Does elevated CO$_2$ alter silica uptake in trees?

Robinson W. Fulweiler$^{1,2,}$*, Timothy J. Maguire$^2$, Joanna C. Carey$^3$ and Adrien C. Finzi$^2$

1 Department of Earth and the Environment, Boston University, Boston, MA, USA
2 Department of Biology, Boston University, Boston, MA, USA
3 The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA, USA

*Correspondence: Robinson W. Fulweiler, Department of Earth and the Environment, Boston University, 685 Commonwealth Avenue, Boston, MA 02215, USA e-mail: rwf@bu.edu

Human activities have greatly altered global carbon (C) and Nitrogen (N) cycling. In fact, atmospheric concentrations of carbon dioxide (CO$_2$) have increased 40% over the last century and the amount of N cycling in the biosphere has more than doubled. In an effort to understand how plants will respond to continued global CO$_2$ fertilization, long-term free-air CO$_2$ enrichment experiments have been conducted at sites around the globe. Here we examine how atmospheric CO$_2$ enrichment and N fertilization affects the uptake of silicon (Si) in the Duke Forest, North Carolina, a stand dominated by *Pinus taeda* (loblolly pine), and five hardwood species. Specifically, we measured foliar biogenic silica concentrations in five deciduous and one coniferous species across three treatments: CO$_2$ enrichment, N enrichment, and N and CO$_2$ enrichment. We found no consistent trends in foliar Si concentration under elevated CO$_2$, N fertilization, or combined elevated CO$_2$ and N fertilization. However, two-thirds of the tree species studied here have Si foliar concentrations greater than well-known Si accumulators, such as grasses. Based on net primary production values and aboveground Si concentrations in these trees, we calculated forest Si uptake rates under control and elevated CO$_2$ concentrations. Due largely to increased primary production, elevated CO$_2$ enhanced the magnitude of Si uptake between 20 and 26%, likely intensifying the terrestrial silica pump. This uptake of Si by forests has important implications for Si export from terrestrial systems, with the potential to impact C sequestration and higher trophic levels in downstream ecosystems.

Keywords: elevated CO$_2$, silicon, forest Si uptake, terrestrial Si pump, active Si accumulation, Si cycling

INTRODUCTION

We are currently conducting a global experiment by exposing Earth’s biosphere to atmospheric carbon dioxide (CO$_2$) concentrations unseen since the early Miocene, some 23 million years ago (Pearson and Palmer, 2000). From the start of the Industrial Revolution we have increased CO$_2$ concentrations by approximately 40% (Pearson and Palmer, 2000) and in the spring of 2014 CO$_2$ levels officially exceeded 400 ppm at the Mauna Loa Observatory (NOAA, 2014). This grand experiment will continue for the foreseeable future, as over the next century CO$_2$ concentrations are expected to increase further (IPCC, 2013).

The impact of increased CO$_2$ concentrations on the terrestrial biosphere has received much research attention over the last several decades. In particular, recent research has focused on how plants have and will respond to rapid CO$_2$ concentration increases in combination with other regional and global climate changes, including warming air temperature and increased N availability (Norby and Luo, 2004; Ainsworth and Long, 2005; Bernhardt et al., 2006; Finzi et al., 2006). Among numerous other impacts, CO$_2$ enrichment can also alter plant stoichiometry (Loladze, 2002). Exposure to elevated CO$_2$ concentrations can cause declines in leaf nutrients, such as N and phosphorus, as well as trace element concentrations (Taub et al., 2008). The mechanism driving this decline is unclear but it has been attributed to nutrient limitation, increased non-structural carbohydrates, lower transpiration rates, or changes in nutrient allocation patterns (Robernitz and Linder, 1999). A compilation of studies on herbaceous and woody plants found that elevated CO$_2$ concentrations decreased foliar element concentrations by up to 15% (Loladze, 2002). Research on rice, a key global crop, found similar declines in essential elements such as N, magnesium, and iron. Such declines in plant elemental concentrations could have serious repercussions for higher trophic levels, including exacerbation of human malnutrition (Loladze, 2002). A meta-analysis by Cotrufo et al. (1998a) found that aboveground N content declined on average by 14% under high CO$_2$ concentrations. Changes in the N content of litter have also been shown to alter rates of decomposition and thus nutrient cycling within terrestrial ecosystems (Cotrufo et al., 1998b). However, changes in foliar elemental composition could also have large-scale impacts on the cycling and transport of nutrients from land to the sea.

Silicon (Si) is the seventh-most-abundant element in the universe and the second-most abundant element in soils, the mineral substrate for most of terrestrial plant life (Epstein, 1994; Tréguer and De La Rocha, 2013). In the ocean, Si is a key nutrient required for diatoms and is used by many species of sponges, radiolarians, silicoflagellates, choanoflagellates, and even pico-cyanobacteria (Baines et al., 2012). Of particular importance are diatoms, as they form the base of many productive marine food webs and they sequester significant amounts of C to the deep ocean. In fact, a recent modeling effort contributes 50% of global ocean productivity to diatoms (Rousseaux and Gregg, 2013). The
primary source of Si to the ocean is the transport of dissolved and biogenic silica (BSi; SiO_2) via rivers, which together account for 78% of the net annual Si oceanic inputs (Tréguer and De La Rocha, 2013). The Si transported by rivers ultimately comes from the weathering of the lithosphere, which is dependent on complex interactions between climate, geology, and biology (Bluth and Kump, 1994; Conley, 2002; Derry et al., 2005). Recently there has been emphasis on the role of biology in altering the timing and magnitude of Si export, specifically in terms of biological uptake by terrestrial vegetation (Conley, 2002; Fulweiler and Nixon, 2005; Gérard et al., 2008; Carey and Fulweiler, 2013b) and the role of human activities in directly altering watershed Si export (Clymans et al., 2008; Carey and Fulweiler, 2013b). Alternatively, because BSi is 7–20 times more soluble than mineral silicates (Cornelis et al., 2010a), plants may also provide an important source of Si on biological times scales.

Within this context we wanted to determine if trees exposed to elevated CO_2 concentrations would exhibit a decline in foliar Si content like those observed for other elements. To do this, we analyzed BSi concentrations of leaf samples from coniferous and deciduous trees from the Duke free-air CO_2 enrichment (FACE) experiments in North Carolina. Additionally, we examined Si content under nitrogen (N) enrichment, as well as under the combined impact of CO_2 and N enrichment. This is the first study to specifically examine the role of CO_2 and N enrichment on Si content in trees.

This study was conducted on leaves collected from CO_2 and N enrichment experiments that took place between 1996 and 2006. The technical details of these studies have been published previously (e.g., Andrews et al., 2000; Luo et al., 2003; Finzi et al., 2007; McCarthy et al., 2010). Briefly, triplicate 30 m diameter treatment plots were exposed to current +200 ppm of CO_2 above ambient during daylight hours in the growing season. Control plots (n = 3) were treated in a similar manner but with the addition of ambient air instead of CO_2 (McCarthy et al., 2010). In 1998, two of these plots were divided in half and N fertilization began (11.2 g N m\(^{-2}\) y\(^{-1}\) as urea). For more detailed information on the experimental design see http://face.env.duke.edu.

For this analysis we used dried green leaf samples from P. taeda and the five broadleaf species listed above, collected in 2002–2003 and 2006, respectively. P. taeda samples (n = 31) were separated and ground into a powder using a mortar and pestle. The premilled deciduous samples (n = 98) each contained composites of several individuals.

Biogenic Si concentrations were determined using a wet alkaline chemical extraction in a 1% Na_2CO_3 solution (Demaster, 1981; Conley and Schelske, 2001). Duplicate samples were weighed to approximately 30 mg (between 28 and 34 mg) and digested in flat bottomed polyethylene bottles in a shaker bath at 85°C and 100 rpm for four hours. We used a Seal AA3 flow injection autoanalyzer to colorimetrically determine DSI from the BSI aliquots using the molybdnum blue colorimetric method (Strickland and Parsons, 1972). Standards made of sodium hexafluorosilicate (Na_2SiF_6) as well as external standards were used throughout the analysis to check accuracy and were always within 4% of the expected value. We report all BSI values as %Si by dry weight.

All statistical analyses were completed using JMP Pro 10.0 and significance was judged with an alpha of 0.05. BSI concentrations across species and treatments exhibited equal variances according to several commonly used unequal variance tests (O’Brien = 0.6385, Brown-Forsythe = 0.3196, Levene = 0.1978). To explore potential drivers of BSI concentrations we used a linear mixed effects model to address if the BSI concentrations were different across species and treatment alone and combined. In this model we treated station as a random effect to assess the potential random station effects of the block design used at the Duke FACE experiment. We used an ANOVA to further explore differences in BSI concentrations across species and followed it by a post hoc means comparison with Tukey’s test for honestly significant differences (HSD).

RESULTS

Across all sample types and treatments BSI values ranged from 0.05 to 3.01 %Si dry wt., with a median of 0.82 %Si dry wt. and mean of 0.98 %Si dry wt. C. florida exhibited the lowest and least variable BSI concentrations, while U. alata had the highest (Table 1; Figure 1). While some species did exhibit a decline in foliar BSI concentrations under elevated CO_2, we found no statistically significant effect of treatment on foliar BSI concentrations (Table 1). In fact, our least squared model showed no effect of treatments, station, or treatment by species.

Because of the lack of statistical difference in plant BSI concentrations across all experimental treatments, we averaged...
Table 1 | The mean foliar biogenic silica (BSi) concentrations (%Si by dry wt. ± SE) under the three treatment types and the control for five deciduous and one coniferous species at the Duke FACE experimental forest.

| Species                          | Control                  | CO₂ enrichment | N enrichment | N and CO₂ enrichment |
|----------------------------------|--------------------------|----------------|--------------|----------------------|
| Cornus florida (dogwood)         | 0.07 (±0.01)             | 0.07 (±0.01)   | 0.07 (±0.01) | 0.08 (±0.01)         |
| Pinus taeda (loblolly pine)       | 0.97 (±0.07)             | 0.90 (±0.36)   | nm           | nm                   |
| Acer rubra (red bud)             | 0.27 (±0.02)             | 0.19 (±0.00)   | 0.16 (±0.02) | 0.50 (±0.21)         |
| Cercis canadensis (red maple)    | 1.06 (±0.12)             | 0.91 (±0.08)   | 0.98 (±0.19) | 0.94 (±0.06)         |
| Liquidambar styraciflua (sweet gum) | 1.08 (±0.16)           | 0.95 (±0.05)   | 0.72 (±0.03) | 0.92 (±0.11)         |
| Ulmus alata (winged elm)         | 2.36 (±0.16)             | 2.57 (±0.23)   | 2.17 (±0.11) | 1.90 (±0.35)         |

nm = not measured.

BSi concentrations by species. Clear species differences exist (Figure 1), as the majority of species are statistically different from one another (p < 0.0001). The exceptions are that P. taeda, A. rubra, and L. styraciflua are not statistically different from each other, but they are statistically different from C. florida, C. canadensis, and U. alata. U. alata exhibited BSi concentrations statistically higher than all other species (p < 0.0001). In all cases, except for C. and C. canadensis, the mean Si foliar content suggests active accumulation (i.e., %Si above 0.46%; Figure 1).

DISCUSSION

In this study we examined foliar BSi concentrations in five deciduous and one coniferous species across three treatments: CO₂ enrichment, N enrichment, and N and CO₂ enrichment. We expected to see a decrease in Si content as CO₂ increased, compared to the control group, as this phenomenon has been observed for a range of other elements such as N, phosphorus, iron, and zinc (Loladze, 2002). In four species (P. taeda, C. canadensis, A. rubra, L. styraciflua) we did observe a decline in BSi concentrations under elevated CO₂ but none of them were statistically significant (Table 1). The largest decrease of 35% was observed in C. canadensis while the others ranged from 7 to 15%. These declines are on par with those reported for essential elements in other plant species and thus, the lack of significance may simply be due to a limited sample number. In one species, U. alata, we observed a small, non-significant increase in BSi concentrations under CO₂ enrichment (Table 1). We know of only one other study that examined the impact of elevated CO₂ on plant BSi concentrations. In that study of cotton (Gossypium hirsutum L. cv. Deltapine 77), the Si concentrations increased by 26%, although the results were also not significant (Huluka et al., 1994).

We observed a decline in BSi concentrations in N enriched trees compared to the control ranging from 8 to 50%, but none were statistically significant (Table 1). Similarly, no significant differences between BSi concentration in CO₂ enriched vs. N enriched were found for any of the species. The combined impact of N and CO₂ enrichment again exhibited mixed results. For three species (A. rubra, L. styraciflua, U. alata) we observed BSi declines from 12 to 21% and in one species (C. canadensis) we observed an increase of 60% (Table 1). Previous work at this same site found no significant differences in leaf N, phosphorus, C, lignin, or total non-structural carbohydrates under elevated CO₂ (Finzi et al., 2001). This is in contrast to other studies that found decreases in N and increases in C concentrations in other tree species (quaking aspen, Populus tremuloides and paper birch, Betula papyrifera; Lindroth et al., 2001). Elevated CO₂ concentrations also decreased concentrations of N, potassium, phosphorus, and sulfur in Norway spruce (Picea abies L. Karst; Roberntz and Linder, 1999). From these and many other studies, foliar chemistry response to elevated CO₂ and N appears to be site-specific. Additionally, although we did not observe statistically significant effects, the trends we document may be ecologically important. For example, Si provides defense against herbivory and the 15% decline we observed in A. rubra could impact feeding preferences of vertebrate and invertebrate consumers. The lack of significance may be in part driven by our sample numbers.
and thus, a larger study with more data may produce different results.

Silicon uptake by plants is divided into three broad categories (active, passive, or rejective). In active accumulation, plants acquire more Si than they would through water uptake alone. In rejective accumulation, also known as excluder accumulation, Si is taken up at a slower rate than water. Finally, in passive accumulation, water and Si have similar uptake rates (Raven, 1983; Ma et al., 2001b). Plants are assigned one of these categories according to various definitions, a thorough discussion of which is beyond the scope of this paper, but see Carey and Fulweiler (2014) in this Special Issue for a full description. Briefly, previous definitions have been based on Si concentrations in aboveground tissues, on the ratio of Si to calcium, and on the relationship between porewater Si concentration and aboveground tissue Si concentrations (e.g., Jones and Handreck, 1967; Takahashi et al., 1990; Ma et al., 2001a, respectively). More recent work has focused on the presence/absence of Si transporter genes in roots (Lisi and Lisi2) and shoots (Lisi6) of rice (Ma et al., 2008; Yamaji et al., 2008).

Research on accumulation modes in trees is surprisingly lacking. Cornelis et al. (2010b) observed both passive and rejective Si accumulation growth in coniferous tree saplings grown hydroponically. And a decrease in Si concentration with depth was observed in a research. In a typical forest to determine a total Si uptake rate (Figure 2), we observed support the idea that forests are a critical component in regulating the flux of Si from land to the sea.

**DUKE FACE SI UPTAKE**

The impact of elevated CO2, N, and combined elevated CO2 and N led to an approximately 28% increase in net primary production (NPP) at the Duke Face site between 1996 and 2004 (McCarthy et al., 2010). We used the mean NPP over this period to estimate the amount of Si taken up by the Duke forest for the control and elevated CO2 treatments. We focused on the CO2 treatment because we do not have BSi concentrations for the P. taeda under N fertilization or the combined elevated CO2 and N fertilization treatments. Additionally, biomass at this site is dominated by P. taeda, which comprises ~98% of the tree basal area (Finzi et al., 2001). We calculated foliar Si:C ratios by dividing the treatment specific median %Si value of either P. taeda alone or all the species together by 0.47, as C concentrations in biomass are well constrained between 45 and 50%. We then multiplied this Si:C ratio by the known amount of C in each treatment to get a treatment specific Si foliar uptake value (Conley, 2002; Carey and Fulweiler, 2012b). We estimated woody biomass Si uptake using the mean temperate woody biomass %Si of 0.08 (Fulweiler and Nixon, 2005) and again divided by 0.47. We then prorated the amount of Si by the proportion of leaves (30%) versus woody biomass (70%) in a typical forest to determine a total Si uptake rate (Figure 2; Litton et al., 2007). Although we observed a decline in Si concentrations under elevated CO2, the total amount of Si taken up by P. taeda was 26% higher at elevated CO2 where NPP was significantly higher compared to ambient CO2 (control: 194 kmol Si km$^{-2}$, elevated CO2: 251 kmol Si km$^{-2}$). Together with the hardwood species, Si uptake rate was 20% higher in the elevated compared to ambient CO2 treatment, although absolute rates of uptake were higher than P. taeda alone (elevated CO2 = 313 kmol km$^{-2}$ y$^{-1}$; ambient CO2 = 266 kmol Si km$^{-2}$, Figure 2). These values are on the high end of those reported for forested systems but well within the reported range. For example, Gérard et al. (2008) reported 157 kmol Si km$^{-2}$ for a Douglas fir forest in France, while Meunier et al. (1999) reported an uptake of over 3400 kmol Si km$^{-2}$ in a bamboo forest.

A review of FACE experiments found that irrespective of ecosystem type, aboveground production increased in the presence of higher CO2 and trees were more responsive than
herbaceous vegetation (Ward et al., 2013). Other studies have found similar increases in global terrestrial production (Melillo et al., 1993; Nemani et al., 2003). In addition, Pan et al. (2013) found that global forest biomass has increased in established forests. Such changes in primary productivity will also alter Si cycling. In fact, Si accumulating vegetation accounts for 55% of terrestrial NPP (33 Gton C y\(^{-1}\)) an amount similar to the C sequestered by marine diatoms (Carey and Fulweiler, 2012b). This terrestrial Si pump has important implications for global climate, as Si cycling helps to control atmospheric CO\(_2\) concentrations through a variety of mechanisms, including chemical weathering of mineral silicates and C occlusion in soil phytoliths (Berner and Berner, 1997; Parr and Sullivan, 2005). In addition, this vegetation also plays a critical role in modulating the amount and timing of Si export from watersheds to downstream receiving waters (Carey and Fulweiler, 2012a, 2013b), which has direct implications for marine C dynamics. Here, we show that anthropogenically driven enhanced NPP may result in an increase in the terrestrial Si pump as forests take up more Si. In turn, the increased terrestrial Si sink may alter Si availability in aquatic systems. Diatoms require N and Si on a one to one molar basis (Redfield, 1963). Thus, the ratio of N to phosphorus to Si (N:P:Si) helps to control the composition and abundance of phytoplankton species assemblages. Human activities, such as fertilizer use and land use change have increased N and P loading to coastal systems worldwide. Phytoplankton respond to these elevated nutrients by increased productivity. At first, diatoms will bloom until all the Si is consumed at which point other non-Si requiring species will flourish (Anderson et al., 2002).

The enhanced Si uptake by forests under elevated CO\(_2\) may be another way in which humans are altering nutrient stoichiometry in coastal receiving waters. Mising from this discussion is the mechanism driving our findings that CO\(_2\) and/or N additions have no significant impact on Si accumulation in aboveground biomass. Of course, with more data and different study sites we might observe a significant impact of these factors on Si accumulation rates in forest or other terrestrial vegetation types. In fact, a recent study found higher Si concentrations in the porewater, sediment, roots, and occasionally the aboveground biomass of a heavily N enriched salt marsh (Carey and Fulweiler, 2013a). Certainly other factors such as changes in water availability and growing season length, as well as warming temperatures, are all factors that might influence foliar BSi accumulation. Here we propose an alternative idea for exploration: we hypothesize that in ecosystems with altered transpiration rates, corresponding changes to leaf Si concentrations will also be observed because Si is delivered to vegetation via water. Higher transpiration rates should, if passive or active accumulation is occurring, result in higher Si concentration in leaves, as Si is typically concentrated at transpiration termini. Conversely, if transpiration rates decline, then less Si will be deposited. Experimental work on Douglas fir saplings found higher Si concentrations that were attributed to greater transpiration in those seedlings (Cornelis et al., 2010b). However, at the Duke FACE experimental site no changes in transpiration were observed and maybe this is why we observed no significant changes in Si concentration (Ward et al., 2013). Complicating these simple ideas is the original hypothesis that motivated this work – enhanced CO\(_2\) lowers elemental composition of leaves such as N, phosphorus, and potassium. Thus, quantifying the interplay between structural changes in vegetation and transpiration rates, as well as water availability under future climate change scenarios, will be a critical next step in our understanding of climate change impacts on terrestrial Si cycling.

**CONCLUSION**

Our data of BSi concentrations in 6 species from the Duke FACE Experiment does not support our initial hypothesis that elevated CO\(_2\) concentrations would decrease foliar Si content. In fact, we observed no consistent or significant impact of any of the treatments on foliar Si content. However, according to the simplest definition based on aboveground tissue Si concentrations, we did find evidence that four out of the six tree species we studied may be active Si accumulators. These tree species had Si concentrations higher than some of the most well-known Si accumulators (e.g., grasses and sedges). Further, the higher NPP values observed under elevated CO\(_2\) resulted in higher Si uptake rates under elevated CO\(_2\) conditions in the Duke forest. Based on this analysis we hypothesize that anthropogenic change, specifically elevated atmospheric CO\(_2\) concentrations, may increase biological Si pumping in forests, increasing the magnitude of the terrestrial Si pump.

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