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Watershed land use alters riverine silica cycling

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Abstract Recent research has highlighted that humans are perturbing the global silica (Si) cycle through land use change. Here we compare in-stream Si biogeochemistry across four rivers that lie along a gradient of land use change in New England, USA. Differences between basins were most notable during the late winter/early spring period when dissolved Si (DSi) concentrations declined significantly in all but the most urban site. Declines in DSi concentration could not be attributed to volumetric dilution by higher discharges, nor in-stream phytoplankton growth, as biogenic Si concentrations did not increase during this period. We provide evidence that uptake of Si by terrestrial vegetation, specifically trees, is responsible for the observed declines of in-stream DSi concentrations (a loss of 2.7 μM day^{-1} at the most forested site). We hypothesize that sap flow during this late winter/early spring period is driving this accretion. We estimate that 68 kmol Si km^{-2} is accreted annually by New England forests, falling well within the range of forest Si accretion rates found in published studies. This analysis increases our understanding of the mechanisms contributing to altered Si biogeochemistry in rivers draining watersheds with different land use.

Keywords Silica · Rivers · New England · Land use/land cover · Terrestrial vegetation

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Introduction

Human induced changes to the global nitrogen (N) and phosphorus (P) cycle are well documented (Vitousek et al. 1997; Rockstrom et al. 2009). We have altered land use and land cover, burned fossil fuels and biomass, mined P, and learned to fix large amounts of N from the atmosphere (Vitousek et al. 1997; Galloway 1998; Smil 2000; Rockstrom et al. 2009). Combined, our activities have doubled the amount of available N in the biosphere (Galloway et al. 2003) and tripled the amount of P mobilized on earth (Smil 2000). In contrast, until recently we considered the global silica (Si) cycle to be unperturbed by these same activities.

Excess N and P loading to coastal waters is known to cause a series of deleterious effects, including eutrophication and subsequent hypoxia (Diaz 2001; Boesch 2002; Turner et al. 2008). While N and P

concentrations have significantly increased, Si concentrations have not, and thus the ratio of N:P:Si in marine receiving waters has changed. Because marine diatoms, the most dominant type of phytoplankton in temperate coastal waters (De La Rocha et al. 2000), require as much N as silica on a molar basis, these changes to water column nutrient ratios favor non-diatom species of phytoplankton. In turn, such shifts in the phytoplankton community can alter the very base of marine food webs (Anderson et al. 2002; Turner et al. 2008). Besides directly adding nutrients to water bodies, humans have also altered water column nutrient ratios and aquatic trophic structure through dam construction. Known as the 'artificial lake effect' (Van Bennekom and Salomons 1981), the damming of rivers to create reservoirs results in lower DSi concentrations in the downstream receiving waters, as Si becomes trapped behind reservoirs in greater proportions than N and P (Admiraal et al. 1990; Conley et al. 2000; Humborg et al. 2006; Triplett et al. 2008).

Recent research has shown that human activities also directly alter Si cycling through land use/land cover (LULC) change. For example, several centuries of agricultural practices in Europe have led to a soil pool depleted in Si (Struyf et al. 2010; Clymans et al. 2011). A study of the Seine River found urban land cover to be a source of Si to the adjacent river from direct runoff of impervious surfaces and effluent from waste water treatment facilities (Sferratore et al. 2006). Most recently, a study in Southern New England (USA) has found LULC to be strongly correlated with riverine Si behavior, with urban land use significantly positively correlated to DSi fluxes, and forested lands significantly negatively correlated with DSi fluxes (Carey and Fulweiler 2011). In addition, Carey and Fulweiler (2011) found that watershed LULC was as, if not more, important than lithology in predicting Si export from the terrestrial to the aquatic ecosystem at the regional scale.

The influence of LULC on riverine Si export is hypothesized to be due in large part to uptake of Si by terrestrial vegetation (Fulweiler and Nixon 2005; Conley et al. 2008; Carey and Fulweiler 2011). Plants take up DSi and deposit it as 'biogenic' (BSi) or 'amorphous' silica (ASi) (Struyf and Conley 2008). Land plants store BSi as phytoliths, siliceous bodies important for plant protection and function (Epstein 1994). As a result, terrestrial vegetation has been recognized as a major factor influencing the global Si cycle (Conley 2002a). In fact, the same order of magnitude of Si is estimated to be fixed annually by terrestrial plants as is fixed by diatoms in the ocean (Conley 2002b). In addition, it is well known that plants play a major role in both the weathering of mineral silicates and the solubility of Si in soil. The concentration of Si in plant tissues is highly variable (Hodson et al. 2005), but can be equal or greater than several macronutrients, including potassium (K) and N (Epstein 1994). Forests typically have tight Si cycling due to continually recycling BSi between soil and vegetation pools (Alexandre et al. 1997). Thus, when these terrestrial plants are removed and land cover is altered, Si fluxes appear to be altered as well. Several other studies have found terrestrial vegetation can impact in-stream Si concentrations (Fulweiler and Nixon 2005; Conley et al. 2008) and soil solution Si cycling (Derry et al. 2005; Cornelis et al. 2010b).

While there is growing evidence that human activities are directly altering the fluxes of DSi from the terrestrial system, the mechanisms driving this phenomenon are not known. For example, it is still unclear whether urban lands are sources of DSi, or compared to the known Si sink of forested lands, they just export more Si relative to vegetated landscapes. It has been proposed that the lower DSi in forested systems is due to sequestration of DSi by terrestrial plants (Carey and Fulweiler 2011). However, it is unclear whether in-steam autotrophic production was also contributing to the lower DSi found in rivers draining more forested watersheds. Because LULC change is also known to impact the fluxes of other nutrients, particularly dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP), enhanced in-stream phytoplankton production may also be responsible for the altered Si biogeochemistry observed in rivers with different LULC change. Alternatively, urbanization often leads to increased loads of total suspended solids (TSS), increasing light attenuation and thus, decreases in stream phytoplankton production (Van Nieuwenhuyse and LaPerriere 1986; Davies-Colley et al. 1992; Wood and Armitage 1997).

The objective of this paper is to examine the impact of land use/land cover (LULC) on Si fluxes, both particulate (biogenic) and dissolved. In addition, we address possible mechanisms influencing such altered Si biogeochemistry. The watersheds we studied lie

along a gradient of urban to rural land cover, each exhibiting different watershed land use characteristics. Being directly adjacent to one another, these watersheds experience very similar climate and temperature regimes. In order to discern the mechanisms influencing Si biogeochemistry in watersheds characterized by different LULC we collected a high temporal resolution data set of weekly river water samples over an annual cycle for dissolved Si (DSi), biogenic Si (BSi), dissolved inorganic nitrogen (DIN), dissolved inorganic phosphate (DIP), chlorophyll *a* (Chl *a*), and total suspended solids (TSS). Further, this is the first high-temporal resolution dataset of BSi ever collected for a river in New England, which will allow us to make a first-order estimate of the amount of BSi exported from these systems.

Methods

To determine the relationship between land use/land cover (LULC) and Si export we collected a highly resolved annual cycle of Si concentrations and fluxes from four watersheds in Central New England (Massachusetts, USA). The watersheds are located adjacent to one another along a gradient of LULC, from urban Boston to the more forested North Shore of Massachusetts (Fig. 1). Each site was located at a United States Geologic Survey (USGS) real-time stream flow gaging station (Table 1) so that fluxes of material could be calculated. We have named the sites in terms of their location along this gradient, in order of increasing forest cover and decreasing developed land—Urban (Aberjona River), Moderate Urban (Ipswich River at South Middleton), Moderate Forested (Ipswich River at Ipswich), and Forested (Parker River). Each watershed has distinctly different dominant land use types making conclusions about the impact of LULC possible (Table 1). Due to the close proximity of the watersheds to one another, the climate conditions are identical. Geologic differences were previously shown to exhibit little difference in terms of riverine Si behavior compared to watershed LULC in this region (Carey and Fulweiler 2011). In addition, the entire region is covered with glacial till, making most of the weatherable substrate uniform across the study area.

We collected samples weekly over the course of 1 year (October 2010–September 2011) (Fig. 2) and measured dissolved silica (DSi), biogenic silica (BSi), DIN (NO_2^-, NO_3^-, NH_4^+), DIP, Chl *a,* and TSS. From a bridge (or the left bank at the Forested site where no bridge existed) a sampling container was lowered into the thalwag of the river and rinsed three times with site water. The sample was then collected approximately 15 cm below the surface. Previously acid washed polyethylene bottles (30 ml) were used to collect water samples. Bottles were rinsed three times with filtered site water before the final sample was captured. Water was filtered using a 60 ml polypropylene syringe. We filtered water samples for DIN and DIP samples through a 0.45 micron glass fiber filter (Whatman GF/F). We filtered water samples for DSi through a 0.40 micron polycarbonate filter and retained the frozen filter for subsequent analysis of BSi concentrations. BSi concentrations were determined using wet alkaline extraction in 1 % Na_2CO_3 solution, digesting filters for 5 h, with sub-samples taken at hours 3 and 4 to allow for a mineral silicate correction (DeMaster 1981; Conley and Schelske 2002).

A SEAL AA3 flow injection analyzer was used to colorimetrically determine concentrations of dissolved inorganic nutrients. DSi from BSi aliquots and water samples was measured using the molybdenum blue colorimetric method and sodium hexafluorosilicate (Na_2SiF_6) as the silicate standard (Strickland and Parsons 1968). DIN was measured using cadmium reduction followed by colorimetric determination of nitrite and DIP was measured by the ascorbic acid method (Grasshoff 1976).

TSS was measured by filtering 150-250 ml river water onto a pre-combusted (400 °C for 4 h) glass fiber filters (Whatman GF/F) which were placed in a drying oven at 60 °C until dry. We measured Chl *a* by filtering 50 ml of river water onto a glass fiber filters (Whatman GF/F), at which point the filters were immediately frozen and kept in the dark until analysis by fluorescence using a Trilogy Fluorometer by Turner Designs (model # 7200-040) and extracting with acetone (90 %) (Yentsch and Menzel 1963; Arar and Collins 1997).

Two methods were used to estimate an annual DSi and BSi flux from the four sites: a simple average and Beale's unbiased ratio estimator. The simple average

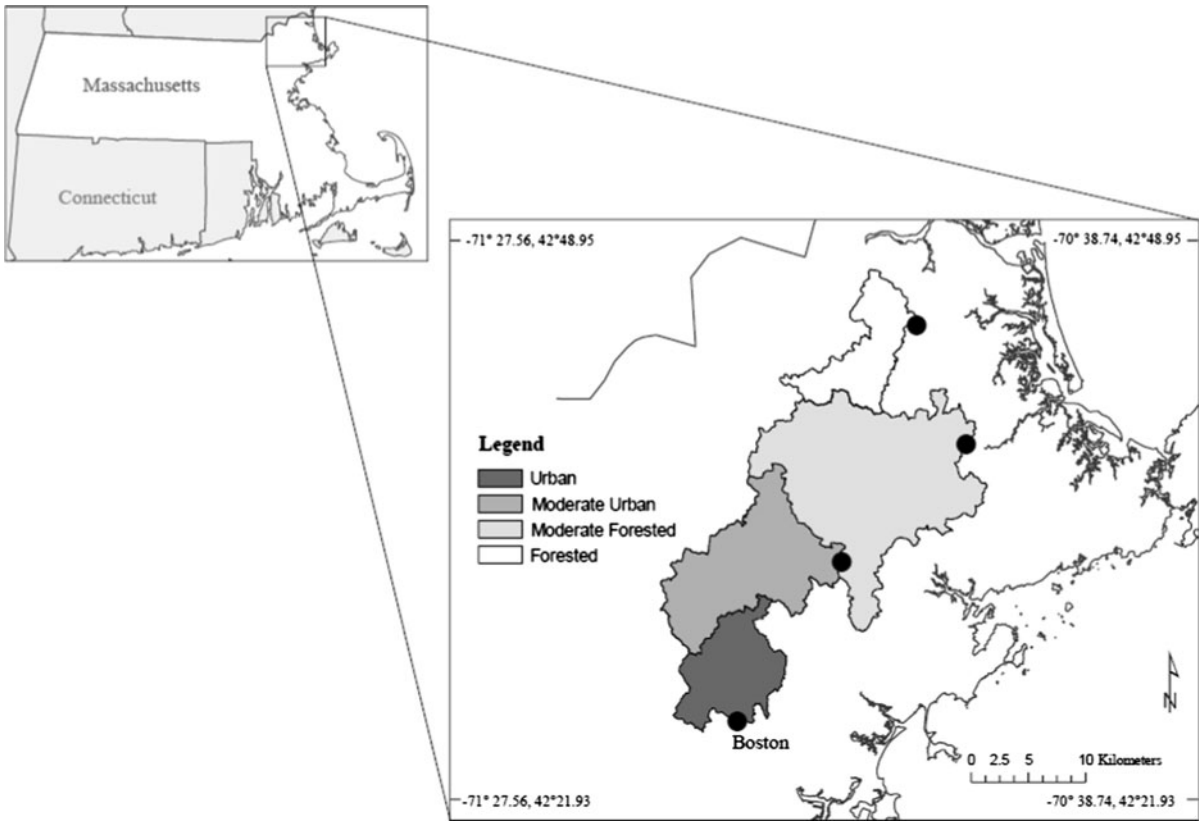

Fig. 1 Map of study sites. *Black dots* indicate sample locations. Watersheds delineated using USGS streamstats software, and other data layers from MA GIS

was done by taking an average of all individual flux measurements (concentration multiplied by the closest recorded 15 min discharge at the time sampled from the USGS flow gage). Beale's ratio estimator multiplies the mean daily discharge for the year by a bias corrected ratio of the mean daily measured fluxes to the mean daily water discharge on days when the fluxes were measured (Beale 1962; Dolan et al. 1981). The Beale's ratio adjusts for biased field sampling which may have missed extreme high or low flows. Beale's estimate is considered a reliable flux estimate if the relationship between discharge and concentration is weak or when the data are not normally distributed (Richards and Holloway 1987; Fulweiler and Nixon 2005). Beale's unbiased estimator is defined as:

$$\tilde{\mu}_y = \mu_X \frac{m_y}{m_x}\left(\frac{1+\frac{1}{n}\frac{S_{xy}}{m_x m_y}}{1+\frac{1}{n}\frac{S_{x^2}}{m_{x^2}}}\right)$$

$$S_{xy} = \frac{1}{(n-1)}\sum_{i=1}^{n} x_i y_i - n m_x m_y$$

$$S_{x^2} = \frac{1}{(n-1)}\sum_{i=1}^{n} x_{i^2} - n m_{x^2}$$

In the above equation, $\tilde{\mu}_y$ is estimated annual flux, $\tilde{\mu}_x$ is the average daily discharge over the entire year, m_y is the mean daily flux on days which concentrations were measured (also equal to the simple average), and m_x is the mean daily discharge for the days sampling occurred. The number of samples is represented by n, while x_i and y_i represent individual concentrations and fluxes, respectively (Dolan et al. 1981). The Beale's ratio estimate was used in our analysis to estimate the total Si flux from the watershed. All other analysis was completed with the individual measurements.

We used several types of analyses to determine how watershed LULC impacts Si biogeochemistry.

Table 1 Land use characteristics of the four sites in this study. All sites located at United Station Geologic Survey (USGS) real-time streamflow gaging stations

Site	USGS ID	Drainage area (km^2)	Elevation (m)	Slope (%)	% Land use (major land use types)								Wetlands
					Open devl	Low intensity devl	Med intensity devl	High intensity devl	All devl	Deciduous forest	Conifer forest	All forest	
Urban	01102500	62	36	4.9	12	20	37	12	81	11	2	13	2
Moderate urban	01101500	115	33	3.0	15	17	14	2	48	18	8	26	18
Moderate forested	01102000	324	32	3.6	10	12	9	1	33	26	11	37	19
Forested	01101000	55	35	4.6	8	6	2	0	17	41	11	51	17

Land use data obtained from the National Land Cover Database (NLCD) 2001, a fifteen-class land cover classification scheme with 30 m. Gradient and slope data obtained from USGS (Zarriello and Socolow 2003)

Devl developed

A Friedman test (Friedman 1939), which is a non-parametric test similar to classical balanced two-way analysis of variance (ANOVA), was used to determine whether the four river sites were behaving differently with respect to water quality constituents, such as DSi, BSi, DIN, DIP, Chl *a*, and TSS. The Friedman test allowed for determining the differences in treatments across sites on our non-normal data. Using the results of the Friedman tests, a multicomparison procedure was used in order to tell which sites had means that were different from each other (see Supplemental Information). In addition, we examined the DSi measurements for relationships with stream temperature and discharge.

We recently developed three multiple linear regression (MLR) models which use combinations of watershed LULC and bedrock geology to estimate DSi fluxes (Carey and Fulweiler 2011). The models are based on long-term (1990–2010) USGS discharge and DSi concentrations from 25 watersheds in New England. In the previous study, we found that LULC alone accounts for 40–70 % of DSi fluxes, while geology alone accounted for 30–55 % of DSi fluxes. The combined LULC_GEOL model accounted for 94 % of the DSi fluxes (see Supplemental Information). In this current study, we used these three models to estimate DSi fluxes with the known LULC and lithological characteristics of our four study sites. We then compared the model estimates to our highly resolved DSi fluxes. Model results were compared to the simple average fluxes, rather than the Beale's estimates, because simple average fluxes from the 25 watersheds were used to create the original MLRs.

In order to further isolate the mechanisms influencing Si biogeochemistry in watersheds with different LULC, we examined the role of terrestrial and aquatic primary production in controlling DSi fluxes. To do this, we focused on the late winter/early spring period (February 13–April 16) when we observed a sharp decline in DSi concentrations at all sites except the Urban River. First, we calculated the slopes and the significance of the spring decline in Si concentrations and compared them across sites. In order to determine whether terrestrial or aquatic primary production was influencing the spring decline in DSi concentrations, the same calculation was completed for concentrations of DIN, DIP, Chl *a*, and BSi during the same period. All statistics were done using Matlab ($\alpha = 0.05$).

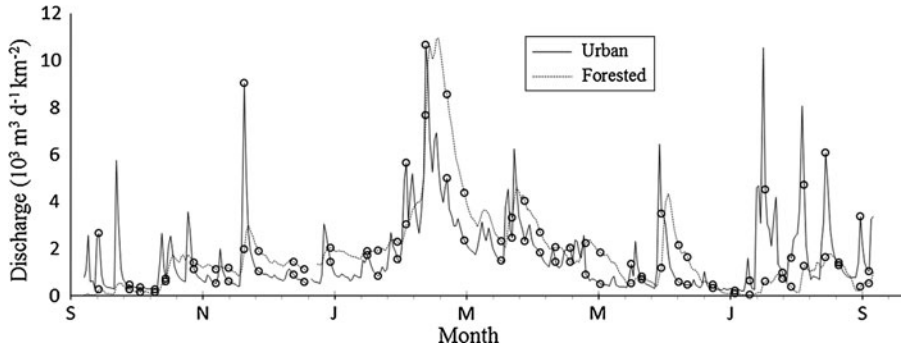

Fig. 2 Annual hydrograph of two end-member sites (urban and forested). *Circles* (o) indicate dates of field sampling. Data from USGS national water information system real-time stream gage network

Results and discussion

Annual water cycle

Discharge during the 2011 water year (October 2010–September 2011) was within 10 % of the long-term (20-year) average median and mean flows at all sites (Table 2). Normalizing discharge for basin size shows no trends towards more or less water at any site (Table 2), making the watersheds comparable once discharge is normalized for drainage area.

We successfully captured a large range of flows that were representative of discharge that occurred during the 2011 year. For example, the range of flows sampled at the Forested site was 0.0022–8.51 × 10^3 m^3 day^{-1} km^{-2}, while the range of flows experienced by the Forested site during the 2011 water year was 0.0186–10.9 × 10^3 m^3 day^{-1} km^{-2}. Field sampling at the Urban site was even closer to capturing the range of flows that occurred in the river throughout the year: sampled discharges ranging from 2.0 × 10^2 to 1.06 × 10^4 m^3 day^{-1} km^{-2} compared to the range of 1.76 × 10^2–1.06 × 10^4 m^3 day^{-1} km^{-2} occurring during all of 2011.

The annual hydrographs reveal the site differences inherent in the river systems. Specifically, discharge over time in the Urban versus Forested sites reveals the typical 'flashy' hydrograph of an urban watershed (Leapold 1968), with higher and earlier peak flows during storm events, and lower base flows compared to the more forested site (Fig. 2). The forested site shows a lag in the timing of peak flow events (Fig. 2) due to longer flowpaths and residence time of water, characteristic of vegetated landscapes.

Silica fluxes across watersheds

Annual fluxes of DSi and BSi were calculated using two methods: a simple average of all flux measurements and Beale's unbiased estimator (Beale 1962; Dolan et al. 1981; Fulweiler and Nixon 2005). Comparing the simple average to the Beale's ratio reveals that the two values are similar for the Moderate Forested and Forested sites (Table 3). Conversely, the simple average DSi flux for the Urban and Moderate Urban Rivers is 41 and 23 % higher, respectively, than the Beale's estimate. The higher simple average values are likely due to field sampling during the

Table 2 Annual water cycle characteristics. The 2011 water year had stream flows within 10 % of the long-term (20 year) average

Site	Long-term record (20 years) (10^3 m^3 day^{-1})		2011 Water year (Oct 2010–Sept 2011) (10^3 m^3 day^{-1})				2011 Water year area-normalized (10^3 m^3 day^{-1} km^{-2})		Percent difference 2011 versus 20-year average	
	Median	Mean	Median	Mean	Min	Max	Median	Mean	Median	Mean
Urban	59.91	95.36	63.57	104.35	11.00	660.18	1.02	1.67	5.94	9.01
Moderate urban	134.24	198.05	145.48	218.96	2.93	1315.47	1.26	1.90	8.04	10.03
Moderate forested	355.03	555.04	343.54	553.91	17.60	3741.03	1.06	1.71	3.29	0.20
Forested	68.46	105.14	75.80	99.20	1.03	601.50	1.37	1.80	10.17	5.82

Table 3 Annual Si fluxes, calculated using the simple average and Beale's unbiased estimator

	Urban	Moderate urban	Moderate forested	Forested
DSi (kmol $year^{-1}$ km^{-2})				
Measured (simple average)	86.5	104.7	79.8	71.8
Beale's ratio estimates	57.2	83.4	72.5	71.8
BSi (kmol $year^{-1}$ km^{-2})				
Measured (simple average)	17.7	11.6	10.1	10.7
Beale's ratio estimates	18.9	13.8	8.8	13.7

higher flows because of the more frequent peaks and the flashy nature of the urban rivers (Fig. 2).

Our DSi flux values (Table 3) fall within the range found in other studies in this region; a 60 % forested watershed in Southern New England reported a DSi export of 50 kmol $year^{-1}$ km^{-2} (Fulweiler and Nixon 2005), and a study on 25 rivers in Central New England found an annual DSi export of 69 kmol $year^{-1}$ km^{-2} (Carey and Fulweiler 2011).

We found a tendency toward lower DSi fluxes from rivers as watershed forest cover increased, and higher DSi fluxes as forest cover decreased. Measured annual DSi fluxes from the Forested site were lower than those at all other sites, although not significantly so (Table 3). There was no trend towards higher or lower BSi fluxes across the LULC gradient (Table 3).

DSi and BSi fluxes were driven by river discharge, rather than concentrations, as depicted by the significant linear relationship between fluxes and discharge ($p < 0.01$) (Fig. 3). This pattern has been found elsewhere in New England rivers (Fulweiler and Nixon 2005) and highlights that river discharge can be a helpful tool for estimating DSi and BSi fluxes. Soils are large reservoirs of BSi (Bartoli 1983), and soil solution and groundwater can be rich in DSi (Cornelis et al. 2010a). It is likely that the significant positive relationship between Si fluxes and discharge is, at least in part, due to Si mobilization from land, where increased over-land water flow mobilizes BSi from the soils, and Si from soil and groundwater.

Modeling DSi fluxes using a multiple linear regression

We compared our measured DSi fluxes from this study to those estimated by our three recently developed multiple linear regression (MLR) models, which use watershed land use land cover (LULC), bedrock geology (GEOL), or the combination of the two (LULC_GEOL) to estimate DSi fluxes (Carey and Fulweiler 2011). We found that the LULC model estimates watershed DSi fluxes within 3.1–50 % of our observed fluxes (Table 4). This type of error was expected, as the LULC model accounted for 40–70 % of observed DSi fluxes in the original analysis (Carey and Fulweiler 2011). Likewise, the GEOL model predicted DSi fluxes within 0.1–36 % of the observed fluxes in this study (Table 4). Again, this type of error was expected given that the GEOL model originally accounted for 35–56 % of observed DSi fluxes (Carey and Fulweiler 2011). Finally, using the best fit model that contains both LULC_GEOL, we found this model estimates DSi fluxes within 0.2–37 % of the measured values (Table 4). Measured DSi fluxes were not consistently lower or higher than the model predictions.

Comparing the precision of the three models across the four different sites, we see that the combined model (LULC_GEOL) is the best fit for the forested site, while the bedrock geology model (GEOL) is the best fit for the Urban site. The better fit of the GEOL model at the Urban site is likely because of the increased importance of lithology in controlling Si fluxes when biology is removed from the watershed.

Unlike the other sites, the precision of all three models was poor for the Moderate Urban river (Table 4), consistently predicted DSi flux 36–50 % lower than our observations. One explanation for this discrepancy between the modeled and measured fluxes could be that wetlands account for almost 20 % of this watershed (Table 1). Wetlands have been shown to directly impact DSi biogeochemistry, often serving as sources of DSi to downstream water bodies (Jacobs et al. 2008; Vieillard et al. 2011). We hypothesize that the large number of wetlands for such an urbanized watershed resulted in abnormal Si biogeochemistry in the Moderate Urban site, compared to the other watersheds used to create the regression models. In

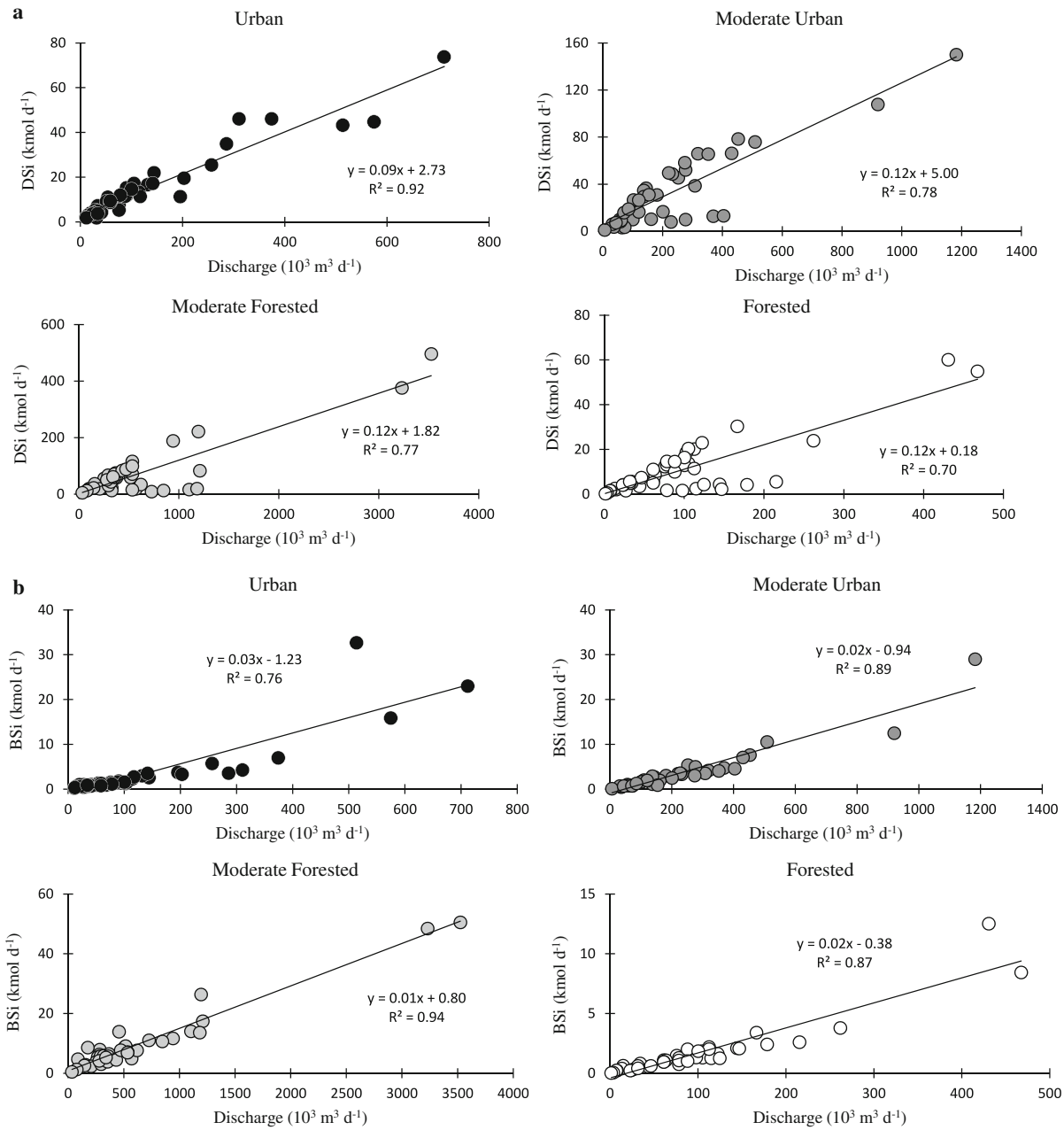

Fig. 3 **a** Daily DSi flux as a function of daily water discharge for each site during 44 days of sampling. **b** BSi flux versus discharge

fact, the average percent of wetlands in watersheds used to create the original models was 7.2 %, less than half the value of the Moderate Urban basin studied here (18 %).

Furthermore, the overall better precision of the models at the more forested sites is likely because the majority of the watersheds used to create this model were on the more forested end of the LULC spectrum (21 of the 25 watersheds used to create the model has at least 30 % forest cover). Therefore, the MLR appears to be more appropriate for predicting DSi fluxes in watersheds with at least 30 % forest cover. While these results indicate the individual LULC and GEOL models predict DSi fluxes reasonably well, the

Table 4 Comparison between measured DSi fluxes and modeled fluxes using multiple linear regression (MLR) model (Carey and Fulweiler 2011). See Supplemental Information for regression equation

Site	Simple avg observed result (mol day^{-1} km^{-2})	Model result (mol day^{-1} km^{-2})			Percent difference model output and observed results		
		LULC_GEOL	LULC	GEOL	LULC_GEOL	LULC	GEOL
Urban	236.9	271.8	271.6	237.1	13.7	13.7	0.1
Moderate urban	286.8	198.2	171.2	198.6	36.5	50.5	36.3
Moderate forested	218.7	198.3	158.8	202.5	9.8	31.7	7.7
Forested	196.7	197.0	190.6	184.0	0.2	3.1	6.7

indices of model goodness of fit (*f* test and correlation coefficient) suggests that including both LULC and lithology characteristics (LULC_GEOL model) is the best method to predict DSi fluxes from a range of watershed types (Carey and Fulweiler 2011).

We also estimated DSi fluxes using the equations developed by Bluth and Kump (1994), which use runoff and dominant bedrock geology as predictor (see Supplemental Data). In each case the fluxes estimated using the Bluth and Kump models were between 1.2 and 1.6 times greater than our measured annual fluxes (Table S1), similar to the results described in Fulweiler and Nixon (2005). Our results indicate that geology and runoff alone may not be the most appropriate metrics to use in estimating DSi fluxes. In addition, this comparison highlights that our recently-developed MLRs do a better job predicting fluxes in New England, compared to global scale models. In sum, while lithology has typically been considered the master driver in Si export from continents to coasts (Bluth and Kump 1994; Jansen et al. 2010), this analysis further highlights that LULC is on par with bedrock geology in controlling river DSi fluxes, especially at the local and regional scale.

Seasonal biogenic silica cycle

This is the first study to collect high temporal resolution (i.e. weekly) BSi measurements in a New England river. We observed no seasonal pattern in BSi concentrations at any site. Our muted BSi seasonal signal at the Moderate Urban, Moderate Forest, and Forested rivers may be due to the nearly 20 % wetland cover in each of these watersheds (Table 1). Previous work has shown that wetlands impact Si biogeochemistry in a similar capacity as dams and impoundments (Hackney et al. 2002). For example, Humborg et al. (2006) found that impounded rivers experienced a muted BSi seasonal signal compared to free-flowing rivers, because dams and reservoirs alter flow regimes and efficiently trap BSi. Alternatively, the lack of seasonal BSi signal at the Urban River may be due to the higher overall in-stream primary production sustained throughout the year at this site, exhibited by the significantly higher average DIN concentrations ($p < 0.01$), and Chl *a* concentrations ($p < 0.01$).

No relationship between BSi concentrations and LULC was observed along the land use gradient. For example, while we observed significantly ($p < 0.01$) higher BSi concentrations at the Urban site (Avg. 21 μM ± 5 μM) compared to all other sites, the Moderate Urban river experienced the lowest BSi concentrations (Avg. 16 ± 5 μM), although not significantly lower than any other site (Table 5). The significantly higher average annual BSi concentrations at the Urban site is likely due to increased nutrient loads which may have stimulated diatom growth throughout the year, reinforced by the fact that average annual Chl *a* concentrations were also significantly higher at the Urban site ($p < 0.01$). In addition, the higher BSi concentrations at the Urban site may be related to the higher concentrations of TSS ($p < 0.01$), as BSi and amorphous Si is often bound to sediment particles (Smis et al. 2011). However, no significant correlation was found between BSi and TSS at any site, indicating that primary production is likely the main cause of the higher BSi concentrations at the Urban site throughout the year.

The minimum BSi concentration measured here was 5.7 μM in the Moderate Urban site, and the maximum BSi concentration was 63.5 μM, found in the Urban site (Table 5). These values fall within the

Table 5 Range of Si concentrations observed at all sites in this study

	Si concentrations			
	Urban	Moderate urban	Moderate forested	Forested
DSi(uM)				
Minimum	54.6	32.5	12.5	14.9
Maximum	208.3	257.7	231.6	207.9
Average	134.8	158.7	138.4	127.1
BSi (uM)				
Minimum	11.9	5.7	8.6	9.6
Maximum	63.5	33.1	53.5	42.6
Average	21.2	15.9	17.7	17.3

range found in other studies. In a study of three rivers draining into the Baltic Sea reported BSi values ranged from nearly zero to 100 μM (Humborg et al. 2006). Similarly, our average BSi concentration (18 ± 2 μM across all sites) falls within the range found in other rivers (e.g., 6 μM in the Daugave River (Humborg et al. 2006), 23 μM in the Rhine River (Admiraal et al. 1990), and the calculated global average of 28 μM (Conley 1997)). Likewise, assessing BSi as a fraction of total Si (DSi + BSi) reveals that our values (11.5 ± 1.8 %) are close to the global average 16 % (Conley 1997).

Seasonal dissolved silica cycle

In-stream DSi concentrations exhibited a distinct seasonal pattern with higher concentrations in the winter and fall and a strong decline in the spring (Fig. 4). This pattern was observed in all sites except the Urban River. The Urban site experienced the most consistent DSi concentrations throughout the year (Avg. 134 ± 38 μM), ranging by only a factor of 3.8. This is a small range compared to the rivers draining the two most forested watersheds, which had DSi concentrations ranging by a factor of 18 (Avg. 138 ± 65 μM) and 14 (Avg. 127 ± 60 μM) in the moderate forested and forested sites, respectively.

Although we did not observe a consistent relationship between watershed LULC and the DSi concentrations, there was a tendency towards higher Si export from the urban watersheds and lower Si export from the more forested watersheds. The Moderate Urban site had the highest average DSi concentrations (Avg. 158 ± 66 μM) ($p < 0.01$) and the forested site exhibited the lowest average DSi concentrations (Avg. 127 ± 60 μM). The minimum DSi concentration (12.5 μM) was observed in the Moderate Forested site while the maximum DSi concentration (257.7 μM) was observed in the Moderate Urban site (Table 5). The world average river DSi concentration is estimated to be 150 μM (Tréguer et al. 1995; Laruelle et al. 2009) and our measured average values (127–159 μM) are very similar (Table 5). Other studies of DSi in temperate river systems found similar DSi values, such as an average of 120 μM in the Connecticut River (Conley 1997) and 136 μM in the Seine River, France (Sferratore et al. 2006).

There are several possible mechanisms that could be driving the observed annual pattern of in-stream DSi concentrations. The increasing DSi concentrations throughout the summer is likely due to BSi regeneration and chemical weathering that occurs with elevated temperatures. The sustained high winter DSi

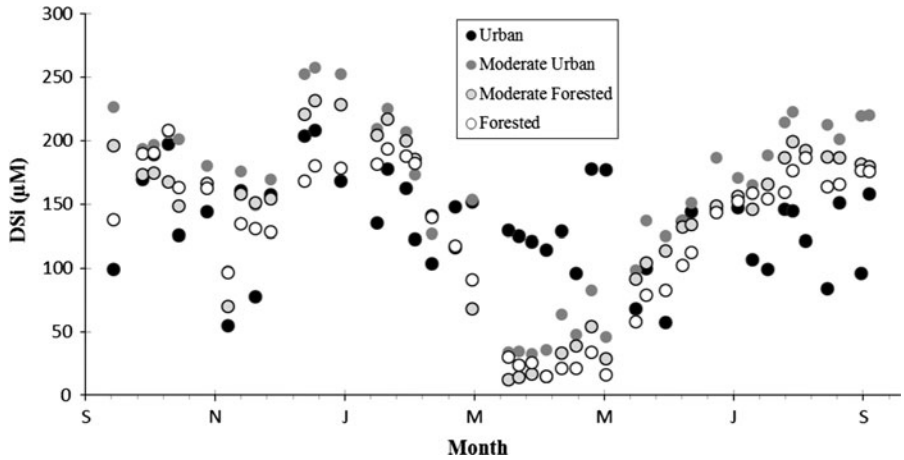

Fig. 4 Annual cycle of DSi concentrations

concentrations are likely due to a lack of DSi uptake by organisms. Finally, the decline in DSi concentrations in the late winter/early spring is typically attributed to in-stream diatom growth and dilution by the spring freshet, both mechanisms we explore here.

A simple volumetric dilution could decrease silica concentrations during the late winter/early spring period if the incoming water was deplete in silica. Given the low concentrations (1.0–6.4 μM) of Si in rainwater (Ladouche et al. 2001; Hofmann et al. 2002; Sferratore et al. 2006), it is possible that the increase of freshwater flow during the spring could dilute the concentrations during this season. If this was the case we would observe a significant decline in concentration as a function of river discharge. However, at all sites except the Urban River, DSi concentrations do not decline with increasing river discharge (Fig. 5). We only observe a significant dilution of DSi concentration with increasing discharge at the urban site ($p = 0.04$, $R = -0.72$) where the spring decline is barely observable. The volumetric dilution occurring at the Urban site is likely a result of the lack of forest cover, reduced infiltration capacity, and increased runoff to the river. This phenomenon has been observed elsewhere: a study of eight rivers draining watersheds with little forest cover (all <30 % forested) in the Scheldt River Basin found significant dilution of DSi concentrations with increasing streamflow (Smis et al. 2011). Moreover, the opposite in-stream behavior is found from more forested watersheds: a river draining a 60 % forested watershed in Southern New England showed no volumetric dilution of DSi with increasing discharge (Fulweiler and Nixon 2005).

Hysteresis patterns of the concentration-discharge relationship during high flow events can be a useful indicator of sources of Si to river systems (Hall 1970; Bowes et al. 2005). Hysteresis illustrates a circular pattern, or 'loop', in plots of concentration versus discharge due to different sources of water at different points on the flood hydrograph (Nagorski et al. 2001; Bowes et al. 2005). Counter-clockwise hysteresis patterns indicate source water more dilute in the rising limb of the hydrograph (Bowes et al. 2005). Consistent with our earlier discussion of a volumetric dilution, we did not see a counter-clockwise pattern. However, during the spring freshet (February 13–April 16), we observed clockwise hysteresis patterns in the two most forested sites (Fig. 6). These clockwise loops suggest that during the spring freshet there is an additional source of water to the river that is rich in DSi (Bowes et al. 2005). It is likely that infiltration of rainwater into the more pervious forested watersheds flushes DSi-rich water into the river during storm events, shown by the clockwise hysteresis loops that indicate a source of DSi-rich water to the river. The size of the hysteresis loops increases with increasing forest cover, indicating increased capacity for DSi storage and subsequent mobilization during rain events in forested watersheds (Bowes et al. 2005). We hypothesize that the source of this rich DSi water is groundwater, since we did not observe this pattern in the more impervious watersheds where streamflow and groundwater are more disconnected (Leapold 1968). In addition, groundwater is known to be rich in Si, often 2–3 times higher than river concentrations (Georg et al. 2009). Considering that groundwater can make up 55–91 % of storm water discharge (Caissie et al. 1996), it seems likely that during the initial portion of the high flow event, Si-rich groundwater is flushed through the more forested watersheds. Thus, it appears that the more forested sites are receiving Si-rich source waters during the period of sharp declines in DSi concentrations, perhaps making the observed decreases in concentrations even greater than they originally appear.

Finally, we explored the relationship between DSi concentrations and stream temperature in order to discern any impact of chemical weathering on the observed DSi behavior during the period of rapid DSi decline. If increased weathering was driving DSi concentrations, we would expect to see a positive relationship between DSi concentrations and temperature (Brady and Carroll 1994; White and Blum 1995). However, as temperatures increase during the spring months, DSi concentrations decline in the river, opposite the pattern one would expect if chemical weathering was driving DSi in the river. In addition, DSi concentrations were not a function of stream temperature at any site. In fact, we observed a distinct pattern between in-stream DSi concentrations and water temperature at all sites except the Urban river (Fig. 7). In both the fall and spring, despite similar stream temperatures, DSi concentrations are markedly different. This pattern is most pronounced at the Forested site where average DSi concentrations are 24 μM in April at 14 °C and 173 μM in October at 11 °C. The rivers draining the more forested

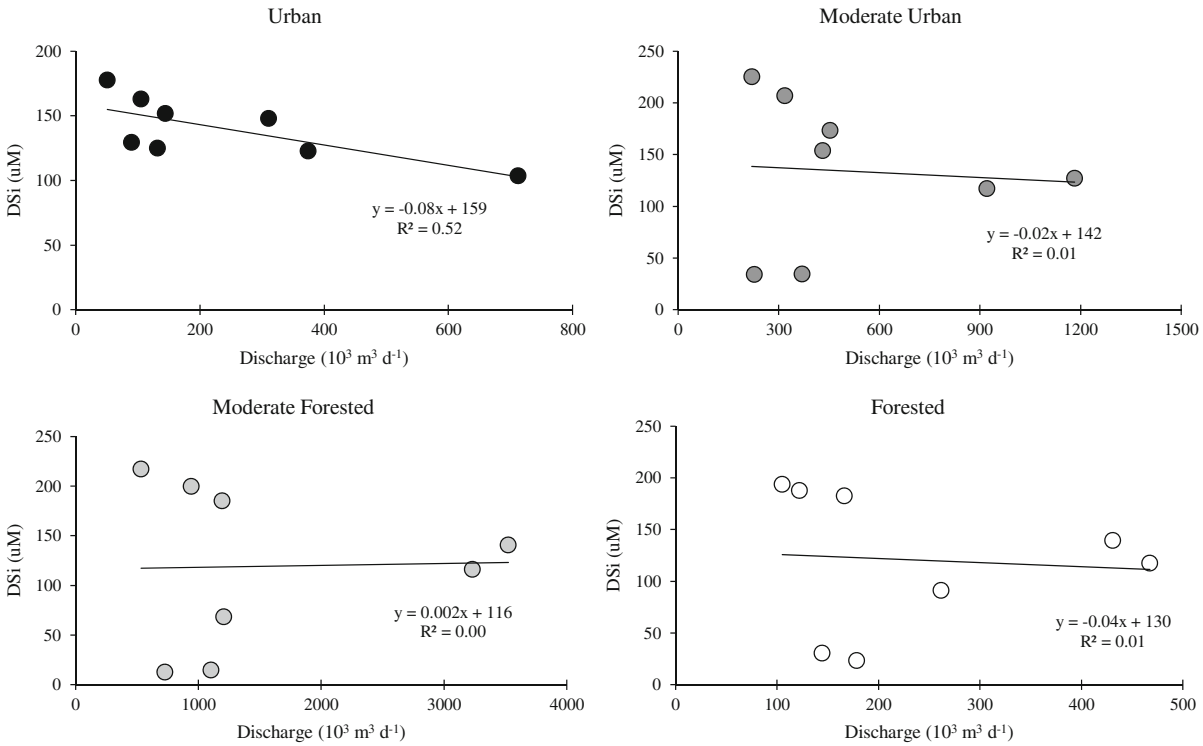

Fig. 5 Lack of volumetric dilution at all but the Urban site during 8 week period of dramatic DSi decline

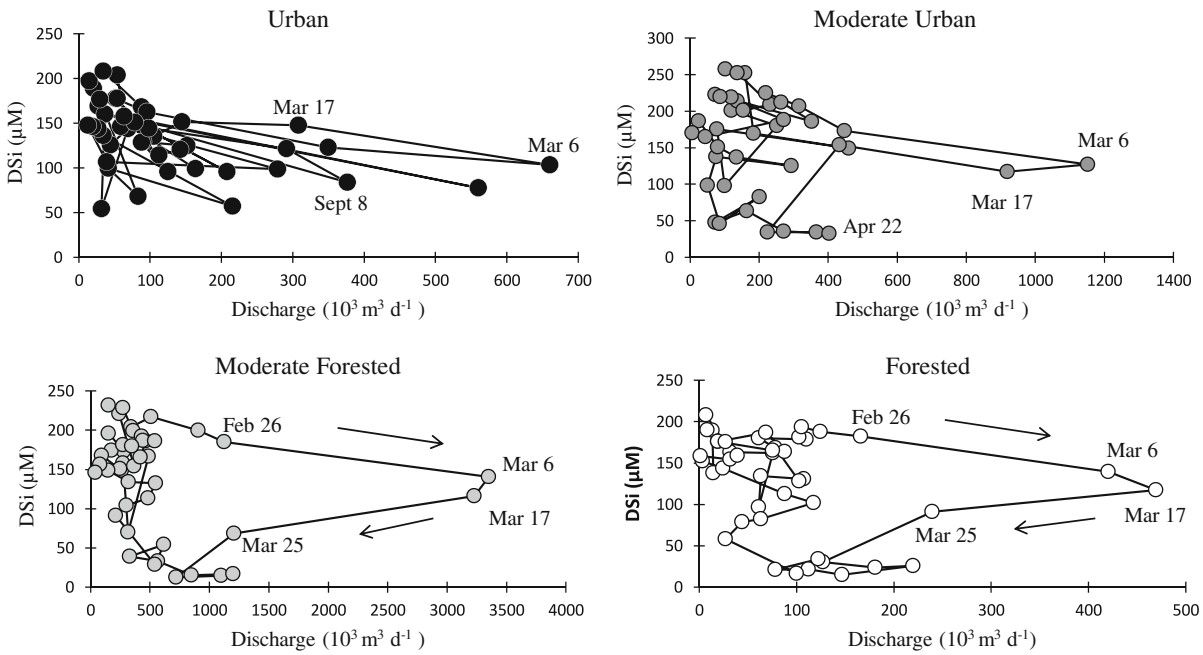

Fig. 6 Hysteresis plots of DSi concentration versus discharge. When followed chronologically, a clockwise pattern, indicating a source of Si-rich water during the rising limb of the hydrograph (Nagorski et al. 2001), is apparent at the two forested sites during the period of active Si drawdown (Feb 13–end of March)

watersheds experienced the largest difference in DSi concentrations at similar temperatures. These patterns are due to the spring drawdown of DSi experienced in all but the Urban site.

Biological uptake

Throughout this study, the clearest differences in Si biogeochemistry between sites were observed in DSi concentrations from February 13 to April 16, where DSi concentrations declined significantly at all but the urban site. We calculated an average loss rate of DSi over the 63 day period of 0.84 and 2.7 μM DSi day^{-1} at the Urban and Forested site, respectively. These values correspond well with the rate of 1.5 μM DSi day^{-1} found in a river draining a nearby 60 % forested southern New England watershed (Fulweiler and Nixon 2005).

In addition, the slopes of change in DSi concentrations over these 8 weeks of late winter/early spring decline were calculated for each site. With increasing percent forest cover, the slope of this decline increased, going from almost no change in DSi concentrations at the urban site, to a highly significant decline in DSi concentrations at the two most forested sites (Table 6). Using a modified analysis of covariance (ANCOVA), the slopes of the decline in DSi concentration were found to be significantly different between sites, with the Urban site having a significantly smaller rate of change compared to the other three sites ($p < 0.01$) (Table 6) (see Supplemental Information). Furthermore, the hysteresis plots of DSi concentrations versus discharge reveal that the more forested watersheds received Si-rich sources of water during this exact period, and thus, the drawdown of Si at these sites may even be stronger than it appears. Given that a volumetric dilution is not the cause of the seasonal decline in Si concentrations, we hypothesize that biology is driving this pattern. Our DIN, DIP, Chl *a* and BSi data provide clues as to the mechanisms influencing the decline in DSi.

Instream primary production

Freshwater aquatic ecosystems are typically limited by DIP availability (Bothwell 1985; Hecky and

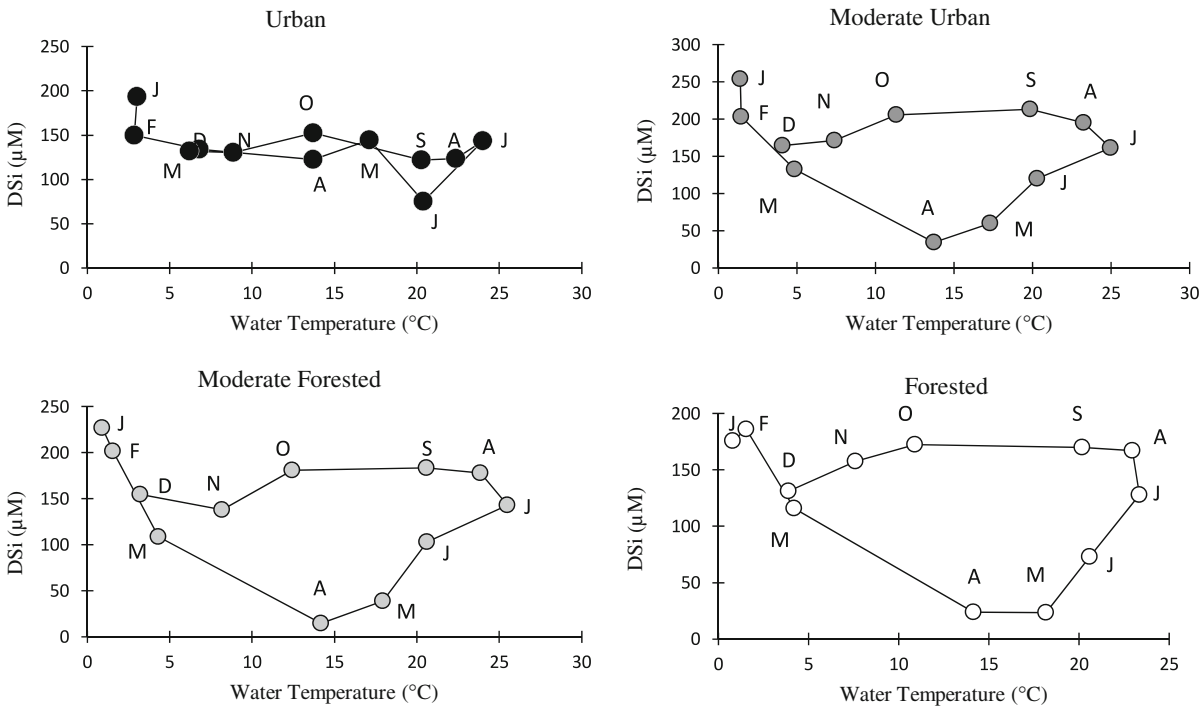

Fig. 7 Average monthly DSi concentrations versus water temperature. The internal diameter of the circle increases with increased percent forest cover, revealing a greater difference in DSi concentrations during months when the water temperature is similar (e.g., spring (April) and fall (October)

Table 6 Slopes, correlations and significance of change in concentrations of DSi (SiO_2) and other indicators of primary production during the period of most rapid DSi decline (February 13–April 16)

	NH_4^{3+}			NO_3^-			DIP (PO_4^{3-})			Chl α			DSi (SiO_2)			BSi ($SiO_2{\cdot}nH_20$)		
	Slope	R	p	Slope	R	p	Slope	R	p	Slope	R	p	Slope	R	p	Slope	R	p
Urban	−0.86	−0.45	0.27	0.14	0.12	0.77	0.00	−0.65	0.08	0.04	0.84	0.01	−0.51	−0.49	0.22	0.03	0.18	0.67
Moderate urban	−0.15	−0.90	0.00	−0.08	−0.12	0.77	0.00	−0.61	0.11	0.01	0.92	0.00	−2.97	−0.93	0.00	−0.03	−0.15	0.72
Moderate forested	−0.08	−0.70	0.05	−0.23	−0.43	0.28	0.00	−0.73	0.04	0.02	0.72	0.04	−3.50	−0.98	0.00	−0.04	−0.24	0.57
Forested	0.15	−0.96	0.00	0.03	0.18	0.67	0.00	−0.75	0.03	0.01	0.74	0.04	−3.00	−0.97	0.00	−0.04	−0.08	0.86

Kilham 1988). Ratios of DIN to DIP over 16:1 indicate P-limitation (Redfield 1958). We observed average ratios of DIN to DIP during the entire year of 1179, 159, 192, 139 in the Urban, moderate Urban, moderate forested and forested sites, respectively. Given these N:P ratios it is likely that in-stream primary production is P limited.

Declines in riverine DSi concentrations are often attributed to in-stream primary production by diatoms (Admiraal et al. 1990; Garnier et al. 1995; Wall et al. 1998). Because our rivers are P-limited, declines in DIP concentrations would indicate in-stream autotrophic production. We examined declines in DIP during the same period of DSi decline in order to determine if in-stream primary productivity was driving the DSi drawdown. Decreases in DIP concentrations were significant in the Moderate Forested ($R = -0.73$, $p = 0.04$) and forested sites ($R = -0.75, p = 0.04$) (Table 6). However, the simultaneous declines in DIP with DSi may not indicate in-stream primary production by diatoms. Unlike DSi concentrations, DIP concentrations decline with increasing river discharge at the two forested sites ($R = -0.40$ and -0.42 at the Moderate Forested and Forested sites, respectively). Thus, the in-stream DIP decline is due, at least in part, to a simple volumetric dilution.

Furthermore, we see no corresponding increase in BSi concentrations during the period of DSi decline (Table 6), indicating the decline in DSi observed at the Moderate Urban, Moderate Forested, and Forested rivers during this 2 month period is not through an increase in diatoms. We do observe a significant increase in Chl *a* concentrations at all sites, possibly indicating non-diatom species bloom (Table 6). This is likely due to the propensity of green algae (Chlorophyceae) to make up river water column phytoplankton species assemblages (Rojo et al. 1994; Descy et al. 2012). Finally, we are hesitant to account for the declines of DSi by in-stream autotrophic production because of how early in the season these declines were observed. While the increases in Chl *a* indicate primary production, this period is typically considered far too early in the growing season to witness a phytoplankton bloom of either diatoms or green algae. Numerous studies of temperate rivers have found little to no in-stream growth until at least May, with peaks in biomass in July and August (Swale 1969; Descy et al. 1987; Rojo et al. 1994; Sin et al. 1999; Descy et al. 2012). These studies are consistent with our observed

peak Chl *a* values occurring much later in the year (May 27, July 28, June 24 and August 11 at the urban, moderate urban, moderate forested and forested sites, respectively).

In addition to changes in DIP, we examined the slope and the significance of the declines in DIN concentrations. While DIN does not change over the 2 month period of DSi decline, NH_4^+ declines significantly at all except the Urban site (Table 6). The in-stream ammonium decline could be driven by several factors, such as phytoplankton uptake or water column nitrification (conversion of NH_4^+ to NO_3^-). However, we see that more NH_4^+ is removed from the system than can be accounted for than through phytoplankton uptake alone. For example, 8.5 μM of NH_4^+ were removed from the water column between February 13 and April 16 at the Forested site. Assuming a ratio close to Redfield for organic matter, we would expect a decline in DIP of roughly 0.53 μM. However, DIP declines only by 0.2 μM during this time, indicating that phytoplankton production may account for some, but certainly not all, of the loss of NH_4^+.

Unfortunately, from our static measurements it is impossible to determine the role of water-column nitrification on regulating NH_4^+ concentrations. At first glance, it appears that nitrification is not occurring due to declines in NO_3^- of 0.01 μM day^{-1}, a trend inconsistent with nitrification. On the other hand, we observe a loss of NH_4^+ at the Forested site (0.14 μM day^{-1}), which falls within the range of summertime river nitrification rates in New England (0.04–1.7 μM NH_4^+ day^{-1}) (Berounsky and Nixon 1993). From our measurements it is not possible to reconcile these conflicting observations, as other instream processes, such as denitrification or algal uptake, could be responsible for these results. Regardless, it appears that the decline in ammonium could be driven at least in part, by terrestrial processes. We hypothesize that processes on land are the primary contributors to the decline in NH_4^+ concentrations.

Terrestrial processes driving DSi concentrations

Most temperate terrestrial ecosystems are nitrogen-limited (Chapin 1980; Brookshire et al. 2012). Trees take up both oxidized and reduced inorganic nitrogen in the forms of nitrate (oxidized) and ammonium (reduced) (Nihlgård 1985). Several studies of temperate forests have found trees with a clear affinity for ammonium over nitrate (Marschner et al. 1991; Gessler et al. 1998); with NH_4^+ uptake rates three to four times higher than nitrate (Marschner et al. 1991). In fact, a study of spruce (*Picea abies*) and beech (*Fagus sylvatica*) trees in Germany found only ammonium uptake and no nitrate uptake during the spring (April and May) (winter not measured) (Gessler et al. 1998). Marschner et al. (1991) calculated that 2.5×10^{-14} mol mm^{-2} s^{-1} NH_4^+ were taken up by spruce (*Picea abies*) at 5 °C. Using the forested area of the Forested watershed (29 km^2), we calculate an ammonium uptake rate of 62.6 kmol day^{-1}. Thus, over the 63 day period of rapid DSi decline, the forested site could potentially take up 3,946 kmol of NH_4^+, which more than accounts for the in-stream loss of 8.5 μM NH_4^+ found at the Forested site over the same period.

Our analysis of ammonium suggests terrestrial vegetation may be influencing in-stream nutrient cycling. We hypothesize that similar processes are impacting in-stream DSi concentrations as well. In order to test our hypothesis that DSi uptake by trees accounts for the decline in riverine DSi concentration, we estimated how much DSi would have been exported from the Forested watershed without the observed late winter/early spring decline. Assuming no spring decline, the average river concentration would be approximately 160 μM. Multiplying this value by the 2011 average annual discharge (99.2×10^3 m^3 day^{-1}), we calculated a theoretical flux of 5,793 kmol $year^{-1}$ at the Forested site. Subtracting our measured DSi flux of 3,832 kmol $year^{-1}$ from this value, we estimate that the forest is accreting 1,961 kmol $year^{-1}$ of Si. Normalizing for the area of forested land in the watershed (29 km^2), we calculate an average forest Si accretion rate of 68 kmol km^{-2} $year^{-1}$. This value falls well within the range of forest Si accretion rates reported by others (26–84 kmol km^{-2} $year^{-1}$) (Bartoli 1983; Markewitz and Richter 1998; Conley 2002a; Fulweiler and Nixon 2005).

Although the decline in DSi concentrations occurs prior to leaf-out, trees are taking up groundwater, and therefore DSi, for sap production during this period. Sap production peaked in Massachusetts forests between January 31 and April 27 during 2011 (USDA 2011), the exact period of DSi decline. Similar to DSi transport, sap is transported through the xylem of the plant. Sap flow is highest when freezing nights are

followed by thawing daytime temperatures (Martin 1958; O'Malley and Milburn 1983; Hacke and Sauter 1996). While there are no known published studies of Si concentrations in sap flow, research on Si in Vermont sugar maples (*Acer saccharum*) found an average DSi concentration in tree sap to be 640 μM (Garvin 2006). Further, average concentrations of DSi in groundwater are between 185 and 1,000 μM (Goudie 1972; Hooper et al. 1990; Hill et al. 1998; Miretzky et al. 2001; Georg et al. 2009), a range matching that of DSi in tree sap. Combining the fact that concentrations in groundwater and tree sap are similar, and that trees take up water and DSi by the same means as sap movement (roots and xylem), it appears likely that sap flow during this period must accumulate DSi as well.

To test if sap flow could account for the in-stream DSi concentration drawdown during this 2 month period we estimated how much DSi trees could accumulate based on water uptake rates and average groundwater DSi concentrations. Rates of water uptake by trees have a large range, from very little (2 l day^{-1} of a suppressed Douglas Fir) (Granier 1987) to 20 l day^{-1} for an apple tree in November (Bar-Yosef et al. 1988) to 600 l day^{-1} for a large sugar maple in the summer (Jackson et al. 2000). We assume an estimate of 56 l H_2O day^{-1}, based on average water intake of a *Picea abies* tree (28 cm diameter at breast height (dbh) at 6.6 °C (Schulze et al. 1985). We also assumed passive Si accumulation and a conservative groundwater DSi concentration of 200 μM (Laruelle 2009). Given these assumptions, a tree could accumulate 11 mM of Si per day. The density of trees on forest land in MA ranges from 15,000 trees km^{-2} (dbh > 28 cm) to 45,000 trees km^{-2} (dbh > 12 cm) (USFS 1999), resulting in a Si accretion rate of 10–32 kmol km^{-2} $year^{-1}$ during the 63 day period of rapid DSi decline. This value is 15–47 % of our estimated annual uptake rate (68 kmol km^{-2} $year^{-1}$), which makes sense considering that DSi uptake by trees should continue throughout the remainder of the growing season. Expanding our estimate over the entire 180-day growing season results in a forest Si accretion rate of 29–91 kmol km^{-2} $year^{-1}$. This range encompasses our estimate of forest Si accretion based on DSi flux values (68 kmol km^{-2} $year^{-1}$) and well within the reported range of forest Si accretion rates. While this is indeed a rough estimate, this analysis highlights the likeliness of terrestrial vegetation in part controlling riverine DSi concentrations.

Considering that water uptake by trees continues into the summer months, one may expect declines in DSi concentrations to persist until fall senescence. In fact, DSi concentrations reach their minimum during May, after which concentrations start to rise. Increasing DSi concentrations throughout the summer is a common pattern in rivers (Admiraal et al. 1990; Fulweiler and Nixon 2005; Triplett et al. 2008), which occurs when sources are greater than the sinks. Sources of DSi during the warm summer months include the remineralization of BSi and chemical weathering of mineral silicates. Both processes are directly related to temperature. Once water temperatures reach 15 °C, BSi dissolution exponentially increases (Yamada and D'Elia 1984). In our case, average monthly water temperatures were below 15 °C until May, at which point they increased reaching their maximum (23–26 °C) in July. While a portion of weathering occurs within the river itself, it is also associated with groundwater-rock interaction. Albeit more thermally buffered than river water temperatures, groundwater also experiences increased temperatures during the summer, especially in the shallow portions closer to the surface (Taniguchi 1993). For example, groundwater one meter below the surface of a temperate wetland varied roughly 15 °C over the annual cycle (Bravo et al. 2002). In addition, plant growth in the summer also stimulates higher weathering rates through alteration of soil pH and exudation of organic acids (Lucas 2001). Consequently, while plants may still be taking up DSi during the summer, declines in DSi concentrations do not persist through the summer likely due to an influx of DSi from BSi remineralization and mineral silicates weathering. The significant declines in DSi that increase with percent forest cover, combined with the lack of increase in river BSi concentrations, provides evidence that terrestrial vegetation (1) may be causing the observed decline in DSi concentrations and (2) can be a stronger influence than in-stream diatoms at controlling DSi concentrations in rivers. Our results augment the hypothesis that terrestrial vegetation controls DSi behavior in rivers, as proposed originally by Fulweiler and Nixon (2005) and highlight how human activities through land use change may be directly perturbing the global Si cycle.

Conclusion

Southern and Central New England experienced major land use changes throughout the last four centuries, characterized by widespread deforestation during the colonial period ($\sim$1650–1800), followed by reforestation as agriculture moved westward (1850–1940), and finally followed by major urbanization and suburbanization (1940–present). Therefore, this study mostly considers the impact of urbanization on Si export, rather than agricultural land uses, as only a small percentage of the study area is currently used for agriculture.

Previous research in the same region has shown urban watersheds to export significantly more DSi than their forested counterparts (Carey and Fulweiler 2011). Here we sought to determine the mechanisms for this difference by comparing in-stream Si biogeochemistry across four rivers that lie along a gradient of land use change. We found the most notable differences in Si cycling between rivers occurred during the late winter/early spring period when rivers draining more vegetated watersheds resulted in higher rates of DSi decline. We hypothesize that the differences between Si export and LULC is due to both hydrology and biology. We provide evidence that by altering the connection between surface and groundwater, in addition to removing the known Si sink of vegetation, urban systems export more DSi than forested systems. Nevertheless, any increase in DSi that occurs through urbanization will likely not offset any of well-known problems associated with DSi-limitation in coastal waters, as export of N increases as well.

Our finding of a lack of impact of LULC on riverine BSi concentrations and fluxes deserves further analysis, considering that the BSi fraction in these rivers is not insignificant (roughly 11 % of total Si loads in our study sites). Higher resolution data and additional field sites may provide more clues as to how the BSi cycle reacts to changes in basin LULC.

The comparison of our measured (simple average) DSi fluxes to a multiple linear regression model (MLR) shows that knowledge of watershed bedrock geology and LULC is all that is needed to predict DSi river export to a reasonably accurate degree (within 2–10 %) in watersheds with at least 30 % forest cover. Future work should test the model predictions with measured DSi fluxes from watersheds in other regions, especially those with different bedrock geology.

Rivers are the central transport mechanism of Si from land to sea. Approximately 82 % of dissolved, biologically available Si in marine ecosystems comes from rivers (Tréguer et al. 1995) and are therefore, appropriate ecosystems to study in order to understand Si biogeochemistry. Given the importance of Si in both aquatic and terrestrial ecosystems, and the degree of land use change ongoing globally, researching the relationship between LULC and Si cycling is critical to understanding how anthropogenic activities influence Si biogeochemistry. Land use change in the form of conversion of forests to agricultural and urban land uses, has greatly altered the global cycling of carbon (C), nitrogen (N), and phosphorus (P). It should now be recognized that land use change also impacts global Si cycling as well.

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