in CWD was calculated assuming that: (1) the species composition of standing vegetation reflects the composition of CWD, and (2) the average residence time of CWD (i.e., 6.2 yr; Siccama et al. 2007) can be translated into a correction factor that accounts for the varying Si losses from CWD of different ages (see Fig. 2). These factors equaled 1.0, 1.3 and 1.3 for American beech, sugar maple and yellow birch respectively. The resulting CWD Si pool is about 2.5% of the total biomass pool (52 ± 6 mol/ha).

Si fluxes: uptake, restitution, decay.—The canopy BSi pool is equivalent to the annual leaf BSi production (ca. $653 \text{ mol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$), as this pool is annually built up and

returned to the forest floor upon abscission of leaves. The pool of BSi in the canopy was stable in 1992–2012, averaging 653 mol/ha. Further, annual woody biomass production, i.e., the additional amount of wood produced compared to the previous year, in W6 was about $3.3 \text{ Mg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ in the stable-biomass period (1992–2012, based on 1997 productivity data in Siccama et al. (2007) and the 5-yr mean of productivity data in Battles et al. 2013). Converting these biomass estimates to vegetation BSi production fluxes, we estimate that $21 \pm 2 \text{ mol Si ha}^{-1} \cdot \text{yr}^{-1}$ was sequestered in wood and bark during the stable-biomass period. Therefore, the annual vegetation Si uptake (woody biomass plus canopy production) averaged $674 \text{ mol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$.

The uptake fluxes are balanced by return of Si to the soil through litterfall and tree mortality. Litterfall is the combined return of leaves, twigs, woody debris, and various other plant parts. Annual litterfall in this deciduous forest equals the canopy production rate of $653 \text{ mol Si ha}^{-1} \cdot \text{yr}^{-1}$. About 90% of this ($585 \pm 116 \text{ mol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$), mainly leaves, is classified as fine litter fall, while the remaining 10% ($68 \pm 14 \text{ mol} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$), called coarse litter, consists largely of twigs and fruits (Fahey et al. 2005). Litterfall accumulates in the forest floor, resulting in a BSi pool of $\sim 33,000 \text{ mol Si per ha}$ (Saccone et al. 2007, 2008).

The biomass of standing dead trees, snags and coarse woody debris at the HBEF has been near steady state,

TABLE 3. Changes in BSi concentrations (mg SiO₂ per kg) in decaying wood and bark tissues of dominant northern hardwood tree species. The means and standard deviations for fresh tissues are shown in the Fresh column. Other columns show the average change in the concentration after 2, 10, and 16 years of decomposition. Values in bold are between species significant differences, while all reported changes are within species differences. Data for within species differences are not shown for cases where $P > 0.05$.

Component	Species	Fresh	2 years	10 years	16 years
Wood	American Beech	190 ± 47		532	225
	Sugar Maple	170 ± 24		103	277
	Yellow Birch	309 ± 84			
	Mean	229 ± 87			
Bark	American Beech	6,634 ± 1,870			
	Sugar Maple	315 ± 45		723	1,008
	Yellow Birch	436 ± 138		361	689
	Mean	2,195 ± 3,045			

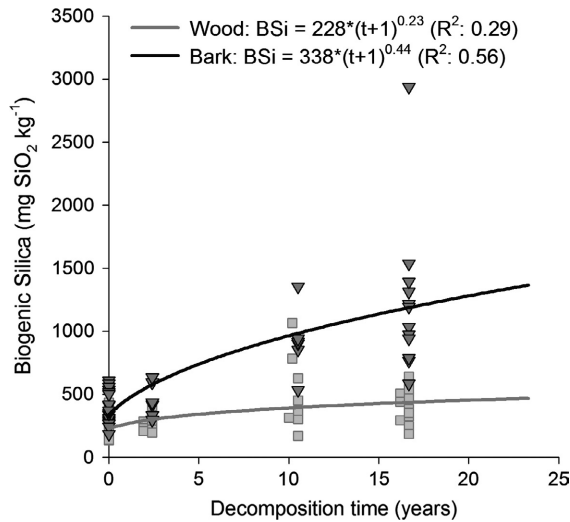


FIG. 1. Increase in BSi concentration with time for wood (grey squares, $BSi = 228 \times (t + 1)^{0.23}$ with $R^2 = 0.29$) and bark without American beech (grey triangles, $BSi = 338 \times (t + 1)^{0.44}$ with $R^2 = 0.56$).

with residence times of 7.5, 15, and 6.2 yr, respectively (Fahey et al. 2005, Siccama et al. 2007). We used mortality data for 1991–2001, reported in Siccama et al. (2007), to estimate Si fluxes going (1) from live standing biomass to dead standing biomass, coarse woody debris (CWD) and decomposition; and (2) from dead standing biomass to CWD. Overall, we estimate that $4.9 \text{ mol Si ha}^{-1} \cdot \text{yr}^{-1}$ is transferred from living biomass to CWD, $5.8 \text{ mol ha}^{-1} \cdot \text{yr}^{-1}$ is converted to dead standing biomass, and $2.6 \text{ mol ha}^{-1} \cdot \text{yr}^{-1}$ is released through decomposition. Finally, about $4.0 \text{ mol ha}^{-1} \cdot \text{yr}^{-1}$ of Si is transferred from the dead biomass pool to CWD. Constant CWD biomass values (Fahey et al. 2005) suggest that decomposition of CWD balances CWD inputs, so about $8.9 \text{ mol Si ha}^{-1} \cdot \text{yr}^{-1}$ is released annually by decomposition of CWD. Together with direct decomposition of dying trees this release results in an additional annual flux of $11.5 \text{ mol Si ha}^{-1} \cdot \text{yr}^{-1}$ to the forest floor (Fig. 3).

DISCUSSION

Vegetation Si dynamics at Hubbard Brook

Global terrestrial BSi production is estimated at 80 Tmol Si per yr of which 2.2 Tmol/yr is attributable to temperate forests (Carey and Fulweiler 2012b). The data underlying this estimate are mostly based on canopy data, and information for woody tissues is sparse (Table 1). The precision and accuracy of annual Si uptake estimates for forest biomes is therefore limited by the lack of BSi concentration data for wood and bark tissues. Our new data covers three dominant tree species occurring in northern hardwood forests of the eastern United States and Canada, and commonly found in other temperate

forests (Bailey 2016). The mean Si concentration of all studied wood specimens ($229 \pm 87 \text{ mg SiO}_2 \text{ per kg}$) is an order of magnitude below concentrations found in tropical woods and is one-third of values reported for Douglas-fir (Table 1). However, our wood concentrations fall in the range of alpine coniferous and dicotyledon species (Torelli and Ćufar 1995, Carnelli et al. 2001, Gérard et al. 2008). Our data on bark indicate an enrichment of Si in the trees' outer layer, particularly for American beech. Interestingly, Cornelis et al. (2010b) reported Si concentrations in bark of European beech (*Fagus sylvatica* L.) and European oak (*Quercus sessiliflora* Smith.) that were similar in magnitude to our values for American beech and maple/birch (Table 1). In addition, we document a slightly higher mean Si concentration ($1,100 \text{ mg SiO}_2 \text{ per kg}$; or $0.28\% \text{ wt SiO}_2$), and Si:C ratio (0.005) for the entire vegetation community in this temperate forest (W6, HBEF) than reported by Carey and Fulweiler (2012b) based solely on canopy data. A canopy contribution of 50% to net primary production at Hubbard Brook, rather than their assumed 30%, explains this difference. Although the magnitude of the global estimate for BSi production by vegetation is robust (Conley 2002), our data emphasize the potential for further refinement of the size of the biological Si "pump" in forested ecosystems by incorporating bole measurements.

Mass balance studies have shown that the production and return of BSi by vegetation is often of a similar or greater magnitude than DSi production from mineral weathering (the ultimate source) and DSi export in

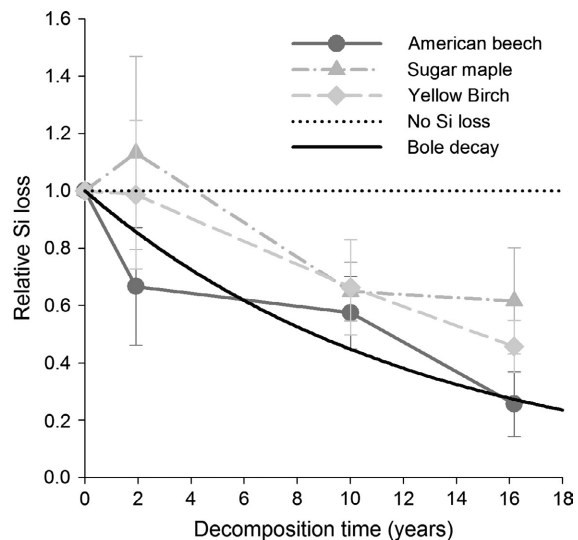


FIG. 2. Fractional gain or loss of Si during decomposition of hardwood tree boles (bark + wood). Values above 1.0 (dotted line) indicate a net gain of Si in the decaying bole, suggesting an external source. Values falling on the wood decay curve have lost Si at a rate commensurate with the decomposition of wood (Relative mass loss = $e^{-0.08 \times t}$ based on Fig. 1 in Johnson et al. (2014); solid line).

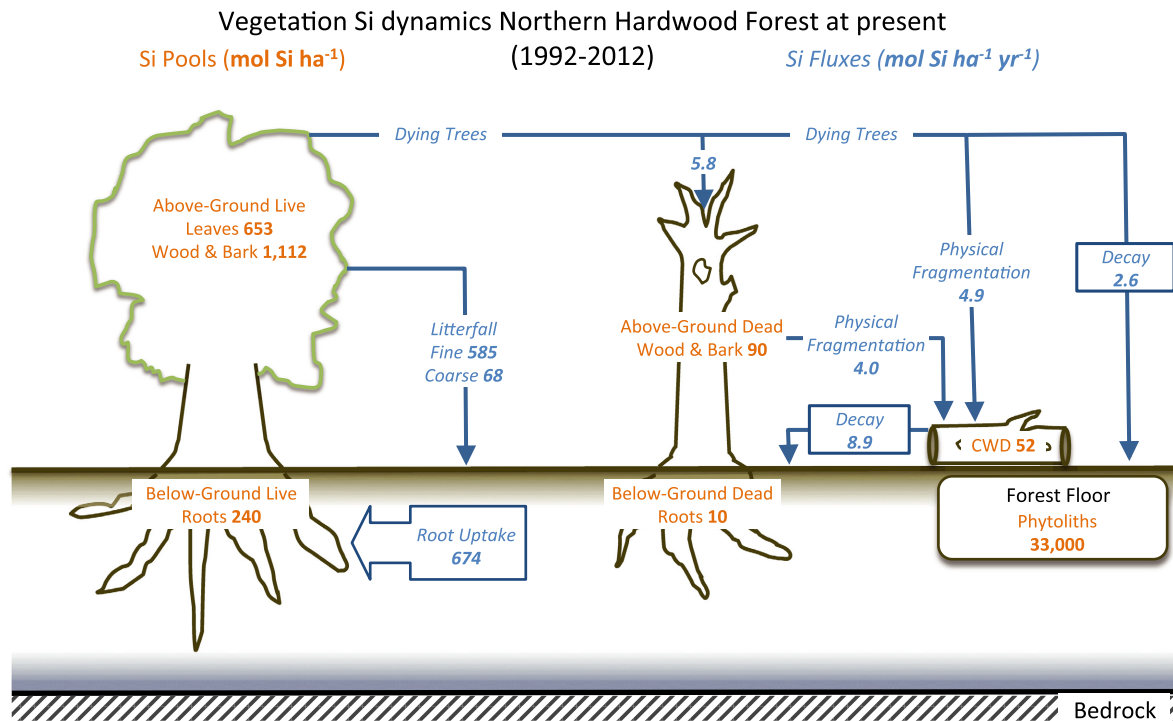


FIG. 3. Ecosystem pools (mol Si per ha, brown) and fluxes (mol Si ha⁻¹ yr⁻¹, blue) of Silicon for a reference watershed (W6) at Hubbard Brook Experimental Forest. Measured Si concentrations of leaves, fresh and decaying boles (this study) were combined with estimates of living and dead biomass (Battles et al. 2013) and tree mortality data (Siccama et al. 2007). The BSi, i.e., phytoliths, pool was previously measured by (Saccone et al. 2008). Values are averages for the period 1992–2012. CWD is coarse woody debris.

streams (the primary loss-term) (Bartoli 1983, Alexandre et al. 1997, Lucas 2001, Cornelis et al. 2010a, Sommer et al. 2013). At the HBEF, silicate weathering supplies about 600 mol Si ha⁻¹ yr⁻¹, while 577 mol Si ha⁻¹ yr⁻¹ was exported from the reference watershed (W6) in the period 1982–1992 (Johnson et al. 2000, assuming a steady-state biological Si cycle). Our data provide a first quantification of the vegetation Si dynamics in this reference

watershed. The standing stock of Si in vegetation is about 2,100 ± 170 mol/ha in the period 1992–2012 (Fig. 3), the majority (65%) of which is stored in the woody biomass of living trees, similar to measurements in a more productive beech forest in Germany (ca. 2,970 mol/ha; 60% in woody biomass) (Sommer et al. 2013). The vegetation BSi pool at the HBEF therefore exceeds annual DSi release by weathering and streamwater DSi export by a factor of four,

TABLE 4. Above and belowground BSi pool (mol Si per ha; with uncertainty and assuming decomposition of standing trees) of live and dead standing trees in W6 of Hubbard Brook Experimental Forest (HBEF) for the period 1992 to present. Biomass data are based on Battles et al. 2015a, b, c, 2016a, b.

BSi Pool (mol Si per ha)	1992	1997	2002	2007	2012
Leaves‡	640 (±127)	644 (±127)	662 (±130)	660 (±131)	692 (±138)
Woody parts					
Live					
Above*	1,143 (±103)	1,141 (±104)	1,122 (±103)	1,068 (±102)	1,116 (±109)
Below†	241 (±37)	243 (±38)	243 (±39)	236 (±40)	251 (±44)
Dead					
Above*	66.4 (±7.7)	66.3 (±7.2)	98.0 (±11.2)	117 (±12.8)	106 (±11.9)
Below†	7.4 (±1.2)	7.5 (±1.1)	10.7 (±1.7)	13.0 (±2.0)	12.1 (±1.9)
Total	2,097 (±167)	2,103 (±168)	2,135 (±170)	2,095 (±172)	2,178 (±182)

*Includes boles, branches and long-term needles. †Includes roots for which no Si measurements are available. ‡standard deviation estimates represents uncertainty on spatial heterogeneity, averaged BSi concentrations for non-measured species, and includes inter-annual differences in BSi leaf concentrations for the period 1998–2012.

while BSi production and dissolution (ca. 674 mol Si ha⁻¹·yr⁻¹; Fig. 3) are of a similar magnitude as the weathering and export fluxes. This analysis emphasizes the importance of vegetation in Si cycling in HBEF, as a minimum of 50% of the DSi annually produced in the soil is derived from BSi dissolution. However, a more precise partitioning of the provenance of DSi leaving the catchment between BSi dissolution and primary mineral weathering requires better constraints on the weathering input and potential immobilization through secondary material formation.

The annual BSi production in the canopy—and therefore in litterfall—in temperate forests has previously been estimated to be between 80 and 1,500 mol Si ha⁻¹·yr⁻¹ (G erard et al. 2008, Cornelis et al. 2010a, Sommer et al. 2013). Our canopy BSi production estimate of 653 mol ha⁻¹·yr⁻¹ (Fig. 3) falls squarely within this range. However, little attention has been paid to the quantification of the contribution of wood decay to Si cycling although this study and others (Sommer et al. 2013) show that the majority of BSi in trees is stored in woody biomass. The dead woody biomass, standing and CWD, accounts for only 5% of the total BSi stock in biomass of the HBEF forest. Approximately 2% of the annual BSi dissolution comes from decaying dead wood (both standing and fallen), indicating that leaf litter is the dominant source of DSi to the forest floor (98%). Between 1982 and 2002, American beech became more prevalent in the HBEF forest, while the biomass of sugar maple and yellow birch declined (Fahey et al. 2005, Siccama et al. 2007). The limited contribution of CWD and the decay of dying wood to the Si supply at HBEF implies that these changes in tree composition have probably had minimal effect on Si dynamics, despite the interspecies differences we observed in Si concentrations and release during decomposition (detailed below). Overall, this finding suggests that the dissolution of BSi hosted in CWD and dying wood is a minor term in a forest Si cycle during periods when annual biomass production rates are relatively stable.

Si release and accumulation during bole decay

Our data show that the mass loss of decaying boles outpaces Si loss for yellow birch and sugar maple, while American beech tracks the whole-bole mass loss (Fig. 2). This result produces a preferential Si retention of 16% and 30% after 16 yr for yellow birch and sugar maple, respectively. The concentrations of Si in decaying boles exhibit high variability (Fig. 1; Table 2), probably due to the environmental factors that influence the mass loss of wood and bark during decay (e.g., temperature, moisture, initial density and microbial community). Despite this variability, we were able to observe significant increases in Si concentrations in the second and third sampling periods (10 and 16 yr) (Table 3; Fig. 1).

The large increases in Si concentrations in both wood (except yellow birch) and bark (except American beech),

up to a factor of 5 over the course of the experiment, correspond with increases observed for several other nutrients (Johnson et al. 2014). Either an additional external source or a preferential Si retention relative to net mass loss can explain the overall Si concentration increase in decaying boles. Input of Si from an external source is unlikely to have precipitated within the bark and wood fraction: the bole samples were positioned to avoid waterlogged sites and Si fluxes in precipitation and throughfall are low (<15 mol Si ha⁻¹·yr⁻¹; G.E. Likens and D.C. Buso, *unpublished data*). The dissolution of leaf litter on the incubating boles might conceivably enrich DSi concentrations in water percolating through the boles, although our data do not permit testing of this hypothesis. The net fractional Si loss from the boles (Fig. 2) supports the interpretation that there are no significant external sources of Si. The increase in wood and bark BSi concentrations is therefore likely to be an enrichment effect; BSi dissolves slower than the wood decomposes.

The half-life of BSi is about 8 yr in decaying American beech boles, and longer than 15 yr for sugar maple and yellow birch. We know that Si phytolith formation is localized in different parts of the stem (e.g., internal surfaces of vessels and fibre, lumina or xylem parenchyma; Scurfield et al. 1974), and therefore the concentration of BSi is heterogeneous within the bole tissue. Evidence from nonstructural carbohydrate to lignin ratios in roots suggests that the initial bole mass loss perhaps occurs in Si-depleted parts of the bole (Fahey et al. 1988), potentially explaining the observed enrichment effect. Alternatively, it may be explained by fungal growth, which enhances wood decay but not BSi dissolution (Alfredsson et al. 2016). More detailed study of deciduous tree species, focusing on Si precipitation and release in relation to the anatomical structure, decay resistance and nutrient concentration of various bole compartments is required to better understand the mechanisms of Si retention in decaying CWD.

Effect of deforestation on Si dynamics

Although CWD decomposition is a minor source of DSi in the steady-state forest, severe disturbances such as ice storms, hurricanes, and pest outbreaks could result in both massive inputs of CWD and lowered biomass production fluxes, potentially contributing to elevated DSi in drainage waters. Following the experimental deforestation in W2 elevated levels of DSi in stream-water were observed (Conley et al. 2008a) and have persisted for five decades (Figs. 4 and 5). The average excess Si flux at the outlet of W2, relative to reference watershed W6, is ~220 mol Si ha⁻¹·yr⁻¹, for a cumulative excess Si export of ca. 10,900 mol Si per ha over 50 years, of which 2,550 mol/ha occurred in the first 6 yr following deforestation (Fig. 4). This excess DSi export was attributed to the reduced biological uptake of Si and the dissolution of BSi from the felled biomass (Conley et al. 2008a). Our new vegetation Si budget,

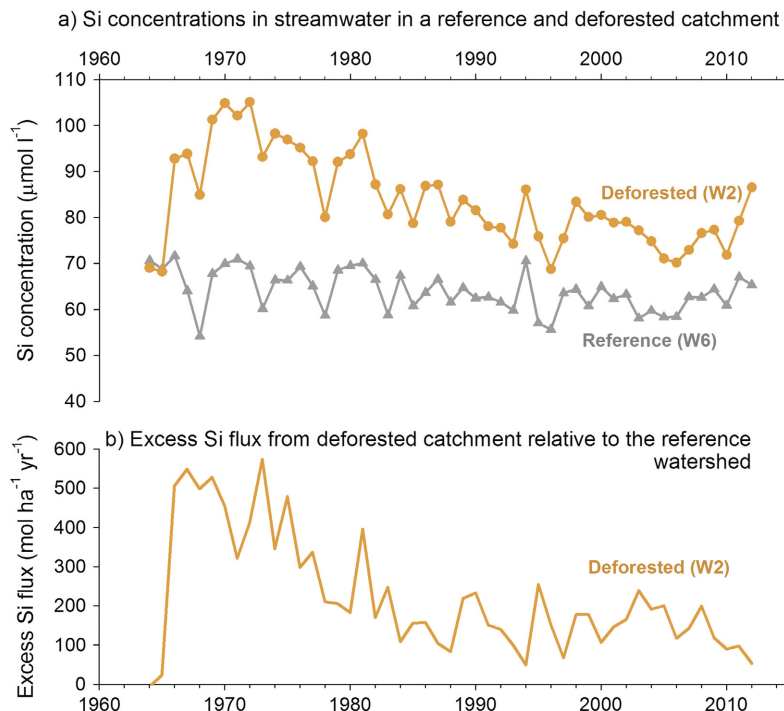


FIG. 4. Silicon (Si) chemistry in stream water of a reference watershed (W6, triangles), and a deforested watershed (W2, circles) at Hubbard Brook Experimental Forest. Flux weighted Si concentration ($\mu\text{mol/L}$) are reported in panel a (updated version of Fig. 1 in Conley et al. 2008a), and the excess Si flux ($\text{mol Si ha}^{-1}\cdot\text{yr}^{-1}$; $W2-W6$) is reported in panel b. [Color figure can be viewed at wileyonlinelibrary.com]

coupled with the results of the bole decay experiments, allows us to evaluate this interpretation.

We combined our fitted power-law functions describing the increase in Si concentrations in wood and bark over time (Fig. 1) with the exponential decay equations reported by Johnson et al. (2014) for the same boles (see Table 1 in Johnson et al. 2014). The Si pool (PSi_t) in the felled biomass at time t (years) is thus described by:

$$PSi_t = M_0 \cdot a \cdot (t + 1)^b \cdot e^{-k_d \cdot t}, \quad (3)$$

in which M_0 is the initial felled biomass, k_d is the mass decay rate constant, and a and b are the coefficients for the power functions (Eq. 2). Equation [3] was calculated separately for each combination of tissue type (wood, bark) and species. For American beech bark, which did not show a significant change in Si concentration during decomposition, we used the average Si concentration in the bark of reference boles (Table 2) as constant a and a b of 0. Arthur et al. (1993) reported initial felled bole wood and stump masses of 116 Mg/ha and 8.8 Mg/ha,

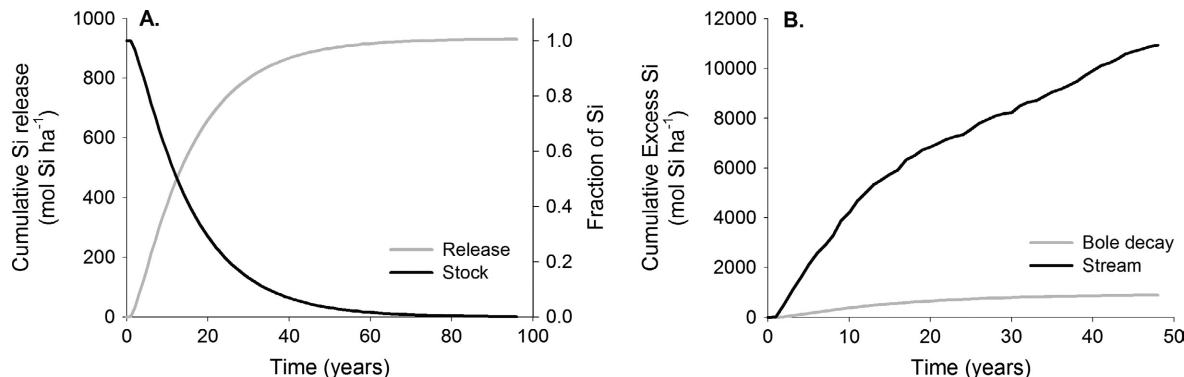


FIG. 5. Si dynamics in coarse woody debris (CWD) following deforestation at W2 in HBEF with the amount/fraction of Si stored in and released from the freshly cut boles, i.e., CWD (A) and compared with the excess Si release measured at the outlet of W2 following deforestation (B). 1964 is the year 0.

respectively, which was distributed in the following proportions: sugar maple, 33%; American beech, 29%; yellow birch, 25%; other, 13%. We allocated the mass of "other" species to the three dominant species in proportion to their aboveground abundances. We then used below-to-aboveground ratios observed for living (0.2) and dead (0.1) wood in W6 (Table 4) to estimate the total cut and decaying bole wood and stump mass (including belowground parts) in W2. Finally, the species-specific bark-to-wood ratios (between 0.06 to 0.10) were applied to estimate the initial masses of wood and bark in the felled boles (M_0).

The deforestation in W2 added *ca.* 931 mol Si per ha to the CWD pool in the winter of 1965–66 in the form of felled trees. Although this input exceeds significantly the annual litterfall input, it represents only 2.8% of the total BSi pool in the forest floor (Saccone et al. 2008). According to our calculations, the dissolution of BSi from this pool was rapid at first and decreased with time. About 50% of the BSi was lost from the felled trees within the first 13 yr after deforestation, while after 50 yr only a small fraction (<5%) of the original Si remained in the decaying boles (Fig. 4).

The decomposition of the felled tree boles was previously suggested to account for a significant amount of the excess Si measured at the W2 outlet (Conley et al. 2008a). Our study demonstrates that decay of wood and bark could only contribute 2–15% of the annual excess Si release. Therefore, other sources (i.e., dissolution of BSi from forest floor soils or mineral weathering) are required to explain the majority of the observed DSi excess. Furthermore, at least one of these additional sources must be extremely labile to explain the immediate response time (<1 yr) of stream water chemistry to the W2 deforestation. We suggest that the elimination of the terrestrial Si filter can explain the short-term excess DSi export, while alterations to the soil weathering regime may explain the longer-term losses.

Role of the biological Si filter.—Conley et al. (2008a) hypothesized that the increase in stream DSi fluxes in W2 from 1965 to present may be due to the disruption of biological Si cycling during the re-establishment of the vegetation after deforestation. In what follows, we investigate the potential for the excess DSi flux to be completely controlled by changes in the biological Si filter (Fig. 5). The decay of the felled boles is insufficient (see previous text; it can account for about 9% of the excess DSi). Instead almost all of the excess DSi after 48 yr (10,900 mol Si per ha) may have been produced through the dissolution of BSi stored in forest soils. In the first 3 yr after deforestation on W2, herbicide treatment virtually eliminated the uptake of Si (and other nutrients) into vegetation. For the next few years, biomass accumulation was low (Reiners 1992). High excess DSi fluxes in the first 5–8 yr after deforestation were therefore likely the result of leaching of DSi that would otherwise have been taken up by vegetation. This hypothesis is supported

by the fact that during the 3 yr of herbicide suppression (1966–1968), the excess DSi (about 600 mol Si ha⁻¹·yr⁻¹) corresponds well with the annual vegetation uptake in the intact forest (674 mol·ha⁻¹·yr⁻¹). Hence, the excess DSi is interpretable as the balance between vegetation uptake and dissolution of the soil BSi pool. The cumulative 48-yr excess DSi loss in W2 of 10,900 mol Si per ha represents a substantial fraction of the BSi in the soil—it is one-third of the forest floor BSi pool (organic horizon) and 4% of the total BSi pool in HBEF soils (257,000 mol Si per ha; Saccone et al. 2008). Therefore, while BSi dissolution can explain the excess DSi export from W2, other mechanisms are likely to have contributed as well.

Deforestation altered not only the biological Si filter but also the geochemistry of soils and drainage waters. For example, secondary clay minerals (e.g., illite, vermiculite) and poorly crystalline phases (e.g., imogolite) are present in soil profiles at the HBEF (Dahlgren et al. 1989). Solution acidity generated by deforestation (Likens et al. 1970) alters soil chemistry and can dissolve primary and secondary silicate minerals (Lucas 2001), releasing Si to soil solutions. The continuing losses of DSi from W2 relative to W6 may therefore be the result of ongoing drawdown of BSi from soil pools, increased mineral weathering rates due to acidification caused by the deforestation treatment, or both.

Implications for increased riverine Si export fluxes.—We show that biology can provide a feasible explanation for pattern of excess Si loss in W2 mostly via a shift in BSi dissolution in the forest floor with a minor contribution from bole decomposition. In a Douglas fir plantation (Beaujolais, France) a chronosequence study showed that it takes about 100–120 yr before the budget between nutrient losses and accumulation in the soil is balanced again (Ranger et al. 2002). Our data confirm that there is still a negative balance almost 50 yr after deforestation in northern hardwood forest. The build-up of the original level of biogenic Si will require an additional couple of decades if regeneration of the original vegetation is allowed.

SUMMARY AND CONCLUSIONS

Our quantification of vegetation Si dynamics in the reference watershed (W6) of Hubbard Brook Experimental Forest (HBEF) confirms the importance of vegetation for Si cycling in northern hardwood forests, as a minimum of 50% of the DSi annually produced in the soil is derived from BSi dissolution.

Generally, little attention has been paid to the role of wood decay in Si cycling. Our study shows that the majority of BSi in northern hardwood forests is stored in woody biomass (65%). In situ incubations of wood boles of the three co-dominant tree species indicated that Si loss from decaying boles either tracks the whole-bole mass loss (i.e., American beech), or results in the preferential retention of Si (i.e., yellow birch and sugar maple) by up to 30% after 16 yr. The decay of wood is a slow

process (half-lives between 8–16 yr), so BSi dissolution from CWD accounts for only 2% of total annual BSi dissolution. Overall, the dissolution of BSi contained in decaying dead wood is a minor term in the Si cycle of a northern hardwood forest when annual biomass production rates are relatively stable.

However, stand-replacing disturbances can still result in large inputs of dead woody biomass, potentially contributing to elevated DSi in drainage waters. Experimental deforestation of W2 at HBEF has elevated levels of DSi in stream-waters for at least five decades. Conley et al. (2008a) attributed this increase primarily to the reduced biological uptake of Si and the dissolution of BSi from the felled biomass. Our vegetation Si budget, coupled with the results of the bole decay experiments, demonstrates, however, that decay of wood and bark could only contribute 2–15% of the annual excess Si release. Therefore, other sources (i.e., dissolution of BSi in forest floor soils or mineral weathering) are required to explain the majority of the observed DSi excess.

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