Biogeochemistry (2005) 74: 115–130
DOI 10.1007/s10533-004-2947-z
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Terrestrial vegetation and the seasonal cycle of dissolved silica in a southern New England coastal river

ROBINSON W. FULWEILER[1,*] and SCOTT W. NIXON[2]
[1]*Graduate School of Oceanography, University of Rhode Island, Narragansett, 02882-1197, USA;* [2]*Graduate School of Oceanography, University of Rhode Island, Narragansett, 02882, USA; *Author for correspondence (phone: +1-401-874-6633; fax: +1-401-874-6207; e-mail: wally@gso.uri.edu)*

Received 11 June 2004; revised in accepted form 6 September 2004

Key words: Little Narragansett Bay, dissolved silica river fluxes, seasonal cycles, watershed export, forest uptake

Abstract. The Pawcatuck river watershed (797 km^2) is located in southern Rhode Island and northeastern Connecticut. The predominant lithology of the area is granite, and over 60% of the watershed remains forested with mixed hardwoods (primarily oak) and eastern white pine. As part of a larger study of nutrient and sediment exports from the watershed to Little Narragansett Bay, we measured dissolved silica (SiO_2) (DSi) concentrations at the river mouth over 70 times between January 14, 2002 and November 29, 2002. Annual export of DSi during our study was 40×10^6 mol or 50 kmol km^{-2}. The United States Geological Survey (USGS) obtained DSi concentrations at this site, at varying frequencies, from 1978 to the present, which allowed for a historical comparison of this study with previous years. River DSi concentrations exhibited a strong seasonal signal that did not vary in a regular way with water discharge or water temperature. DSi and dissolved inorganic nitrogen (DIN) concentrations were significantly related over the annual cycle ($p < 0.0001$) and both decreased substantially during the spring. Dissolved inorganic phosphorus (DIP) did not covary at any time with silica or nitrogen, suggesting that in-stream biological uptake was not responsible for the seasonal decline in silica. The spring decline in river silica concentrations may be due to silica uptake by terrestrial vegetation. We estimate a net forest silica accretion rate of 41 kmol km^{-2} y^{-1}, a value that is stoichiometrically consistent with other measurements of net carbon accretion in nearby forests.

Introduction

Dissolved silica (DSi) concentrations in rivers are a product of chemical weathering, the interaction of the hydrological cycle with soils, and biological uptake and dissolution on land and in surface waters (Derry et al. 2001; Conley 2002). Weathering rates are determined through complex interactions of climate (Bluth and Kump 1994; White and Blum 1995), geology (Bluth and Kump 1994), and biology (Berner 1992; Hinsinger et al. 2001; Conley 2002). Lately, emphasis has been placed on the cycle of DSi between soils and terrestrial vegetation. Alexandre et al. (1997) found that in an equatorial rainforest the dissolution of silica from phytoliths, the opaline silica components in plants, was about twice the rate of silica release from weathering reactions in the ecosystem. More recently, Conley (2002) reported that the flux of silica in river waters is significantly modified by the terrestrial biogeochemical silica cycle, and that the current weathering rate models may therefore not yield accurate silica export predictions for forested watersheds.

The purpose of this paper is to report a highly resolved annual cycle (1/14/02–11/29/02) of DSi concentrations in, and an annual DSi flux from, the Pawcatuck Watershed in southern Rhode Island. DSi concentrations were measured on more than 70 occasions and an annual flux of silica was determined using various statistical techniques. We also examine the effects of temperature, precipitation, dam obstructions, and terrestrial vegetation on the observed silica concentrations and fluxes.

Methods

Site description

Two main drainage systems, the Wood River and the Pawcatuck River, form the Pawcatuck watershed. While most of the 797 km^2 area is in Rhode Island, 20% of it extends into neighboring Connecticut. The Pawcatuck River (47 km) runs east to west and then southwest to the Pawcatuck River estuary and Little Narragansett Bay. The Wood River (29 km), considered the most unpolluted in Rhode Island, runs from north to south and meets the Pawcatuck River at Wood River Junction (Figure 1) (Wood Pawcatuck Watershed Association 2003). The watershed contains 15 km^2 of ponds and lakes and approximately 60 tributaries. Streams are first and second order, softwater, and humic laden (Burkholder and Sheath 1985; Rosenblatt 2000). Average annual precipitation in the Pawcatuck watershed amounts to 1.2 m and the Pawcatuck River 60 years mean daily discharge is 1.46×10^6 m^3 d^{-1}. Historically, the Wood and Pawcatuck Rivers supported 24 small dams, but only 15 remain, including six constructed before 1900 [Rhode Island Department of Environmental Management (RIDEM 2003)]. Together these dams increase the mean annual residence time of the Wood and Pawcatuck Rivers by approximately four days (Fulweiler 2003). Bedrock in the Pawcatuck Watershed is predominantly granite with vitreous quartzite, quartz mica schist, and pink and gray-layered gneisses (Ehinger et al. 1978; Hermes et al. 1994). Soils are approximately 55% glacial till, 30% glacial outwash, and 10% organic and alluvial (Rosenblatt et al. 2001). Rosenblatt et al. (2001) report that Inceptisols, Histosols, and Entisols are the predominant soil orders within the watershed. Over 60% of the watershed remains forested with mixed oak hardwoods (mainly *Quercus rubra* and eastern white pine (*Pinus strobus*). Agriculture accounts for about 8% of the total land use and is mostly dedicated to turf production (Table 1). Approximately 18% of the area is urban, though the watershed as a whole is not densely populated (70 people km^{-2}). The watershed's most densely

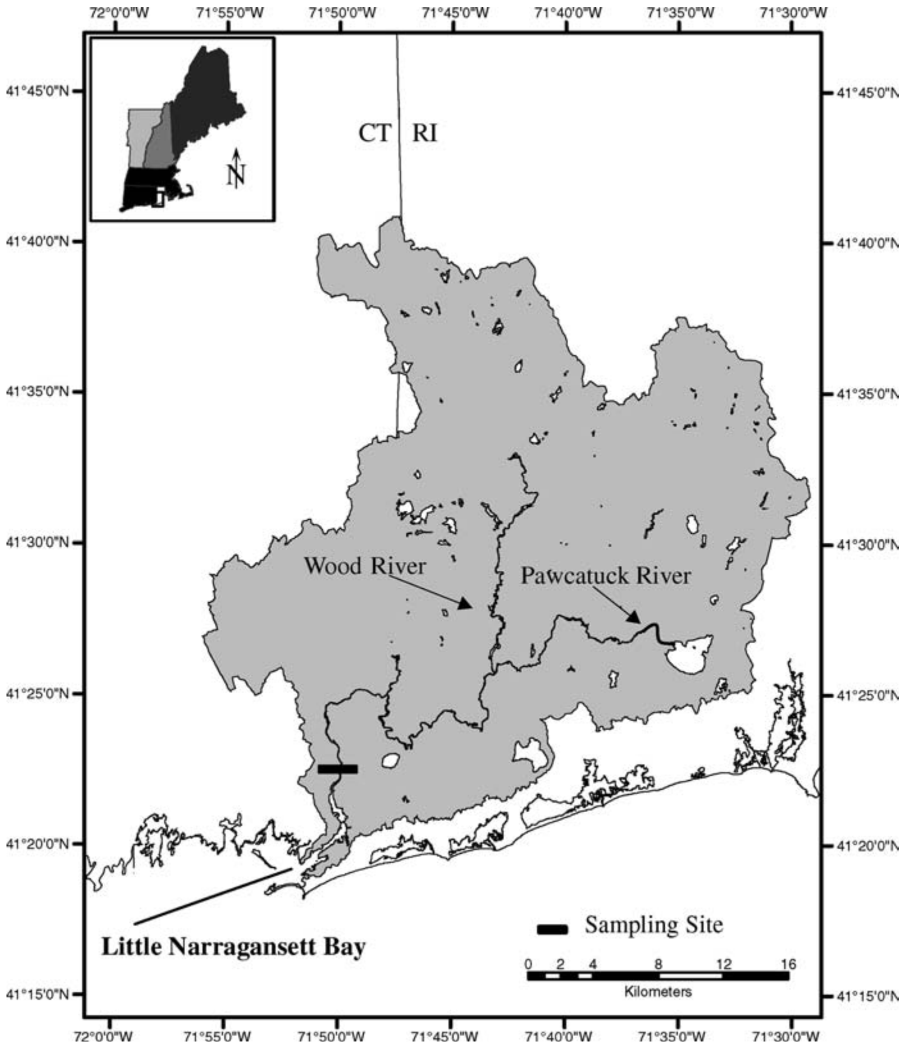

Figure 1. Location of the Pawcatuck watershed. The bar marks the water sampling site used in this study and USGS water discharge gage (41°23′01″; 71°50′01″) in Westerly, Rhode Island. Cartographic data were obtained from the Rhode Island Geographic Information Systems (RIGIS).

populated area is below our sampling site in Westerly, Rhode Island with a population of 23,000 (240 people km^{-2}).

Field sampling

Located in Westerly, Rhode Island, the Stillmanville blockage is the last dam before the Pawcatuck River meets tidal intrusion. We collected water samples

Table 1. Pawcatuck River and watershed characteristics.

River	
Length	47 km
Drainage Basin	797 km^2
Mean Daily Discharge (1941–2001)[1]	1.46×106 m^3 d^{-1}
Mean Study Discharge (11/01–12/1/02)	0.83×106 m^3 d^{-1}
Watershed land use (%)	
Agriculture[2]	8
Urban[3]	18
Forest[2]	61
Wetland[2]	13

[1]At USGS gauge number 01118500, Westerly, Rhode Island.
[2]Rhode Island Geographic Information Systems 2003.
[3]Population density determined for the Rhode Island portion of the watershed only by MANAGE (Kellog et al. 2000).

at this site from January 14, 2002 to November 29, 2002 over a wide hydrographic range (Figure 2). Approximately 70 m below this site the United States Geological Survey (USGS) has been measuring water discharge since 1941. Discharge is determined from stage height every 15 min. The gauged area (764 km^2) accounts for 95% of the total watershed area.

Facing upstream, water samples were collected using polyethylene bottles (500 ml) that had been rinsed and leached with deionized water. Each bottle was rinsed with river water three times before the final sample was taken and stored on ice for later processing in the laboratory (< 3 h). DSi samples were filtered using a 60 ml polypropylene syringe and 0.45 μm membrane filters. The filtrate was collected in 60 ml acid washed and deionized water-leached polyethylene bottles and stored in the dark at room temperature until analysis. No laboratory glassware was used in the collection, storage, or analysis of the samples.

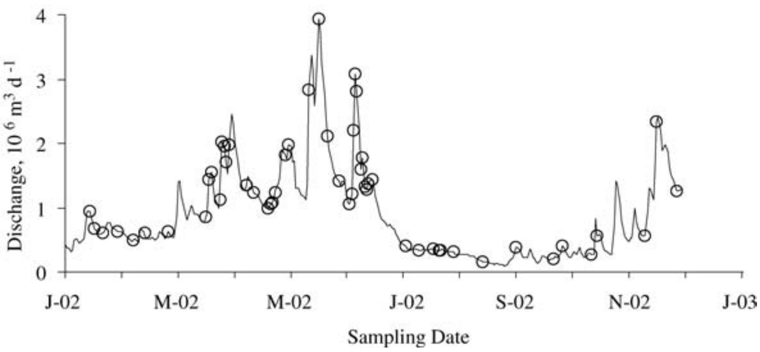

Figure 2. Mean daily water discharge for the study period (1/14/02–11/29/02) at Westerly, Rhode Island. Open circles represent days in which water samples were taken for analysis of DSi and other nutrients. USGS flow data were obtained at 15 min intervals and averaged over 24 h periods.

Analytical methods

A Lachat Instrument QuikChem 8000 flow injection analyzer was used to colorimetrically determine concentrations of dissolved silica (SiO_2) (Parsons et al. 1984; Lachat QuikChem methods 2000). According to Dietzel (2000) silica polymers persist in acidic waters (> 1 year) and could interfere with silica analysis. However, the Pawcatuck River mean pH level of 6.9 ($\pm$0.43 standard deviation) allows for rapid (~30 min) depolymerization of silica molecules and thus silica polymers should not be a factor in our analysis. Sodium hexafluorosilicate (Na_2SiF_6), dried overnight (110 °C) and cooled in a vacuum dessicator, was used for the silicate standard (Strickland and Parsons 1968). We also checked this standard against a performance evaluation sample from Ocean Scientific International. The Ocean Scientific International sample was made from a sodium hexafluorosilicate standard as described above and checked against a fused silicate standard. Ocean Scientific International found that their hexafluorosilicate standard matched their fused silica standard within 0.4–0.8%. The performance evaluation standard we analyzed was a 400 μM solution for which we obtained an average of 400 $\pm$ 16 μM.

Data analysis

We used four methods to estimate an annual DSi flux from the Pawcatuck River: simple averaging, a geometric mean regression, a log-linear regression, and Beale's unbiased ratio estimator. The simplest technique, the average, is the mean daily DSi concentration multiplied by the mean daily water discharge (Bierman et al. 1988). When applied strictly, the regression estimate requires that the data be normally distributed (Jacquez and Norusis 1973; Zar 1999). Because neither silica concentration nor flux data were normally distributed, a log-transformation was applied to the raw data (Preston et al. 1989). All of the log-transformed data were normal according to the Shapiro-Wilk test ($p > 0.05$). The log-transformed data were then used to compute both the log-linear regression and geometric mean regressions. A geometric mean functional regression was used because the independent variable, water discharge, was subject to error (Ricker 1973). Beale's ratio estimate 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). Beale's ratio estimator is defined as:

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

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

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

where $\tilde{\mu}_y$ is equal to the estimated load, $\tilde{\mu}_x$ is mean daily discharge over an annual cycle, m_y is the mean daily loading for days on which concentrations were determined, m_x is the mean daily discharge for those days on which concentrations were determined, and n is equal to the number of days on which concentrations were determined. Individual measured flows and concentrations are represented by x_i and y_i, respectively (Dolan et al. 1981). Beale's ratio estimate has proven to be highly reliable and is recommended if the relationship between discharge and concentration is weak, if the data are skewed, and if the data are not normally distributed (Richards and Holloway 1987; Richards 1999). Data are available upon request to the first author.

Results and discussion

Seasonal water cycle

Although this study was conducted during a severe drought, we sampled a wide range ($0.09–3.93 \times 10^6$ m^3 d^{-1}) of water discharges (Figure 2). The mean daily water discharge observed during this study (0.83×10^6 m^3 d^{-1}) was only 40% of the 60 years mean daily discharge (1.46×10^6 m^3 d^{-1}). Historically, the Pawcatuck River has exhibited highest discharge in March and April and lowest discharge in September. During this sampling period, however, maximum daily discharges, averaged over monthly intervals, occurred in May and June.

Silica flux

Daily DSi flux exhibited a strong positive relationship with increasing water discharge (R^2 = 0.90) (Figure 3). Each of the four estimation techniques we used, except the simple average, gave comparable annual DSi fluxes (Table 2). The consistency of these techniques may be due to the large sample size of the study. The use of a simple average of measured concentrations and mean daily water discharge did not provide a reliable estimate of annual flux even with a large data set. Unfortunately, this approach is common in the literature (e.g. Ohowa et al. 1997; Prego and Vergara 1998; Justic et al. 2003). Throughout the

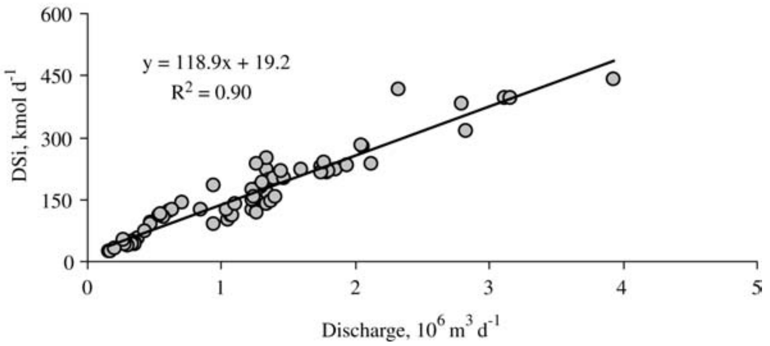

Figure 3. Daily DSi flux as a function of daily water discharge from the Pawcatuck River during 2002.

Table 2. Pawcatuck River annual DSi flux estimate calculated using various techniques (see text).

	10^6 mol y^{-1}
Simple average	76.8
Beals's ratio estimate	39.9
Log-linear regression[1]	40.8
Geometric mean regression[2]	40.8

[1]Based on log-linear flux regression, $0.89x + 2.13$, $R^2 = 0.92$.
[2]Based on geometric flux regression, $0.92x + 2.13$, $R^2 = 0.92$.

remainder of this paper, we use the annual flux of 40×10^6 mol yr^{-1} calculated by Beale's ratio. This is equivalent to an export of 50 kmol DSi km^{-2} y^{-1} from the watershed.

Seasonal cycle of silica

Dissolved silica concentrations varied by a factor of two over the annual cycle, with a minimum of about 90 μM in late spring and early summer and a maximum of about 200 μM during winter (Figure 4). The decline is not a product of the drought because the historical USGS record also shows an annual spring decline. At first this was surprising, since it might be assumed that seasonal warming would increase the dissolution of silica (White and Blum 1995; Schlesinger 1997). The USGS measures water temperature continuously in another Rhode Island river, the Ponganset, 64 km North of our sampling site. Mean monthly DSi concentrations in the Pawcatuck and mean monthly water temperature in the Ponaganset displayed only a weak inverse correlation ($R^2 = 0.33$). Moreover, when mean monthly DSi concentrations are plotted as a function of water temperature, it is clear that concentrations are lower during spring than they are during fall at equivalent water

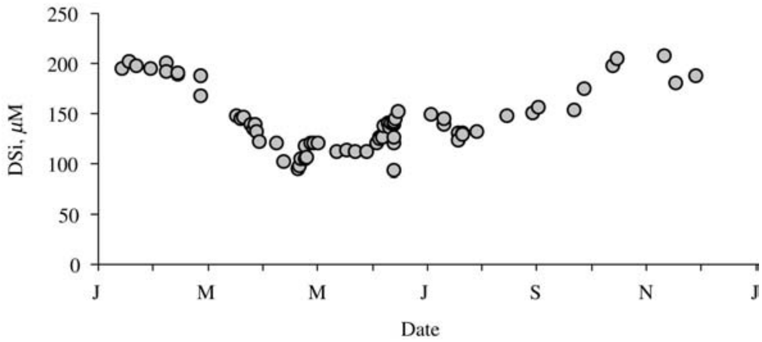

Figure 4. Dissolved silica concentration as a function of time for the study sampling period (1/14/02–11/29/02) at the Stillmanville dam in Westerly, Rhode Island.

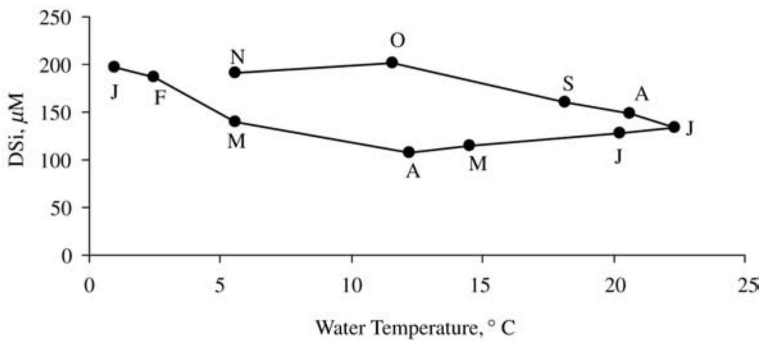

Figure 5. Dissolved silica concentration at the mouth of the Pawcatuck River during 2002 as a function of water temperature measured by the Ponaganset River, 60 km North.

temperatures (Figure 5). For example, the lowest monthly average DSi concentration and the highest occurred at approximately 12 °C (108 μM in April and 201 μM in October).

With a simple volumetric dilution excluded, it is still possible that the spring DSi decline might reflect dilution of older, more silica rich groundwater by rainwater which is not a significant source of silica. Hysteresis patterns can be used to determine which geochemically distinct sources in a watershed dominate streamflow at a particular time (Nagorski et al. 2001). Clockwise loops in chronological plots of DSi concentration verse water discharge would show that DSi concentrations are higher during the rising limb of the hydrograph than during the fall and suggest that water sources with higher constituent concentrations dominate streamflow during increased periods of discharge. Counterclockwise loops may suggest that dilution by water with less DSi is occurring. The width of each loop reflects the concentration difference between each water source (Nagorski et al. 2001). Neither of these patterns is found in the Pawcatuck River data leading us to exclude changing water sources as well as simple volumetric dilution as explanations for the spring DSi decline. We are left to conclude that biological uptake, either in the river or on land, is providing the spring-summer decline of in-stream DSi concentrations.

Few studies have reported detailed seasonal DSi concentration data for rivers, and those that do attribute the spring decline to diatom production (Capblanq and Tourenq 1978; Admiraal et al. 1990; Garnier et al. 1995; Wall et al. 1998). While this is may be the case in larger and more slowly flowing river systems, it is unlikely that planktonic diatom blooms are an important feature of the Pawcatuck River because it is a fast flowing dark water system with a short residence time, especially during spring. Throughout the summer much of the river is heavily shaded. Unfortunately, we did not measure chlorophyll *a* concentrations as part of this study. However, the University of Rhode Island's Watershed Watch program measured chlorophyll *a* at two sites along the Pawcatuck River, Bradford and Alton, approximately 10–15 km,

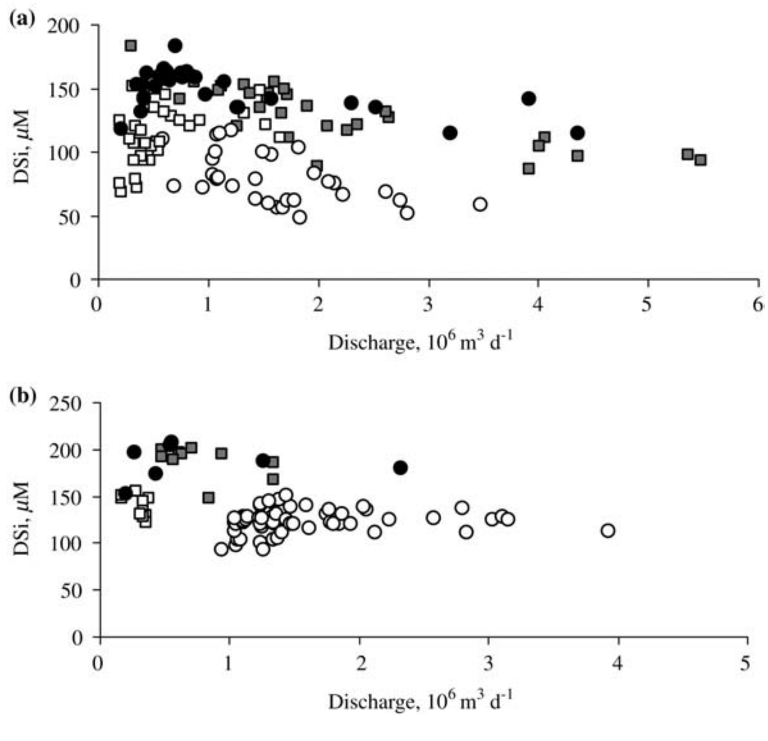

Figure 6. (a) Long-term DSi concentrations, reported by the USGS and (b) those measured during this study as a function of water discharge for the Pawcatuck River at Westerly, Rhode Island. Data have been separated seasonally: winter (■) December 21–March 20; Spring (●) March 21–June 20; Summer (□) June 21–September 20; and Fall (○) September 21–December 20. USGS data were collected at varying frequencies (4–12 y^{-1}) from 1974 to 1996.

respectively, above our sampling site from May to October. At these two sites the average chlorophyll *a* concentration was 2.6 μg L^{-1} over the five month period and ranged from 0.71 to 5.1 μg L^{-1} ± 2.0. At Bradford on August 8 chlorophyll concentrations reached 26.8 μg L^{-1}, however DSi concentrations showed no response.

It is also unlikely that epibenthic or epiphytic diatom accumulations are responsible for the spring DSi decline. We measured dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) concentrations in the river along with DSi (Fulweiler 2003). While DIN concentrations and DSi concentrations were significantly related during the spring decline (Pearson correlation $p < 0.0001$), DIP and DSi concentrations were not (Figures 7a, b). Our interpretation of this observation is that the spring decline of DSi and DIN in the river is largely due to uptake of DSi and DIN from the groundwater by terrestrial vegetation (Epstein 2000, 2001). Since groundwater is almost certainly not a significant source of inorganic P to the river it should not co-vary with nitrogen and silica if terrestrial uptake is the major DSi and N sink. Over the study, inorganic P ranged from 0.3 to 3 μM and appears to come mainly from a single point source that discharges to the

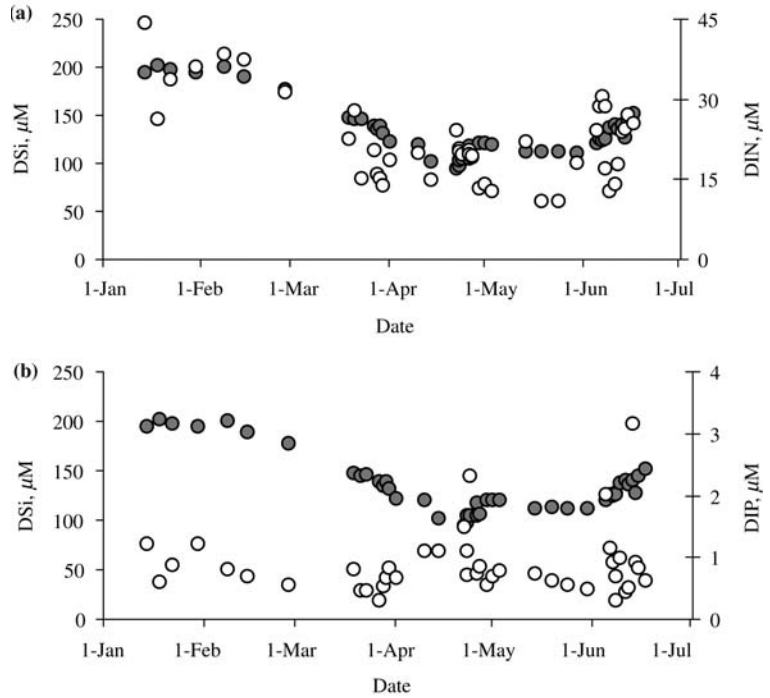

Figure 7. (a) Dissolved silica (●) and DIN (○) and (b) dissolved silica (●) and DIP (○) as a function of time over the period of strongest silica decline (January–July).

river (Fulweiler 2003). Nonetheless, if the nitrogen and DSi uptake were occurring in the river, we would expect a corresponding uptake of DIP. A linear regression, applied to the period of strongest DSi and nitrogen decline (February to April), shows a concentration decline of about 1.5 μM d^{-1} of DSi and 0.30 μM d^{-1} of nitrogen. According to the Redfield ratio, the latter should correspond to a DIP decline of about 1.7 μM over the 90 day period. However, the mean DIP concentration during this time was only 0.74 μM $\pm$ 0.32. In fact, there was actually a slight increase in DIP concentration (+0.01 μM d^{-1}) during the period of DSi and DIN concentration decline. The decline in DSi is also very large relative to the decline in DIN. Nutrient ratios can vary widely from Redfield in freshwater systems when nutrients are limiting (Hecky et al. 1993), but neither nitrogen nor phosphorus appears to be limiting in this system. Throughout the study the average concentration for DIN and DIP was 28 μM $\pm$12 and 1.1 μM $\pm$0.91, respectively (Fulweiler 2003). The ratio DSi to DIN uptake by diatoms varies around 1 (Lynn et al. 2000) compared with the 6:1 ratio observed in the Pawcatuck River, another indication that in-stream biological uptake may not be driving the spring DSi decline in this system.

Silica and terrestrial vegetation

Silica is found in terrestrial plant tissues at levels similar to and even exceeding those of many macronutrients (0.1–10% of dry weight) (Epstein 1999). Variations in silica content among plants have been attributed to three modes of silica uptake: active or accumulator plants, which take up more silica than water; passive or nonaccumulator plants, where water and silica uptake are similar; and rejective or excluder plants, where silica uptake is slower than water (Raven 1983; Takahashi et al. 1990; Marschner 1995; Tamai and Ma 2003). Most studies of silica uptake in higher plants have focused on important agricultural crops (i.e. rice, wheat, soybean, barley) and the beneficial effects of silica. Plants lacking in silica are more susceptible to biotic and abiotic stresses, can exhibit abnormal growth, and are structurally weak (Epstein 1994; Marschner 1995). While studies on the effects of silica application on crop species (Epstein 2001) are abundant we know of only one study where the influence of silica application on the physiology of trees was determined. Emadian and Newton (1989) report that silica application to loblolly pine (*Pinus taeda)* positively influenced seedling growth, suggesting that a mechanism may exist where silica is actively accumulated in the seedling. Our hypothesis that terrestrial vegetation is responsible for the spring decline in river DSi requires that the trees must be actively accumulating silica. Unfortunately, data are not yet available to address this question directly.

In order to test the proposition that uptake by terrestrial vegetation is a reasonable explanation for the riverine DSi concentration decline in spring, we calculated what the annual DSi flux would have been without the spring deficit. If the DSi concentration was constantly 200 μM (Figure 4), the annual DSi flux would have been approximately 60×10^6 mol y^{-1} or 1.5 times the measured flux. If we divide the difference between the expected and measured flux by the total forest area in the Pawcatuck watershed, we calculate a forest silica accretion rate of 41 kmol km^{-2} y^{-1}, well within the range of reported DSi accretion rates (26 kmol km^{-2} y^{-1} to 84 kmol km^{-2} y^{-1}) from an admittedly small number of forested sites (Bartoli 1983; Markewitz and Richter 1998; Conley 2002). As a further test we compiled a list of carbon to silica molar ratios in wood and leaves of various tree genera (Table 3). Unfortunately, the available data are heavily weighted by conifer studies while the Pawcatuck watershed forest contains large numbers of oak as well as white pine. Combining the leaf C:Si ratio for oak (98) and pine (580) with our calculated silica

Table 3. Carbon to silica ratio (molar) for various tree leaves and wood.

	Leaf C:Si	Wood C:Si
Angiosperm		
Quercus serrata[a]	98	
Fraxinas sp.[a]	109	
Gymnosperm		
Abies[b]	204	
Arucaria[b]	137	
Cedrus[b]	1289	
Chamaecyparis[b]	94	
Cryptomeria[b]	645	
Cunninghamia[b]	1934	
Cuperssocyparis[b]	67	
Juniperus[b]	2901	
Juniperus nana[c]	1601	
Larix[b]	53	719
Larix decidua[c]		
Picea[b]	48	193
Picea abies[c]	132	
Pinus[b]	580	630
Pinus cembra[c]	1027	
Pinus densiflora[a]	190	5679
Pinus mugo[c]		
Pinus thunbergii[a]	288	1628
Pseudolarix[b]	1934	
Pseudotsuga[b]	117	
Sequiadendron[b]	298	
Taxodium[b]	1451	
Taxus[b]	414	
Thuja[b]	1934	
Tsuga[b]	270	

[a]Jones and Hay (1975).
[b]Hodson and Sangster (1999).
[c]Carnelli et al. (2001).

accretion rate suggests a very preliminary estimate of annual net carbon accretion of 50–290 g C m^2 y^{-1}. This is consistent with detailed studies of carbon accumulation in reforested areas of varying ages approximately 60 km from the Pawcatuck watershed, where Hooker and Compton (2003) found net carbon accumulation of about 210 g C m^2 y^{-1}. Other vegetation within the watershed may be taking up silica as well. For example 8% of the watershed is agriculture, with much of this land dedicated to turf farms, and 13% of the watershed is wetland (Table 1). Both turf and wetland grasses have high silica content and are known to be silica accumulators (Raven 1983; Hull 2004). However, these plants would only have access to surficial groundwater and thus may not be a major sink for DSi.

At this point we can only conclude that the hypothesis that terrestrial vegetation in a re-growing forested watershed may reduce the flux of silica to coastal marine waters during spring and early summer appears reasonable and consistent with the data available. Confirmation must await further study of silica accumulation processes in this or similar forests.

Predicting chemical weathering in the Pawcatuck watershed

During 2002, the Pawcatuck watershed lost approximately 50 kmol km^{-2} y^{-1} of DSi. This is 80% of the 11 years mean rate reported from Hubbard Brook, New Hampshire, a more heavily forested New England watershed (Likens et al. 1977). Bluth and Kump (1994) reported an empirical regression model of silica flux relationships dependent on basin bedrock type and annual runoff from a wide range of watersheds. Using the Bluth and Kump equation, corrected for log bias, and runoff for the period of study (38 cm y^{-1}), the predicted flux of DSi from the Pawcatuck watershed is 40 kmol km^{-2} y^{-1}, 80% of the flux we measured. Since our study took place during a drought, however, we also used the log-linear regression equation from Table 2 and the 60 years mean daily flow of the Pawcatuck River (1.46×10^6 m^3 d^{-1}) to estimate a more typical annual flux of 87 kmol DSi km^{-2} y^{-1}, or almost double the flux found during the drought. The log-linear regression for DSi flux as a function of water discharge obtained in this study was not statistically different from the log-linear regression of the long-term USGS data. If the Bluth and Kump equation is applied to the 60 years mean runoff from the watershed (67 cm y^{-1}), it predicts a long-term average silica loss that is almost three times greater than that calculated from our regression for the Pawcatuck. Applying the Bluth and Kump equation to Hubbard Brook also over estimated the reported silica weathering rate by a factor of 2.5. While the Bluth and Kump (1994) regression may be useful on a global scale, it appears that basin lithology and runoff alone are not very reliable indicators of DSi flux in forested watersheds where the influence of terrestrial vegetation appears to be important (Epstein 1994, 1999; Conley 2002).

Acknowledgements

We thank Betty Buckley and Stephen Granger for help throughout this project. The manuscript was improved by helpful comments from Art Gold, Michael Pilson, Dan Conley, Emanuel Epstein, Michel Meybeck, and Martin Hodson. We also thank two anonymous reviewers for their insightful comments, Elizabeth Herron from the Watershed Watch Program at the University of Rhode Island and Linda Comeau from USGS. This research was supported in part by the Rhode Island Sea Grant College Program.

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