

Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest

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Abstract

Globally significant increases in the riverine delivery of nutrients and suspended particulate matter have occurred with deforestation. We report here significant increases in streamwater transport of dissolved silicate (DSi) following experimental forest harvesting at the Hubbard Brook Experimental Forest, NH, USA. The magnitude of the streamwater response varied with the type of disturbance with the highest DSi export fluxes occurring in the manipulations that left the most plant materials on the soil surface and disturbed the soil surface least. No measurable loss of amorphous silica (ASi) was detected from the soil profile; however, ASi was redistributed within the soil profile after forest disturbance. Mass-balance calculations demonstrate that some fraction of the DSi exported must come from dissolution of ASi and export as DSi. Land clearance and the development of agriculture may result in an enhanced flux of DSi coupled with enhanced erosion losses of ASi contained in phytoliths.

Keywords: amorphous silica, biogeochemistry, deforestation, Hubbard Brook, mass balance, streamwater export

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Introduction

The accelerating rate of deforestation and conversion to agricultural land and other land uses is a globally significant problem with only 21% of indigenous forests remaining on the Earth. Most studies of the impact of these perturbations are focused on reductions in biodiversity, increases in atmospheric CO₂ concentrations and soil erosion losses. Experimental removal of forests has shown large increases in the land–ocean flux of many nutrients (e.g. Likens *et al.*, 1970), especially nitrogen as NO₃⁻. The subsequent loss of soil fertility with deforestation is especially severe in the tropics (Buschbacher, 1986).

Forests recycle substantial amounts of silicon (Si) through the uptake of dissolved silicate (DSi, e.g. ortho-silicic acid) from soil solutions and deposition of amorphous silica (ASi) in vegetation primarily in the form of phytoliths, although nonphytolith ASi is also

present in plants (Watteau & Villemin, 2001). This ASi is returned to surface soils through litterfall and tree death. The ASi is stored in soils and released through dissolution as DSi back to the soil solution (Bartoli, 1983). The fluxes and pools within the terrestrial biogeochemical Si cycle are poorly constrained, with only a handful of mass-balance studies available [reviewed in Conley (2002)], making it difficult to assess the response of the Si cycle to disturbance and changes in land use. Nevertheless, enhanced losses of DSi have been observed following deforestation (Likens *et al.*, 1970) and redistribution of silica in soil has been observed with the conversion of forest lands to agriculture (Kelly *et al.*, 1998).

Recognition of the importance of the coupling between terrestrial and oceanic systems to global Si cycling has increased in recent years (Conley, 2002). Land–ocean fluxes of DSi have been considered relatively invariant over the Holocene, though it has been recognized that reductions in DSi transport have occurred through the building of dams on rivers (Humborg *et al.*, 2000) and through eutrophication-induced losses on the

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continents (Schelske *et al.*, 1983) and continental shelves (Turner & Rabalais, 1994). Knowledge concerning the inputs of DSi to the oceans is important for predicting global C fluxes. The transfer of DSi to the oceans influences the proportion of diatoms in food webs and promotes diatom production and sedimentation thereby sequestering carbon in the oceanic reservoir (Rague-neau *et al.*, 2006).

Here, we present results from experimental forestry practices and long-term monitoring of experimental watersheds in the northeastern USA at the Hubbard Brook Experimental Forest (HBEF) that show large and persistent increases in the transport of DSi to streams following forest disturbance. We suggest that the increase in transport of DSi is partially related to the mobilization of ASi from cut vegetation remaining in the watersheds. Redistribution of soil ASi was observed within the soil profile, but no measurable losses of ASi from the soil occurred. We suggest that increases in the land-ocean flux of DSi have occurred with deforestation and conversion to agriculture and other land uses.

Materials and methods

The HBEF basin is located in central New Hampshire, USA (43°56'N, 71°45'W). The bedrock lithology is a complex system of metamorphosed sedimentary and igneous rocks. Soils are mainly Spodosols of sandy-loam texture with a thick organic layer at the surface (Likens & Bormann, 1995). The experimental watersheds discussed in this paper are composed of a mixture of American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*). However, at a higher elevation, less-abundant species including red spruce (*Picea rubens*), white birch (*Betula papyrifera*) and balsam fir (*Abies balsamea*) dominate the overstory (Likens & Bormann, 1995). The mean above-ground biomass of vegetation at the HBEF in the reference watershed (W6) was estimated to be 123 Mg ha⁻¹ in 1965 (Whittaker *et al.*, 1974) and forest biomass has not changed significantly since 1982, averaging 196 Mg ha⁻¹ (Likens *et al.*, 1994). Schad (1996) reported a species-weighted Si content of 3.0 mg SiO₂ g⁻¹, providing a watershed biomass Si content of 369–588 kg SiO₂ ha⁻¹. The ASi content of aboveground biomass at the HBEF, which is stored in plant tissues, compares favorably with estimates of Bartoli (1983) for a deciduous forest in France (386 kg SiO₂ ha⁻¹) dominated by European beech (*Fagus sylvatica*).

The Hubbard Brook Ecosystem Study has used a number of long-term, whole-watershed experimental manipulations including various types of forest removal (Likens & Bormann, 1995). Watersheds 1 (11.8 ha) and 6 (13.2 ha) have been maintained as refer-

ence watersheds, although W1 was chemically manipulated in 1999, but this treatment will not be discussed here. In W2 (15.6 ha), all trees, shrubs and woody vegetation were cut with a chain saw in the winter of 1965–66 and left on the ground to determine how the elimination of plant uptake affected hydrologic and hydrochemical outputs. Herbicides were applied for 3 years following cutting to prevent regrowth and then vegetation was allowed to regrow thereafter. W4 (36.1 ha) was divided into lateral, elevational strips and every third strip was cut in 1970. Another one-third of the strips were cut in 1972, and the remaining strips in 1974. W5 (21.9 ha) was cut in a whole-tree harvest in the winter of 1983–84, removing all aboveground biomass greater than 5 cm diameter at breast height (1.37 m).

Stream discharges are monitored continuously with streamwater samples collected both at weekly intervals and during hydrologic events. Measurement of DSi (equivalent to ortho-silicic acid) was made using the molybdenum blue colorimetric technique from 1964 through 1984, and by ICP from 1984 to the present (Buso *et al.*, 2000). Stream-water exports were calculated using measured and averaged DSi concentrations multiplied by daily discharge, and compiled into monthly and annual mass fluxes. Annual, volume-weighted DSi stream concentrations were derived by dividing the annual DSi mass export by the annual water flow. An excess DSi concentration was determined by subtracting the long-term volume-weighted mean DSi concentration for the period of record when there were no experimental manipulations by the annual volume-weighted mean DSi concentration for each year following the manipulation. A running 3-year mean DSi concentration was then calculated.

Soil samples were collected and stored air-dried in the sample archive at the HBEF. Only postharvest samples were available for W2, and no soil samples were available for W4. Soil samples from W5 were quantitatively collected by digging a vertical soil pit with a 0.5 m² template. The purpose was to quantify soil mass per unit area for five soil layers: Oi + Oe horizon, Oa horizon, top 10 cm of mineral soil, 10–20 cm mineral soil layer and from 20 cm horizon to the bedrock (Johnson *et al.*, 1991).

ASi in soils was determined by wet chemical extraction with 1% Na₂CO₃ at 85 °C for 5 h in a heating shaking bath. Subsamples taken at 3, 4 and 5 h were measured for DSi using the molybdenum blue colorimetric technique and extrapolation to the intercept was used to correct for the dissolution of minerals in order to estimate the ASi content (Saccone *et al.*, 2007). ASi is a chemical estimate that is comprised of both ASi from plants, including phytoliths, and from inorganic ASi

(Sauer *et al.*, 2006; Saccone *et al.*, 2007). Soil ASi pools were calculated by multiplying the ASi concentration by soil mass as estimated by Johnson *et al.* (1991).

Results

Large increases in stream concentrations of DSi occurred following deforestation at the HBEF (Fig. 1), with increases still persisting up to 40 years after disturbance. Annual volume-weighted DSi concentrations

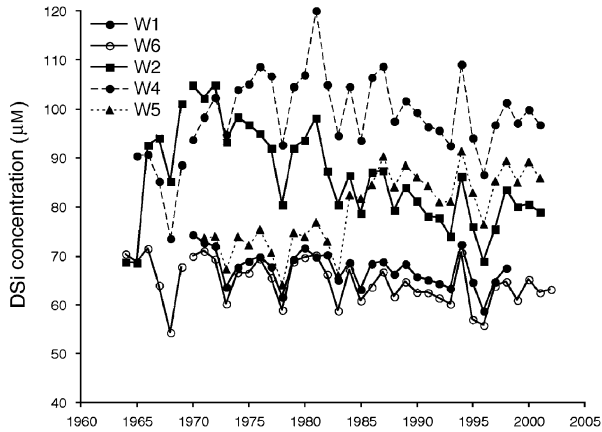


Fig. 1 Mean annual flow-weighted dissolved silicate (DSi) concentrations from different watersheds in the Hubbard Brook Experimental Forest following experimental manipulations. In W2, all trees, shrubs and woody vegetation were cut in the winter of 1965–66 and left on the ground with herbicides applied for 3 years. W4 was divided into lateral, elevational strips and every third strip was cut in 1970. Another one-third of the strips were cut in 1972, and the remaining strips in 1974. W5 was cut in a whole-tree harvest in the winter of 1983–84, removing nearly all the aboveground biomass.

in undisturbed watersheds (W1 and W6) ranged from 54 to 74 μM with an overall mean DSi concentration of $66 \pm 4 \mu\text{M}$ (Fig. 1). In W2, W4 and W5, DSi concentrations increased by 10–40 μM following deforestation. In order to more closely examine the response of stream-water DSi to deforestation and minimize year-to-year variations, a 3-year running mean of excess DSi concentrations was calculated (Fig. 2). The long-term variations in DSi concentrations in both disturbed and undisturbed watersheds are synchronous. The reference watersheds both showed significant long-term decreases in DSi concentrations of 0.16 and 0.20 $\mu\text{M yr}^{-1}$ in W1 and W6, respectively (Fig. 2a). The precise cause of these long-term declines is not known.

The magnitude of the response in DSi concentrations (Fig. 2b) varied with the amount of detrital vegetation remaining after cutting. The W2 manipulation, where vegetation was left on the ground after clear cutting and herbicide application for 3 years, had the highest DSi concentrations and export fluxes as compared with the other manipulations. The response in excess stream DSi concentrations was intermediate in the strip-cutting treatment (W4), where trees were limbed and crowns and branches left behind. The whole tree harvest manipulation (W5), where 93% of all aboveground biomass was removed from the watershed after cutting, produced the smallest response in DSi.

Mean ASi concentrations in the upper O soil horizon from W5 were $25.5 \pm 10.8 \text{ mg SiO}_2 \text{ g}^{-1}$ ($n = 109$; Oi + Oe and Oa horizons combined) in 1983 before harvesting and decreased significantly to $16.6 \pm 8.55 \text{ mg SiO}_2 \text{ g}^{-1}$ ($n = 79$) in the 1986 postharvest samples ($P < 0.001$). When converted to a watershed mass basis, there were no significant losses of ASi integrated over the entire soil profile (Table 1). No soil samples were available from

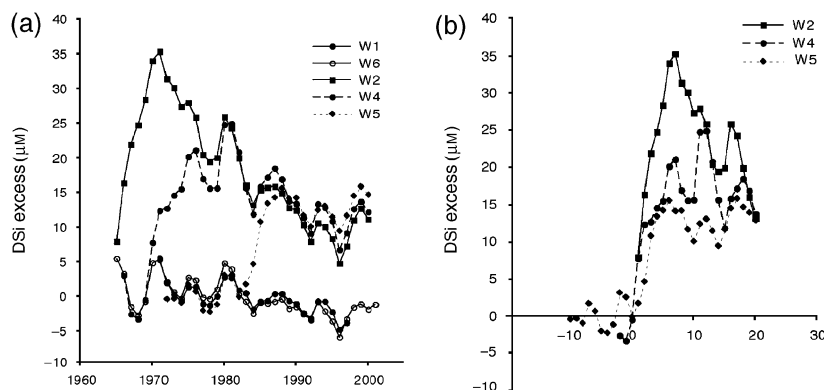


Fig. 2 A 3-year running mean of the excess dissolved silicate (DSi) from different watersheds in the Hubbard Brook Experimental Forest following experimental manipulations. Excess DSi was calculated by averaging volume-weighted DSi concentrations for the period of record when there were no experimental manipulations and then subtracting that average from the period of record following the manipulation. (a) Excess DSi concentration vs. time. Both W1 and W6 act as reference watersheds and the excess DSi is the deviation from the mean DSi concentration. (b) Excess DSi concentrations for the harvested watersheds plotted from time (years) after cutting.

Table 1 Amorphous silica (ASi) content ($\text{kg SiO}_2 \text{ ha}^{-1}$) of watershed 5 integrated over the O horizon (Oie + Oa) and over the profile from the surface to the mineral horizon before (1983) and after (1986) whole-tree harvesting (Saccone *et al.*, 2008)

	1983 (kg ha^{-1})	1986 (kg ha^{-1})
O horizon	2030 (228)	2277 (333)
Integrated profile	17 416 (5485)	17 467 (6092)

Standard error in parenthesis.

Table 2 Overall mean amorphous silica (ASi) content ($\text{mg SiO}_2 \text{ g}^{-1}$ dry soil) of all samples from undisturbed watersheds of Hubbard Brook Experimental Forest (HBEF) by horizon (Saccone *et al.*, 2008) as compared to ASi content of Watershed 2 in 2004, 39 years after cutting

Horizon	Undisturbed watersheds (mg g^{-1})	Watershed 2 (mg g^{-1})
O	25.3 (2.23) <i>n</i> = 31	9.25 (1.90) <i>n</i> = 15
A	14.0 (3.72) <i>n</i> = 7	26.4 (3.91) <i>n</i> = 5
E	5.76 (0.92) <i>n</i> = 12	3.70 (0.53) <i>n</i> = 6
B	3.52 (0.24) <i>n</i> = 51	3.22 (0.71) <i>n</i> = 21
C	4.84 (0.60) <i>n</i> = 37	1.17 (0.08) <i>n</i> = 2

The standard error is in parenthesis and *n* is the number of samples analyzed.

W4; however, samples collected in 2004 from W2 also had lower ASi concentrations in upper soil horizons than samples from the undisturbed watersheds (Table 2).

Discussion

Origin of the excess DSi

Likens *et al.* (1970) hypothesized that the initial increase in stream DSi concentration after deforestation of W2 was due to the increased weathering of primary silicate minerals. Bailey *et al.* (2003) suggested that enhanced primary silicate weathering was modest and lasts only the first few years after harvesting. A more likely explanation is that the excess DSi originates from the dissolution of a biologically derived pool of ASi. The ASi is abundant (Saccone *et al.*, 2008) and is orders of magnitude more reactive and susceptible to dissolution than is the geologic substrate (Bartoli & Wilding, 1980).

Table 3 Comparison of the amount of ASi remaining on the watershed contained in vegetative debris after experimental manipulation and the excess DSi exported from streams integrated over the first 20-year period following manipulation

Watershed	ASi in remaining vegetation (kg ha^{-1})	Excess DSi exported (kg ha^{-1})
W2	369–588*	599
W4	110–176†	265
W5	26–41‡	122

It was assumed that 30% of the biomass remained in W4 after all merchantable materials were removed and 10% remained after whole-tree removal in W5.

*Schad (1996).

†Approximately 30% of the biomass remained after all merchantable materials were removed.

‡Seven percent of the biomass remained after whole-tree removal.

The higher postharvest losses of DSi in streamwater from W2 as compared to W4 and W5 likely originated from the decomposition and dissolution of ASi contained in vegetation that was cut and left lying on the soil surface. Average excess DSi fluxes via streams over the period of measurement were 23.7, 12.2 and 9.2 $\text{kg SiO}_2 \text{ ha}^{-1}$ for W2, W4 and W5, respectively, and varied according to experimental manipulation. The treatment with the largest amount of biomass remaining in the watershed (W2) had the highest excess DSi flux and the treatment with the largest aboveground biomass removal (W5) had the smallest excess DSi flux (Table 3). The excess DSi exported over a 20-year period was of the same order of magnitude as the amount of ASi in vegetation remaining on the soil surface in W2. However, W4 and W5 both exported more DSi than could be accounted for only in vegetation.

A contribution to the excess DSi fluxes could also arise from the dissolution of ASi from the large soil pool (ca. 17 400 $\text{kg SiO}_2 \text{ ha}^{-1}$, Table 1). The largest amount of ASi is found in soils and is typically orders of magnitude larger than found in vegetation biomass (Conley, 2002; Blecker *et al.*, 2006). At Hubbard Brook, for example, the aboveground biomass ASi pool (369–588 $\text{kg SiO}_2 \text{ ha}^{-1}$) is only 2–3% of the soil ASi pool. Therefore, it is likely that some fraction of the excess DSi export arises from the large soil pool. However, because the amount of excess DSi is small compared with the soil pool (0.7–3.4%), changes in the soil ASi pool could not be detected within the error limits (Table 1).

We have observed significant postharvest decreases in ASi concentrations in upper soil horizons, but no

significant changes in ASi pools integrated over the soil profile following harvesting in W5 (Saccone *et al.*, 2008). Changes in the mass of O horizons and the upper mineral horizons have been observed after harvesting due to mixing caused by logging operations (Johnson *et al.*, 1991). As a result of these physical changes in the soil profile, ASi has been redistributed within the soil profile. Additional translocation of Si within the soil results from the leaching of ASi from logging residues and the O horizon through dissolution to DSi, transport to lower soil horizons in soil solution, followed by reprecipitation in lower soil horizons (Saccone *et al.*, 2008). This process appears to have been especially pronounced in W2, where there was a delayed re-establishment of plant growth through herbicide treatment. Forty years after cutting, ASi concentrations in the O horizon of W2 are 62% lower than in comparable watersheds, whereas ASi concentrations in the A horizon are nearly double in W2 (Table 2). Lysimeter data from W5 provide direct evidence of translocation of ASi downward in the soil profile. In the first 5 years after harvesting, DSi concentrations in soil solutions draining the Oa horizon in W5 were significantly greater than DSi concentrations in soil solutions in undisturbed control sites (Dahlgren & Driscoll, 1994).

Finally, DSi leaching may also be enhanced by rapid plant growth during re-establishment of vegetation after harvesting. The quantity of Si exported from a watershed is a dynamic balance between the generation of DSi from ASi (Bartoli, 1983) and primary or secondary minerals, and the formation of ASi from DSi by biological uptake. Forest growth following deforestation may stimulate the rate of weathering (Bailey *et al.*, 2003). Although plant uptake may consume a proportion of the newly (re)-generated DSi, some fraction will be exported. Thus, a rapidly aggrading ecosystem may still export more DSi than a slowly growing forest through leakage of DSi as long as there is an available pool in the soil to draw from. This response might also help to explain the continued high exports from DSi in the experimentally manipulated watersheds even after vegetation is re-established, as well as the declining trends in DSi export from the reference watersheds, themselves recovering from early 20th century disturbance.

Long-term trends in DSi

To our knowledge, few long-term datasets exist that can document changes in DSi concentrations. At the scale of the watersheds studied here (<4 km²), there was a remarkable similarity between streams in long-term DSi concentrations (Fig. 1). This pattern is even clearer in the 3-year running mean of excess DSi concentrations

(Fig. 2), suggesting that the same forcing pattern operates at the scale of the watershed with the probable basis of the variations being climatic forcing.

The long-term decreases in DSi concentrations and export in W1 and W6 that we observed may be due to the reduced weathering potential of the slowly aggrading forest at HBEF. There have been significant declines in the concentrations of base cations, hydrogen ion and sulfate, comprising some 95% of the ionic charge in the reference watersheds at HBEF over the last 40 years (Likens *et al.*, 2002). Because the forest biomass at HBEF has been in a steady state since 1982 (Likens *et al.*, 1994), the uptake of DSi into vegetation has likely remained constant. Therefore, declining DSi concentrations in watershed streams likely reflect lower rates of DSi production through the dissolution of ASi in the soil and weathering of primary minerals.

Most long-term trends previously reported for aquatic ecosystems have been strongly influenced by anthropogenic activities such as eutrophication or damming (Conley *et al.*, 1993). Long-term declines in DSi have also been observed in western Virginia, USA, streams, and the declines in concentrations coincided with gypsy moth defoliation (Grady *et al.*, 2007). Defoliation leads to greater sunlight penetration to streams, hence diatom growth, which utilizes DSi. Initial studies at HBEF found that algae were not present, but more recent studies indicate the presence of algae and that green algal blooms occur just after spring snow melt and before leaf out of the deciduous forest canopy in some years (Bernhardt *et al.*, 2005). However, the increase in diatom biomass is not currently sufficient to remove significant quantities of DSi. By contrast, increasing DSi concentrations have been observed in lakes in the Bohemian Forest, Czech Republic, and attributed to recovery from acid deposition and changes in Al biogeochemistry (Vesely *et al.*, 2005).

Upscaling to the global biogeochemical cycling of silica

The HBEF data represent one of the few studies available reporting DSi concentrations and fluxes following deforestation. No increases were observed in DSi concentrations at Biscuit Brook, NY, USA (Peter Mudroch, U.S. Geological Survey, personal communication) with a partial cut of 40% of the original basal area (Wang *et al.*, 2006) and only a 6% increase was observed in the Bavarian Alps with forest thinning (Bäumler & Zech, 1999). Both these watersheds have sandstone bedrock. Saccone *et al.* (2007) reported low ASi concentrations (<10 g SiO₂ kg⁻¹) for soils formed on sandstones. In addition, the ASi content of soils is strongly dependent upon the amount of ASi in vegetation (Jensen *et al.*, 1999; Saccone *et al.*, 2008). Thus, the more modest

responses observed at Biscuit Brook and in the Bavarian Alps may reflect smaller pools of ASi in soils and differences in vegetation in the Alps.

Can we use these data from HBEF to infer changes on the global scale? The global delivery of DSi to the oceans has probably changed on geological time-scales, as hypothesized by Conley (2002), due to enhanced weathering with the evolution of land plants (Berner, 1992) and uplift (Raymo *et al.*, 1988). In addition, Froelich *et al.* (1992) have suggested that during glacial periods, DSi inputs to the oceans are higher than during interglacial time periods as evidenced by changing Ge:Si ratios. Our data from the HBEF suggests that the flux of DSi has probably increased to the oceans through forest harvesting and deforestation. Unfortunately, to our knowledge there are no other published studies to test the generality of increases in DSi transport following deforestation. However, the mechanisms described above should be universal and occur in other landscapes that are deforested or brought into agriculture.

In addition to enhanced DSi transport, clearing of forested ecosystems and development of agricultural land leads to the erosion of upper soil horizons (e.g. Pimentel & Kounang, 1998). Because phytoliths are concentrated in the upper soil profile (Alexandre *et al.*, 1997), enhanced erosion should also lead to the export of ASi from soils, although no data are available to examine this process. Development of agricultural land can also lead to changes in the compartmentalization of Si in the soil profile and increase in the export of DSi. Kelly *et al.* (1998) showed that the proportion of acid oxalate-extractable Si in soils was significantly reduced when Hawaiian rainforests were subjected to deforestation and converted to pasture. More data are needed before quantifying the effect of deforestation on DSi and ASi transport in rivers.

The evidence suggests that previous estimates of DSi export fluxes by rivers may be underestimates because of changes in landscape management with deforestation and the long-term development of agriculture during the Holocene. These changes should affect the oceanic Si mass-balance reported by Tréguer *et al.* (1995). Recently, biogenic silica accumulation rates in the Southern Ocean have been recalculated, reducing the estimates of storage in these deep ocean sediments as much as 35% (DeMaster, 2002). To maintain a balance in the world ocean, DeMaster (2002) hypothesized a new sink for biogenic silica on the continental margins, although there are no data to support this hypothesis. Rather than invoking this scenario to maintain a balance in the global silica budget, we hypothesize here that it is more likely that the global oceanic silica cycle is currently out of balance, which exhibits higher DSi inputs

than can be balanced by oceanic burial losses, due to increases in DSi and ASi transport with changes in terrestrial landscape such as those caused by deforestation. Interestingly, decreases in Si transport by rivers have occurred in the last decades with the building of dams (Humborg *et al.*, 2000); these decreases in Si transport are recently compared to the historical increases due to deforestation and agricultural development through human history.

A better understanding of the dynamics of DSi transport across the land–ocean interface improves not only our understanding of the complex biogeochemistry of Si, but also our understanding of global C fluxes (Ragueneau *et al.*, 2006). Over geologic timescales, biologically mediated weathering processes influence atmospheric carbon dioxide content and global climate because the net effect of silicate weathering is the transfer of atmospheric carbon dioxide to bicarbonate. These fundamental weathering processes further influence atmospheric carbon dioxide due to the net transfer of DSi to the oceans, which promotes diatom production and sedimentation thereby adding carbon to the oceanic reservoir. Therefore, long-term changes in the delivery of DSi to the ocean may have a significant effect on C sequestration in oceanic sediments.

References

- Alexandre A, Meunier J-D, Colin F, Koud J-M (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochimica Cosmochimica et Acta*, **61**, 677–682.
- Bailey SW, Buso DC, Likens GE (2003) Implications of sodium mass balance for interpreting the calcium cycle of a northern hardwood ecosystem. *Ecology*, **84**, 471–484.
- Bartoli F (1983) The biogeochemical cycle of silicon in two temperate forest ecosystems. *Ecological Bulletin*, **35**, 469–476.
- Bartoli F, Wilding LP (1980) Dissolution of biogenic opal as a function of its physical and chemical properties. *Soil Science Society of America Journal*, **44**, 873–878.
- Bäumler R, Zech W (1999) Effects of forest thinning on the streamwater chemistry of two forest watersheds in the Bavarian Alps. *Forest Ecology and Management*, **116**, 119–128.
- Berner RA (1992) Weathering, plants, and the long-term carbon cycle. *Geochimica Cosmochimica et Acta*, **56**, 3225–3231.
- Bernhardt ES, Likens GE, Hall RO Jr *et al.* (2005) Can't see the forest for the stream? In-stream processing and terrestrial nitrogen exports. *BioScience*, **55**, 219–230.
- Blecker SW, McCulley RL, Chadwick OA, Kelly EF (2006) Biologic cycling of silica across a grassland bioclimate sequence. *Global Biogeochemical Cycles*, **20**, 1–11.
- Buschbacher RJ (1986) Tropical deforestation and pasture development. *BioScience*, **36**, 22–28.
- Buso DC, Likens GE, Eaton JS (2000) *Chemistry of precipitation, streamwater, and lake water from the Hubbard Brook Ecosystem Study: a record of sampling protocols and analytical procedures.*

- Gen. Tech. Rep. NE-275, Newtown Square, PA. USDA Forest Service, Northeastern Research Station.
- Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. *Global Biogeochemical Cycles*, **16**, 1121, doi: 10.1029/2002GB001894.
- Conley DJ, Schelske CL, Stoermer EF (1993) Modification of silica biogeochemistry with eutrophication in aquatic systems. *Marine Ecology Progress Series*, **101**, 179–192.
- Dahlgren RA, Driscoll CT (1994) The effects of whole-tree clear-cutting on soil processes at the Hubbard Brook Experimental Forest, New Hampshire, USA. *Plant and Soil*, **158**, 239–262.
- DeMaster DJ (2002) The accumulation and cycling of biogenic silica in the Southern Ocean: revisiting the marine silica budget. *Deep Sea Research Part II: Topical Studies in Oceanography*, **49**, 3155–3167.
- Froelich PN, Blanc V, Mortlock RA, Chillrud SN, Dunstan W, Udomkit A, Peng T-H (1992) River fluxes of dissolved silicate to the ocean were higher during glacials: Ge/Si in diatoms, rivers and oceans. *Paleoceanography*, **7**, 739–767.
- Grady AE, Scanlon TM, Galloway JN (2007) Declines in dissolved silica concentrations in western Virginia streams (1988–2003): Gypsy moth defoliation stimulates diatoms? *Journal of Geophysical Research*, **112**, G01009, doi: 10.1029/2006JG000251.
- Humborg C, Conley DJ, Rahm L, Wulff F, Cociasu A, Ittekkot V (2000) Silica retention in river basins: far-reaching effects on biogeochemistry and aquatic food webs in coastal marine environments. *Ambio*, **29**, 45–50.
- Jensen JE, Cooper SR, Richardson CJ (1999) Calibration of modern pollen along a nutrient gradient in Everglades Water Conservation Area-2A. *Wetlands*, **19**, 675–688.
- Johnson CE, Johnson AH, Huntington TG, Siccama TG (1991) Whole-tree-cutting effects on soil horizons and organic-matter pools. *Soil Science Society of America Journal*, **55**, 497–502.
- Kelly EF, Chadwick OA, Hilinski TE (1998) The effect of plants on mineral weathering. *Biogeochemistry*, **42**, 21–53.
- Likens GE, Bormann FH (1995) *Biogeochemistry of a Forested Ecosystem*, 2nd edn. Springer-Verlag, NY.
- Likens GE, Bormann FH, Johnson NM, Fisher DW, Pierce RS (1970) Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. *Ecological Monographs*, **40**, 23–47.
- Likens GE, Driscoll CT, Buso DC *et al.* (1994) The biogeochemistry of potassium at Hubbard Brook. *Biogeochemistry*, **25**, 61–125.
- Likens GE, Driscoll CT, Buso DC *et al.* (2002) The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry*, **60**, 235–316.
- Pimentel D, Kounang N (1998) Ecology of soil erosion in ecosystems. *Ecosystems*, **1**, 416–426.
- Ragueneau O, Schultes S, Bidle K, Claquin P, Moriceau B (2006) Si and C interactions in the world ocean: importance of ecological processes and implications for the role of diatoms in the biological pump. *Global Biogeochemical Cycles*, **20**, GB4502, doi: 10.1029/2006GB002688.
- Raymo ME, Ruddiman WF, Froelich PN (1988) Influence of late Cenozoic mountain building on ocean geochemical cycles. *Geology*, **16**, 649.
- Saccone L, Conley DJ, Koning E *et al.* (2007) Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. *European Journal of Soil Science*, **58**, 1446–1459.
- Saccone L, Conley DJ, Likens GE, Bailey SW, Buso DC, Johnson CE (2008) Factors that control the range and variability of amorphous silica in soils in the Hubbard Brook Experimental Forest. *Soil Science Society Journal of America*, **72**, in press.
- Sauer D, Saccone L, Conley DJ, Herrmann L, Sommer M (2006) Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry*, **80**, 89–108.
- Schad D (1996) *The biogeochemistry of silicon and sodium at the Hubbard Brook Experimental Forest*. MS thesis, Syracuse University, Syracuse, NY.
- Schelske CL, Stoermer EF, Conley DJ, Robbins JA, Glover R (1983) Early eutrophication in the lower Great Lakes: new evidence from biogenic silica in sediments. *Science*, **222**, 320–322.
- Tréguer P, Nelson DM, van Bennekom AJ, DeMaster DJ, Leynaert A, Quéguiner B (1995) The silica balance in the world ocean: a reestimate. *Science*, **268**, 375–379.
- Turner RE, Rabalais NN (1994) Coastal eutrophication near the Mississippi river delta. *Nature*, **368**, 619–621.
- Vesely J, Majer V, Kopacek J, Safanda J, Norton SA (2005) Increasing silicon concentrations in Bohemian Forest lakes. *Hydrology and Earth System Sciences*, **9**, 699–706.
- Wang X, Burns DA, Yanai RD, Briggs RD, Germain RH (2006) Changes in stream chemistry and nutrient export following a partial harvest in the Catskill Mountains, New York, USA. *Forest Ecology and Management*, **223**, 103–112.
- Watteau F, Villemin G (2001) Ultrastructural study of the biogeochemical cycle of silicon in the soil and litter of a temperate forest. *European Journal of Soil Science*, **52**, 385–396.
- Whittaker RH, Bormann FH, Likens GE, Siccama TG (1974) The Hubbard Brook Ecosystem Study: forest biomass and production. *Ecological Monographs*, **44**, 233–252.