

AN EXPLORATORY STUDY OF THE TERRESTRIAL BIOGEOCHEMICAL  
SILICON CYCLE AT A FORESTED WATERSHED IN NORTHERN VERMONT

A Thesis

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by

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## ABSTRACT

The importance of the global silicon cycle is becoming increasingly recognized because of its role in the consumption of atmospheric CO<sub>2</sub>. However, the terrestrial component of the silicon cycle is insufficiently understood, especially in temperate regions, since the majority of past research has ignored the effects of vegetation on the cycle. This study examines the terrestrial biogeochemical silicon cycle at a 40.5-ha sub-basin of the Sleepers River Research Watershed in Danville, VT. In particular, we examine the role of plants in the silicon cycle by analyzing silicon and germanium in plant leaves and cores, stream water, groundwater, soil water, bedrock, and soil obtained throughout 2005 from the watershed. Our results show that the amount of Si cycled by the vegetation is roughly the same as the amount weathered from bedrock and soil minerals. We also predict significant storage of Si in phytoliths in both the soil and the living biomass, slowing the rate of Si export from the watershed. Additionally, there appears to be a seasonal shift in the source of Si to the stream. We suggest this is because phytolith dissolution contributes more significantly in the early growing season than late in the season, when stream-flow is dominated by Si derived from mineral weathering.

## BIOGRAPHICAL SKETCH

Christopher Garvin grew up in New Paltz, NY, at the foot of the Shawangunk Mountains. After graduating from New Paltz High School in 1999, he attended Williams College in Massachusetts, where he majored in Geosciences and ran on the cross country and track teams. Christopher graduated from Williams in the spring of 2003 and arrived at Cornell that fall, working under the guidance of Professor Louis Derry. Once finished at Cornell, Christopher hopes to find a job he enjoys, preferably one playing major league baseball.

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## TABLE OF CONTENTS

Biographical sketch.....	iii
Acknowledgments.....	iv
Introduction .....	1
Silicate weathering .....	4
The role of plants in terrestrial ecosystems.....	4
Silicon in plants .....	5
Determining Si fluxes with Ge/Si ratios .....	9
Site description.....	11
Procedures.....	15
Results and Discussion .....	22
Plant chemistry .....	22
Deciduous leaf silicon.....	22
Si increase during growing season .....	22
Si versus tree size .....	24
Coniferous needle Si .....	28
Carbon and nitrogen in leaves and cores .....	28
Leaf C/Si.....	30
Leaf Ge/Si.....	32
Leaf N/Si.....	32
Wood silicon .....	32
Soil chemistry .....	33
Water-extractable silicon .....	33
Water-extractable Ge/Si .....	34
Soil carbon and nitrogen .....	37
Sap chemistry .....	37

Water chemistry .....	42
Stream water silicon .....	42
Stream water Ge/Si .....	43
Stream hysteresis.....	57
Soil water and groundwater silicon.....	61
Soil water and groundwater Ge/Si .....	69
Chemistry summary .....	72
Sleepers River Si cycle model .....	80
Si flux from soil solution to plant .....	81
Si flux from plant to soil phytolith reservoir .....	82
Si flux from soil phytolith reservoir to soil solution .....	82
Long-term phytolith burial .....	83
Si flux from soil solution to stream water .....	83
Si flux from mineral weathering to soil solution .....	87
Plant Si reservoir.....	88
Soil solution Si reservoir.....	89
Soil phytolith Si reservoir .....	91
Si model summary .....	93
Conclusions .....	96
Appendix I: Procedural details.....	99
Phytolith extraction .....	99
Si analysis .....	99
Ge/Si analysis .....	101
Appendix II: Data tables.....	103
Appendix III: Bedrock mineralogy.....	106
References .....	109

## LIST OF TABLES

Table 1 Sleepers River watershed W-9 characteristics .....	12
Table 2 Leaf phytolith Si .....	23
Table 3 Comparison of leaf Si between this and other studies .....	29
Table 4 Weight percent nitrogen and carbon in leaves .....	30
Table 5 Tree leaf chemistry and tree diameter .....	31
Table 6 Soil carbon and nitrogen .....	37
Table 7 Sap chemistry .....	41
Table 8 Lysimeter and well depths .....	69
Table 9 Stream water Si and Ge/Si.....	103
Table 10 Lysimeter and well water Si and Ge/Si.....	105
Table 11 Water-extractable Si and Ge/Si.....	105

## LIST OF FIGURES

Figure 1 Maps of Sleepers River watershed .....	13
Figure 2 Photograph of soil pit .....	17
Figure 3 Diagram of continuous-flow setup .....	20
Figure 4 Plot of maple leaf Si vs. tree diameter .....	26
Figure 5 Plot of water-extractable Si vs. soil depth .....	35
Figure 6 Plot of water-extractable Ge/Si vs. soil depth .....	38
Figure 7 Plot of stream water Si vs. discharge .....	44
Figure 8 Stream water seasonal Si vs. discharge.....	46
Figure 9 Stream water Si vs. discharge following dry periods .....	48
Figure 10 Stream water Ge/Si vs. discharge.....	51
Figure 11 Plot of stream water Ge/Si vs. Si .....	53
Figure 12 Stream water Ge/Si vs. 1/Si .....	55
Figure 13 Plot of stream water Ge/Si vs. discharge for June and August .....	58
Figure 14 Stream water hysteresis using Si vs. discharge .....	62
Figure 15 Stream water hysteresis using Ge/Si vs. discharge .....	64
Figure 16 Lysimeter water Si variation throughout the growing season.....	67
Figure 17 Well water Si variation throughout the growing season .....	70
Figure 18 Lysimeter and well water Ge/Si vs. depth .....	73
Figure 19 Lowland lysimeter water Ge/Si variation throughout growing season.....	75
Figure 20 2003 Sleepers River hydrograph and Si concentrations .....	85
Figure 21 Schematic model of the terrestrial Si cycle at Sleepers River .....	94
Figure 22 Bedrock x-ray diffraction patterns.....	107

## **Introduction**

The global biogeochemical Si cycle has become increasingly relevant to climate research because of its role in controlling atmospheric CO<sub>2</sub> levels; weathering of silicate minerals results in the transfer of CO<sub>2</sub> from the atmosphere to the lithosphere. Therefore, in order to better understand the natural CO<sub>2</sub> cycle and make predictions about future global warming, it is important to detail the Si cycle and all of its individual components.

One such component, the terrestrial biogeochemical Si cycle, has received relatively little attention for its part in the global Si cycle. Instead, most research has examined the oceanic Si cycle (Treguer et al., 1995) or the weathering release of Si (Berner, 1992). However, the rate of biological Si cycling in the terrestrial environment [estimated to be 60-200 Tmol yr<sup>-1</sup> (Conley, 2002)] is of the same magnitude as the 240 Tmol yr<sup>-1</sup> cycled in the marine environment (Treguer et al., 1995). In addition, the terrestrial biological turnover of Si is significantly greater than the global rate of silica release from weathering of silicate minerals (Berner and Berner, 1998; Kump et al., 2000). Thus, the terrestrial biogeochemical Si cycle deserves at least as much attention as the more intensively studied facets of the global Si cycle.

The few studies that have looked at terrestrial biogeochemical Si cycling have revealed generally consistent results. Specifically, most have found a strong biological component to the terrestrial Si cycle such that the export flux of Si from a watershed is modified by the biological cycle (Lucas et al., 1993; Alexandre et al., 1997; Meunier et al., 1999; Carnelli et al., 2001; Lucas, 2001, and references therein; Derry et al., 2005). Recognizing and quantifying the impact of plants on the global terrestrial Si cycle is an important step toward determining the relationship between the Si cycle and the CO<sub>2</sub> cycle.

In an equatorial rainforest, Alexandre et al. (1997) found that 92.5 % of the Si input to the soil is rapidly recycled by plants, while the other 7.5 % maintains a stable pool of phytoliths with a slower rate of turnover. Dissolution of silica from phytoliths in this rainforest is about twice the rate of silica release from weathering reactions. Balancing the Si cycle at this site requires uptake by the vegetation of Si that would otherwise be available for mineral neoformation or export through regional drainages. This complements the findings of Lucas et al. (1993), which show that constant supply of Si in litterfall to the topsoil in a rain forest allows for kaolinite stability in the shallow soil layers. In underlying soil, where there is a lack of a continuous Si source, kaolinite is weathered to gibbsite. The observed succession of kaolinite in the shallow soil and gibbsite in the deeper soil is the opposite of that predicted by most geochemical soil formation models, and it demonstrates the importance of considering the effects of vegetation on the terrestrial Si budget.

Meunier et al. (1999) examined Si cycling in a tropical bamboo forest and concluded that the storage of biogenic silica in soils may be significant and may retard the output of silica to rivers. They determined that biogenic Si dissolution controls soil solution Si. Similarly, Derry et al. (2005) reported that most of the Si released to stream water in Hawaii has passed through the biogenic Si pool. They suggest that other systems containing little Si in soil and/or high Si uptake rates by biomass will also have strong biological control over Si cycling and export.

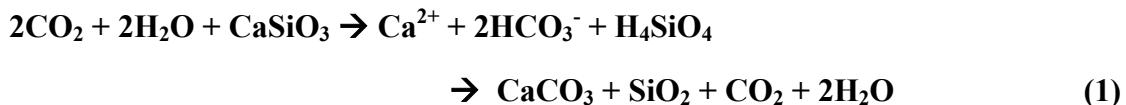
Our current understanding of terrestrial biogeochemical Si cycling is based primarily on these and other similar studies of tropical ecosystems. This tropical bias has resulted in an incomplete understanding of temperate terrestrial Si cycling and, almost certainly, a limited picture of the global terrestrial biogeochemical Si cycle. The few studies examining temperate forest Si cycling have demonstrated the influence of vegetation on Si dynamics in these settings. Bartoli's (1983) model of the

biogeochemical cycle of silicon in a forested ecosystem shows the potential for a strong biological cycle and moderate weathering release of Si in a temperate climate. In a study at a loblolly pine forest in South Carolina, the accumulation of Si in aboveground biomass and forest floor organic matter was found to augment the annual weathering release of Si by 82% (Markewicz and Richter, 1998). Additionally, in a recent paper, Fulweiler and Nixon (2005) demonstrate evidence for a strong seasonal signal in river Si concentrations in a Rhode Island watershed. It is difficult, however, to draw conclusions about the temperate forest Si cycle from the few existing papers on this subject. It is therefore necessary for other studies to build on the current understanding of temperate terrestrial Si cycling in order to ultimately create a more complete picture of the global Si cycle.

The small watershed approach has long been used to develop element budgets and relate these data to larger scale biogeochemical cycles (Bormann and Likens, 1967). The goal of our study was to use the small watershed approach to develop a preliminary understanding of terrestrial Si cycling in a temperate climate. Specifically, we created a model on which future studies could build to help elucidate the temperate terrestrial Si cycle. We quantified fluxes and reservoirs of Si in a headwater catchment of the Sleepers River Research Watershed in northern Vermont. We also attempted to determine the effect of seasonal changes in the hydrologic cycle on the Si cycle using Ge/Si as a tracer of Si source. Prior to the study, we hypothesized that the Si cycle at this location would display a stronger seasonal component than had been observed in tropical locations. More specifically, we expected that the Si (particularly of biogenic origin) in the stream export flux would vary in response to seasonal variations in plant water-use. We also expected the internal biological cycle of Si to be significant and to increase the watershed residence time of Si released by weathering.

### *Silicate weathering*

Silicon is the second most abundant element in the Earth's crust behind oxygen, though only a small fraction takes part in biogeochemical cycles (Conley, 2002). Silicates comprise 90% of the minerals in the Earth's crust and dominate many water-rock systems (Heaney and Post, 1992). The weathering of silicate minerals converts soil organic carbon (derived from atmospheric CO<sub>2</sub> via photosynthetic pathways) into dissolved HCO<sub>3</sub><sup>-</sup> and finally into CaCO<sub>3</sub>. The overall process can be represented by the following equation (France-Lanord and Derry, 1997):



where one mole of CO<sub>2</sub> is sequestered as marine carbonate for each mole of Ca derived from silicate weathering. This transfer is a significant control on atmospheric CO<sub>2</sub> levels on geologic timescales (Berner, 1992).

### *The role of plants in terrestrial ecosystems*

For many years, the weathering of rocks was ascribed primarily to circulating waters. More recently, many important feedbacks between weathering and plants have become appreciated. For example, plants can enhance weathering rates by releasing organic acids, increasing mineral surface area, and raising soil water residence time (Drever, 1994; Berner, 1997; Lucas, 2001). Plants also play a role in the distribution of nutrients in the soil. In the case of Si, it is taken up in soil solution by plant roots, accumulates in plant tissue in opal phytoliths, and is eventually transferred back to developing soils after litterfall. This plant uptake of Si increases the chemical weathering rate without increasing the denudation rate (Alexandre et al., 1997). After litterfall and the ensuing decay of plant organic matter, phytoliths accumulate in the underlying soil, where the silica can be redissolved and taken up

again by plants. As a result, Si phytoliths in soils are ubiquitous, having been found in rainforests (Lucas et al., 1993; Alexandre et al., 1997; Runge et al., 1999; Meunier, 1999; Derry, 2005), grasslands (Runge et al., 1999), temperate deciduous and evergreen forests (Bartoli, 1983), and wetland areas (Norris and Hackney, 1999). By cycling Si, plants can slow its release to stream water, thereby increasing its residence time in the watershed (Meunier, 1999; Conley, 2002). The effect of plants on the Si cycle should be especially evident in temperate systems, where plant activity is highly seasonal.

Plants also have significant control over water dynamics within a watershed (Lucas, 2001). Trees in forested watersheds represent a major pathway through which soil water and groundwater re-enter the hydrologic cycle. For example, during dry periods, some large trees (in particular, sugar maples) demonstrate a phenomenon called hydraulic lift. Dawson (1993; 1996) defines hydraulic lift as the nocturnal transport of deep groundwater through roots to the dry upper soil layers. The water that is released into the upper layers is utilized the following day when transpiration demand exceeds water uptake by deep roots alone. For large trees, 80 liters of water per night can be transported through this process (Dawson, 1996). Hydraulic lift essentially creates a second, shallow water reservoir from which both large and small trees can draw during the daylight hours, thus permitting a greater total water flux (Dawson, 1996; Caldwell et al., 1998). As a result, mixed-age stands may have a greater impact on hydrologic balance than old stands, because trees in mixed stands draw water from both soil water and groundwater reservoirs (Dawson, 1996).

### *Silicon in plants*

Despite silicon's prevalence at the Earth's surface, its role in plant nutrition has been mostly neglected by researchers. This is especially surprising because Si is

present in plants at similar levels to other macronutrients, such as Ca, Mg, and P, and in grasses often at higher levels than any other inorganic component (Epstein, 1999). However, Si is not considered to be essential to plant growth, as plants are able to complete their life cycle without it (Raven, 2003). Instead, it has been called “pseudo-essential”, because it is nonetheless recognized as being important to plant health.

Silicon’s role in plant growth, nutrition, and strength, as well as resistance to disease, herbivory, and adverse chemical conditions in the soil has been documented (Raven, 1983; Epstein, 1994, 1999; Datnoff et al., 2001; Conley, 2002). Like lignin, silica is a compression-resistant structural component of some cell walls (Epstein, 1994). However, silica is energetically cheaper to incorporate (3.7 % the energetic cost of lignin), making it a suitable alternative for many plants (Raven, 1983). Plants amply supplied with silica assume a more upright position, and their leaves are full and rigid; these characteristics all favor light interception and thus promote photosynthesis (Epstein, 1994). Additionally, silica deposition in plant tissues creates a hard outer layer that serves as a defense against herbivory and infection (Sangster and Hodson, 2001).

The extent of silicon’s role in plants appears to be somewhat species-dependent (Raven, 1983; Carnelli et al., 2001); plants that actively take up Si are the most sensitive to a Si deficit. Such plants (Si-accumulators - see description below) require more Si than they would otherwise obtain through passive uptake and are therefore more likely to suffer from a Si deficit. In studies of Si-accumulators grown in a Si-free medium, Si-deficient symptoms, such as abnormal growth, structural weaknesses, and susceptibility to abiotic stress and disease, have been noted (Epstein, 1999; Marschner, 1995).

Furthermore, there is evidence that Si plays a role in alleviating heavy metal toxicity in plants (Ma and Takahashi, 1990; Hodson and Evans, 1995; Cocker et al.,

1998; Epstein, 1999; Sangster and Hodson, 2001; Carnelli et al., 2001). It appears that Si may reduce Al bioavailability by forming aluminosilicate and hydroxyaluminosilicate complexes that can co-precipitate in plant tissues (Cocker et al., 1998). This Al-Si association could function as a mechanism for sequestering Al, thus detoxifying the soil solution taken up by the plant (Hodson and Sangster, 1999). In addition, Fe and Mn are immobilized by Si in the roots where they can be oxidized to their less toxic forms before being transported to the plant shoots (Ma and Takahashi, 1990).

Most studies of the physiological role of silicon in terrestrial plants have focused on important agricultural crops, such as rice, wheat, barley, and soybean (e.g. Epstein, 1994, 1999; Marschner, 1995; Tamai and Ma, 2003). Understanding the function of silica in crops is of obvious economic importance and has undoubtedly motivated many of these studies. Conversely, very little is known about silicon in natural plants, and only one known study has focused on the physiological role of silicon in trees. In that study, silica applied to loblolly pine was shown to encourage seedling growth, suggesting the existence of a mechanism in which silica is actively accumulated in the seedling (Emadian and Newton, 1989). Si clearly provides many benefits to crop plants and appears to be important to natural plants, as well (Richmond and Sussman, 2003).

Silicon in the soil is available for uptake by plants as monosilicic acid ( $H_4SiO_4$ ) that is generated by the dissolution of biogenic silica in the soil, but ultimately originates from the weathering of silicate rocks (Carnelli et al., 2001). After being taken up by roots, silicic acid enters the transpiration stream, in which it is transported into the shoots toward transpiration termini. As water evaporates in the plant tissue, the silicic acid becomes supersaturated with respect to solid hydrated silica and precipitates as hydrated opal-A (phytoliths) (Hart, 2001; Carnelli et al. 2001; Raven,

2003). Phytoliths are returned to the soil as single silicified cells and cell fragments (ranging in size from a few to tens of microns) after plant death and decomposition of organic matter (Carnelli et al., 2001). Once in the soil, most are dissolved, though a small fraction are preserved and buried (Alexandre et al., 1997).

Opal deposition can be intracellular (opal silica occupying the cell) or extracellular (filling the intercellular spaces or forming a layer on epidermal cells) (Alexandre et al., 1997; Carnelli et al., 2001). Once deposited in plant tissues, opal silica is not remobilized and cannot be transported to other parts of the plant (Raven, 1983). Because of this, as well as the fact that dissolved silica is an uncharged molecule, its translocation within the plant is more strongly influenced by the transpiration stream than is the case for other elements. Therefore, Si in plants tends to accumulate at the terminal sites of the transpiration stream (Epstein, 1999; Sangster and Hodson, 2001). Phytoliths in plants have also been found in xylem vessels and the endodermis of roots (Raven, 1983).

The amount of silica deposited in plant tissue depends on the amount of silicic acid in the transpired water and the overall amount of water transpired (Raven, 2003). Variations in silica content in plants are a result of three different types of uptake: active uptake, by which plants take up silica at a higher rate than water; passive uptake, by which water and silica are taken up at similar rates; and rejective uptake, by which silica is taken up at a slower rate than water. Plants exhibiting these modes of uptake are categorized as accumulators, non-accumulators, and excluders, respectively (Raven, 1983; Takahashi et al., 1990; Marschner, 1995; Tamai and Ma, 2003). Silica levels in terrestrial plant tissues vary from 0.1-15% dry weight (Epstein, 1999). Accumulators include primitive plants, such as horsetails and wetland Gramineae (paddy-grown rice), and have the highest measured Si values (4.5-15%) (Epstein, 1999). The roots of these plants must deplete the silicic acid from the soil water

adjacent to their roots allowing additional silicic acid to diffuse toward the roots (Hull, 2004). Non-accumulators, including dryland grasses (e.g. rye and oats) and sugarcane, absorb as much Si as is transported to their roots by the flow of transpirational water and have intermediate levels of Si (0.5-1.5 %) (Epstein, 1999; Conley, 2002). Finally, excluders, including some dicotyledonous species, typically have less than 0.25 % (Epstein, 1999; Conley, 2002; Hull, 2004). In these plants, water is absorbed more rapidly than the silicic acid it contains.

Studies have shown that the silica content of plant tissues increases with age; older plant tissues sometimes contain five times the amount of silica present in younger tissues (Carnelli et al., 2001; Sangster and Hodson, 2001). This applies to the needles and leaves of trees, and is the result of a one-way flow into the needle from the xylem and little return flow into the phloem (Hodson and Sangster, 1999).

#### *Determining Si fluxes with Ge/Si ratios*

Germanium and silicon display remarkably similar chemical characteristics; both are group IV elements and have identical outer electron structures. As a result, Ge follows Si through its biogeochemical cycle, and germanium is considered a “pseudo-isotope” of silicon. Additionally, Ge-O and Si-O tetrahedral bond lengths are nearly the same (1.75 Å and 1.64 Å, respectively), thus Ge can substitute readily for Si in the tetrahedral sites of silicate minerals (the principle of camouflage; Goldschmidt, 1958). Therefore, crustal rocks tend to display uniform Ge/Si ratios on the order of  $10^{-6}$  (Mortlock and Froelich, 1987). Weathering of silicate minerals from these rocks is the primary source of dissolved Ge and Si in terrestrial systems (Murnane and Stallard, 1990).

Ge/Si ratios do not remain constant throughout the biogeochemical cycle, but are instead fractionated during weathering and plant uptake. In the case of weathering,

fractionation results from the sequestration of Ge during the initial precipitation of secondary soil aluminosilicates, which have weakly polymerized silicate tetrahedra (Murnane and Stallard, 1990; Kurtz et al., 2002; Kurtz and Derry, 2004).

Consequently, soils have higher Ge/Si ratios than the parent material on which they form (Murnane and Stallard, 1990; Chillrud et al., 1994, Anders et al., 2003).

Similarly, Ge/Si ratios in modern uncontaminated (i.e., unaffected by pollution or hydrothermal inputs) rivers are lower than the Ge/Si ratios of the silicate bedrock they drain. Ge/Si ratios of rivers range from  $0.3\text{--}1.2 \times 10^{-6}$ , while the typical ratios in the continental crust are roughly  $10^{-6}$  (DeArgollo and Schilling, 1978; Bernstein, 1985; Mortlock and Froelich, 1987; Murnane and Stallard, 1990).

During plant uptake, Ge is discriminated against relative to Si, resulting in opal phytolith Ge/Si ratios of  $0.05 \times 10^{-6}$ . The exact mechanism of the fractionation is not currently known, but phytoliths in plants and soils, as well as the water draining these soils, all have low Ge/Si signatures.

Ge/Si ratios are particularly useful for tracing silica delivery sources to streamwater. Fractionation during weathering and plant uptake results in source areas with distinctly different Ge/Si ratios. Incongruent dissolution of primary minerals results in a solution with high [Si] and low Ge/Si. Dissolution of secondary clay minerals under more intense chemical weathering yields a low [Si], high Ge/Si solution. Dissolution of amorphous (biogenic) silica gives a solution with high [Si] and low Ge/Si (Kurtz and Derry, 2004; Derry et al., 2005).

The use of Ge/Si as a tracer has been tested in various tropical settings containing different vegetation and bedrock regimes. In Puerto Rico, stream water Ge/Si measurements by Kurtz and Derry (2004) indicate a two-component source of silica. During base flow, Ge/Si ratios are low and [Si] is high, consistent with measurements from lysimeter samples from near the bedrock-saprolite interface.

During storm events, Ge/Si ratios increase and [Si] drops, suggesting a switch in silica source from the bedrock-saprolite interface to saprolite pore waters that were flushed out during the storm. There was little evidence of biologically cycled Si contributing to the stream water Si flux.

In Hawaii, the Ge/Si signal is strongly influenced by export of biologically cycled silica, which contributes ~80% of the Si delivered to the streams. Thus, Ge/Si ratios in the Hawaiian streams trace the mixing of plant phytolith-derived Si from surface soils and secondary mineral-derived Si from deeper soils. Only during high discharge in streams draining well-developed soils are Ge/Si ratios ever high (Kurtz and Derry, 2004; Derry et al., 2005).

### **Site Description**

The Sleepers River Research Watershed, located near Danville, Vermont, is a rolling-to-mountainous 111.25 km<sup>2</sup> sub-basin of the Passumpsic River Basin (Figure 1a) (Shanley et al., 1995). Sleepers River is one of five sites for research on Water, Energy, and Biogeochemical Budgets (WEBB) under the USGS Global Change Hydrology program and has a long-term (>40 years) hydrologic and meteorological database. Samples for this study were collected from the W-9 headwater catchment of Sleepers River (Figure 1b). The USGS maintains a network of groundwater wells, lysimeters, stream samplers, and stream gauges throughout the 40.5 ha headwater catchment.

Stream flow measurements are taken at a V-notch weir at W-9 (Hornbeck, 1997), while precipitation is measured at an adjacent clearing, and snow water equivalent is measured at the snow survey station 1.5 km south of the W-9 weir (Ohte, 2004). W-9 has an elevation range of 520-675 m and is completely forested (Hornbeck, 1997; Shanley et al., 1995). The forest is evenly aged 70-80 years

(Hornbeck, 1997) and consists primarily of northern hardwoods, including sugar maple, yellow birch, American beech, and white ash. Conifers are also present and include balsam fir, red spruce, tamarack, and white cedar (Shanley et al., 2002). The W-9 watershed is underlain by a calcareous granulite bedrock interbedded with quartz mica phyllite (Appendix II; Newell, 1970). The bedrock is blanketed by 1 – 4 meters of fine silty calcareous till derived from local bedrock. Stream chemistry is controlled mainly by dissolution of calcite in the till and bedrock, resulting in a stream water pH of 7-8 (Shanley et al., 1995). Inceptisols and podzols have developed on the till to an average depth of 70 centimeters (Kendall et al., 1999). Histosols dominate in riparian zones, while up to 2 m of peat is present in swampy areas near the headwaters (Shanley et al., 2002).

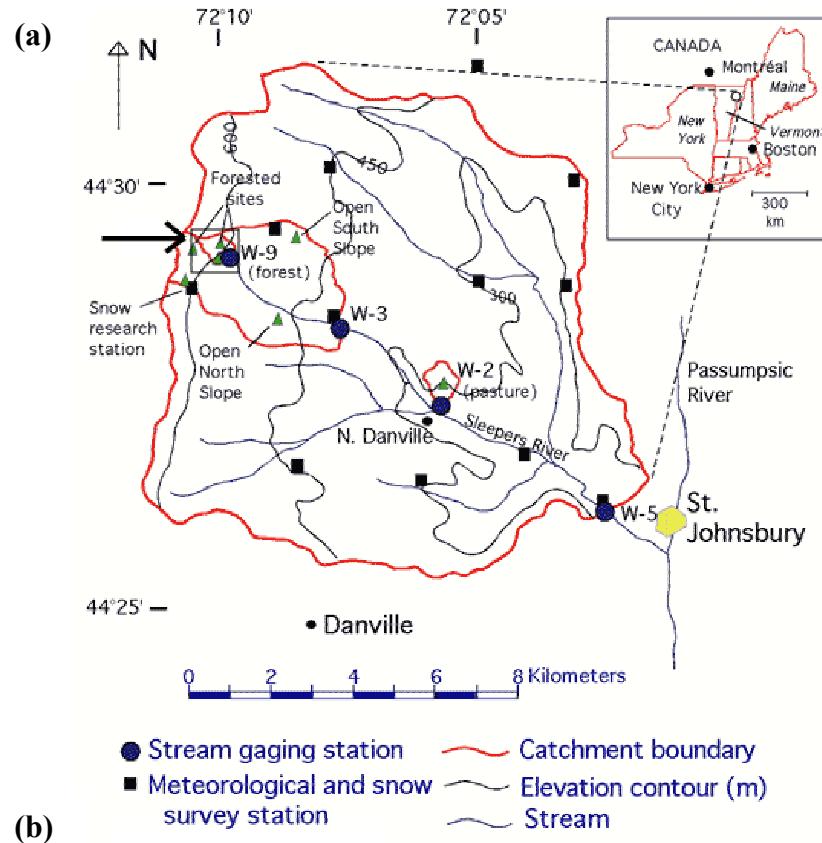
**Table 1** Sleepers River W-9 watershed site characteristics

Catchment Area	40.5 ha
Elevation	520-675 m
Mean slope	22 %
Aspect	South
% Forest	100 %
Forest age	70-80 years
Precipitation	1300 mm/yr
Runoff	740 mm/yr
Mean Annual Temperature	4.6° C
Soil Types	Inceptisols and Podzols
Bedrock	Calcareous granulite; Quartz-mica phyllite

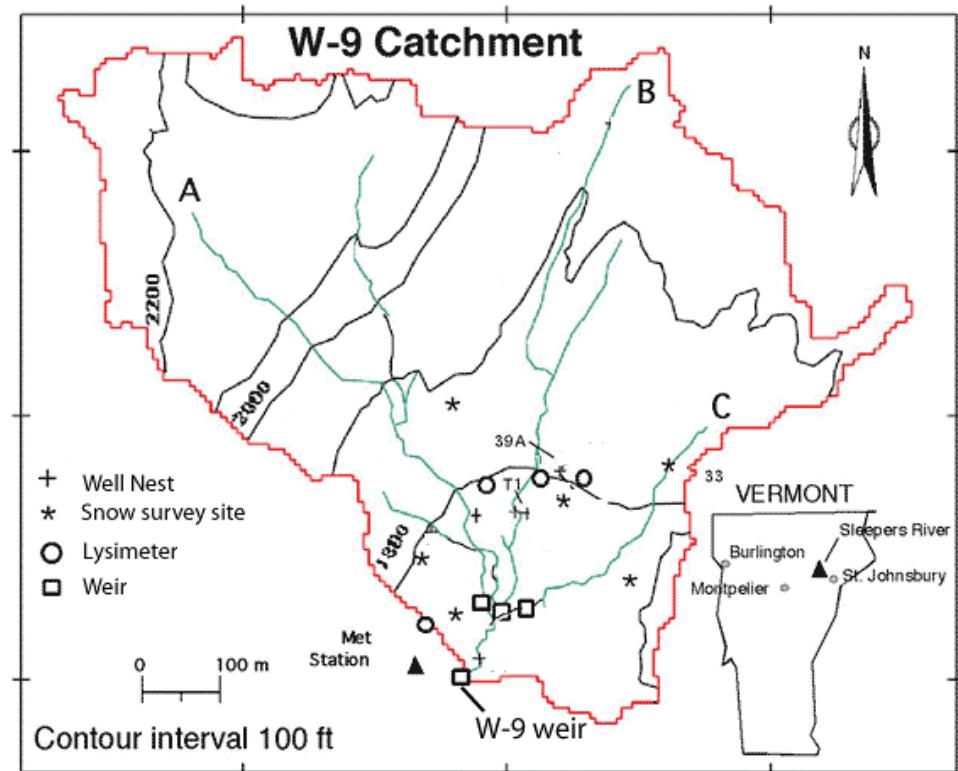
The climate at the Sleepers River watershed is typified by long, cold winters ( $-10^{\circ}\text{C}$  40-year average) and relatively cool summers ( $12^{\circ}\text{C}$  40-year average). Historically, temperatures have ranged from -38 to  $30^{\circ}\text{ C}$ , with an average annual temperature of  $4.6^{\circ}\text{ C}$  (McGlynn et al., 1999). W-9 receives about 1300 mm precipitation annually, 25-30% of which falls as snow (Kendall et al., 1999). Snow

**Figure 1a** (top) Map of the entire Sleepers River Research Watershed, located in Danville, Vermont. The small W-9 sub-watershed is denoted by a rectangular box and an arrow.

**Figure 1b** (bottom) Expanded map of the W-9 watershed, showing the location of wells and lysimeters that were sampled for this project. Also note the location of the soil pit and the W-9 weir.



(b)



cover typically persists from mid-November to late April, with peak runoff occurring during snowmelt (Shanley et al., 1995). Minimum flow usually occurs between July and October (Shanley et al., 1995).

Recent studies at Sleepers River have included work on nitrogen dynamics (Campbell et al., 2004; Ohte et al., 2004), snow melt and riparian zone hydrology (Shanley and Chalmers, 1999; Kendall et al., 1999; McGlynn et al., 1999; Shanley et al., 2002; Ohte et al., 2004), acidification processes and weathering (McDonnel et al., 1999; Hornbeck et al., 1999; Peters et al., 2004; Shanley et al., 2004), and mercury fluxes (Shanley et al., 2005; Dennis et al., 2005). This partial list of recent publications demonstrates the intensity of current research at Sleepers River by both the USGS and outside collaborators. Sleepers River offers us the opportunity to test our hypotheses about the temperate terrestrial Si cycle within an established framework found at few other temperate sites.

## Procedures

All fieldwork took place at the W-9 headwater catchment of the Sleepers River watershed in Danville, VT (Figure 1b). We sampled soil in mid-August at 5-20 centimeter intervals, to a depth of roughly one meter, from the walls of a freshly dug soil pit. Leaf litter samples were taken from the forest floor adjacent to the soil pit. The soil pit (Figure 2) was located in a topographically flat area, far enough from steep slopes and the stream bank to limit the possibility of past modification by geomorphic processes such as erosion or colluviation. Water-extractable silica was obtained from the soil samples by the saturation paste method (Lajtha et al., 1999). Soils were placed in 250-mL Nalgene bottles, a prescribed amount of QD water was added, and, after stirring, the mixtures were allowed to sit for two weeks. They were then centrifuged at 3000 rpm for 30 minutes, and the supernatant water was poured off

and filtered through 0.22- $\mu\text{m}$  cellulose nitrate membrane filters. This water was analyzed for Si and Ge as described below.

Stream water samples were taken by the USGS throughout 2005 from a point just upstream of the W-9 weir. Water was sampled weekly during dry conditions and more frequently during summer storm events. Stage height and discharge were measured at the weir at the same time the water was sampled. Deep soil water and groundwater (from wells) and shallow soil water (from zero-tension lysimeters) were sampled by the USGS throughout the year, as well. All water samples were filtered through 0.22- $\mu\text{m}$  cellulose nitrate membrane filters and acidified in the field. They were stored in acid-washed Nalgene bottles and kept refrigerated in the laboratory.

We sampled plant tissue from trees located within 50 meters of the W-9 weir. Canopy leaves were sampled, in June and August, with a slingshot and well-aimed rocks. Each tree from which leaves were taken in August was cored three times with a Haglof increment borer. Leaf and core samples were stored in plastic bags. At Cornell, all plant samples were dried in an oven at 55° C for 24 hours. After drying, the leaf samples were powdered in a Spex Certiprep freezer/mill. Phytoliths were extracted from these samples, and Ge and Si content determined, as described in Appendix I.

In April, we sampled phloem sap water from sugar maples (*Acer saccharum* Marsh.) throughout the Sleepers River W-9 watershed. To obtain the sap, we drilled a hole one to two inches into each tree sampled, placed plastic taps in the holes, and allowed the sap to run through the taps and into waiting acid-washed Nalgene bottles. In the laboratory, the sap was treated with H<sub>2</sub>O<sub>2</sub> (1 mL peroxide to 5 mL sap) to dissolve organic matter.

We sampled bedrock with a rock hammer from exposed surfaces near the streambed. In the lab, rock samples were ground into small pieces with a rock grinder

**Figure 2** Photograph of the upper portion of a soil pit near the W-9 weir in the Sleepers River watershed, with a tape measure for scale. Note the presence of a thick organic-rich horizon above the mineral soil. The pit was dug in a flat area under a stand of sugar maples, 20-30 meters from the stream. Samples were collected every 10-20 centimeters from the wall of the pit.



and then powdered using a mortar and pestle. The powdered rock samples were analyzed by x-ray diffraction with the help of Dr. Maura Weathers in the Department of Geological Sciences at Cornell University.

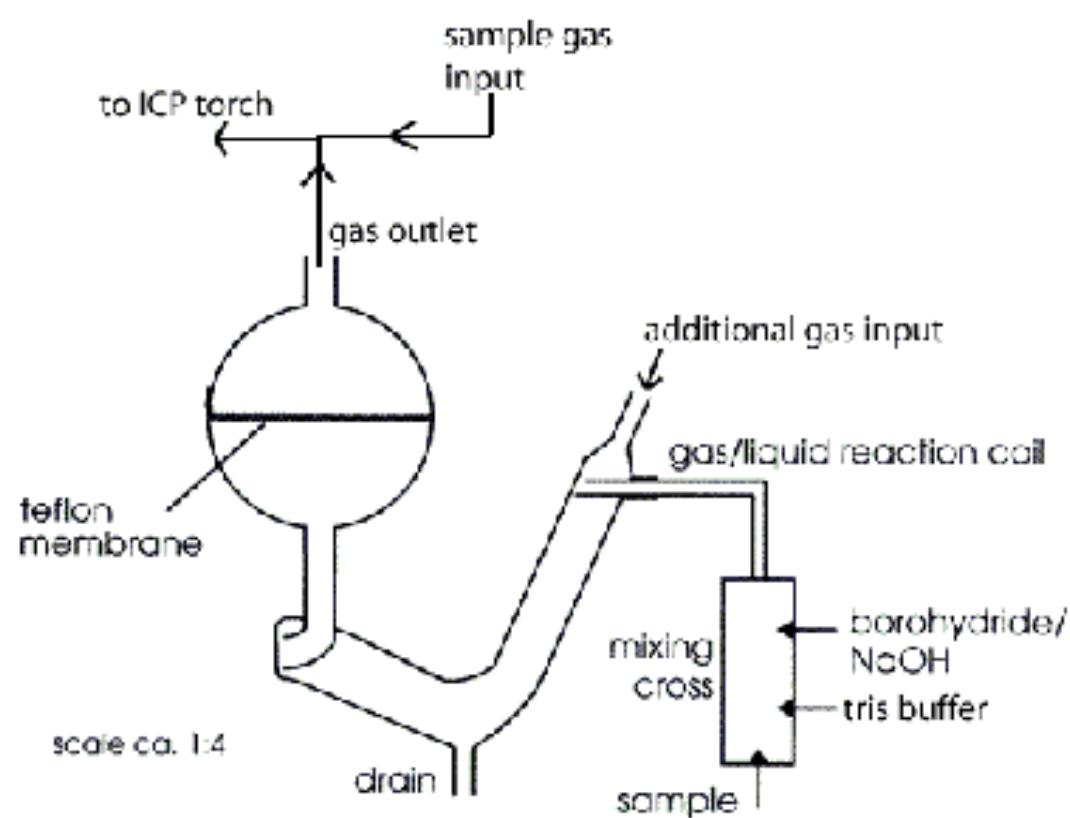
Dissolved silica concentrations in stream water, groundwater, soil water, and sap water were determined by molybdate-blue spectrophotometry (see Appendix I for details). Silica concentrations were also determined on selected sap and stream samples by ICP-optical spectroscopy by Dr. Matthew Gorring at Montclair State University. These results were comparable to those obtained by molybdate-blue spectrophotometry to within 5%. Germanium concentrations in stream water, groundwater, soil water, and sap were determined by continuous flow isotope-dilution hydride generation (Figure 3; Appendix I).

Major elements (Ca, Mg, K, Na, Sr) in stream water and sap water were measured by inductively coupled plasma optical emission spectroscopy by Dr. Matthew Gorring at Montclair State University and by ion chromatography at Cornell University. %C and %N of dried core, soil, and powdered leaf samples were determined by Art Kasson on a Carlo Erba NC2500 elemental analyzer at Cornell University. Long-term averages of stream water discharge and Si concentration were determined using the geometric mean equation:

$$\text{Geo. Mean } (a_1, a_2, a_3, \dots, a_n) = (a_1 * a_2 * a_3 * \dots * a_n)^{1/n} \quad (2)$$

where  $a_i$  is a data point, and  $n$  is the total number of data points in the series. The geometric mean equation was used instead of the arithmetic mean because the latter is too strongly influenced by large peaks and valleys in the data and thus yields an average value unrepresentative of highly variable data sets like stream discharge and concentration. More complicated formulae, such as Beale's ratio and a log-linear

**Figure 3** Diagram of the continuous-flow hydride-generation setup used to introduce samples to the ICP-MS for Ge analysis (modified from Klaue and Blum, 1999). The sample, sodium borohydride, and tris buffer are simultaneously pumped into a tube where the hydride generation reaction takes place. The Ge hydride is then swept along by argon gas (“additional gas” in diagram), through a Teflon membrane filter, and into the ICP-MS torch with the aid of another flow of argon (“sample gas”). The reaction waste is removed via the drain at the bottom of the diagram.



regression, can also be used to determine annual stream discharge and concentration fluxes, but Fulweiler and Nixon (2005) found the results of these to be no different than those of the geometric mean.

## **Results and Discussion**

### **Plant Chemistry**

#### *Deciduous leaf silicon*

Leaves from the three dominant deciduous species – sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.), and yellow birch (*Betula alleghaniensis* Britt.) – were sampled at Sleepers River. Silicon concentrations in leaf phytoliths from these trees ranged from 1.05 to 8.79 mg/g dry weight (Table 2). The Si concentrations in beech and birch leaves were similar to those reported by Bartoli and Souchier (1978), while maple leaf Si has not previously been measured. According to the Si uptake classification scheme noted by Epstein (1999) and Conley (2002), the moderate Si levels in sugar maple and American beech leaves indicate that they are non-accumulators of Si, while the low leaf Si in yellow birch might mean that it is a Si-excluder. However, more research on the uptake mechanisms of these trees is needed to make any definitive remarks on their classification.

#### *Si increase during growing season*

Samples were taken on two separate occasions, two months apart (June 13 and August 14), during the 2005 growing season. While an admittedly small number of samples were collected on the early date, there nonetheless appears to be an increase in leaf phytolith Si in samples of each species between mid-June and mid-August.

**Table 2** Leaf phytolith Si concentrations (number of samples analyzed in parentheses).

	June Mean mg Si/g dry leaf weight	August Mean mg Si/g dry leaf weight	August Si Range
Sugar Maple	1.7 (3)	6.30 (10)	3.03 – 8.79
Yellow Birch	0.24 (2)	1.49 (3)	1.05 – 2.01
American Beech	0.77 (2)	7.27 (3)	6.03 – 8.55
Balsam Fir	-----	0.069 (3)	0.025 – 0.15

Between the two sampling dates, mean Si concentrations in American beech leaves increased from 0.77 to 7.2 mg/g, in yellow birch from 0.24 to 1.6 mg/g, and in sugar maple from 1.7 to 5.6 mg/g. While it is widely accepted that other elements, such as Ca, Mg, and Fe, accumulate in leaf tissue throughout the growing season (Schlesinger, 1997), ours is among the first evidence of Si increasing with leaf age in deciduous tree species (Farmer et al., 2005, and references therein). This finding supports recent evidence from coniferous forests in which Si was found to continuously accumulate in needle tissue throughout development (Hodson and Sangster, 1998; Carnelli, 2001). As noted in the introduction, dissolved Si is an uncharged molecule ( $H_4SiO_4$ ), so its translocation in the plant is more strongly controlled by the transpiration stream than is true of other elements. Therefore, the observed increases were likely due to the continuous input of Si-carrying water to the leaves via the transpiration pathway during the growing season.

The differences between the June and August Si concentrations allow us to calculate rough Si accumulation rates in the leaves of each species for the period between each sampling (~60 days). According to these calculations, American beech added 105.4  $\mu\text{g}$  Si per gram per day, yellow birch added 22.3  $\mu\text{g}/\text{g}$  per day, and sugar maple added 63.9  $\mu\text{g}/\text{g}$  per day. However, these rates should be considered nothing more than rough estimates because the small number of leaf samples taken during

June increases the likelihood of error in the mean leaf Si concentration from that date. In the future, leaf samples should be collected more frequently during the growing season to better define a rate of Si accumulation for each species. Regardless, the apparent trend of Si accumulation between June and August is important when examining seasonal effects on the Si cycle, and the above rates provide a starting point for future work.

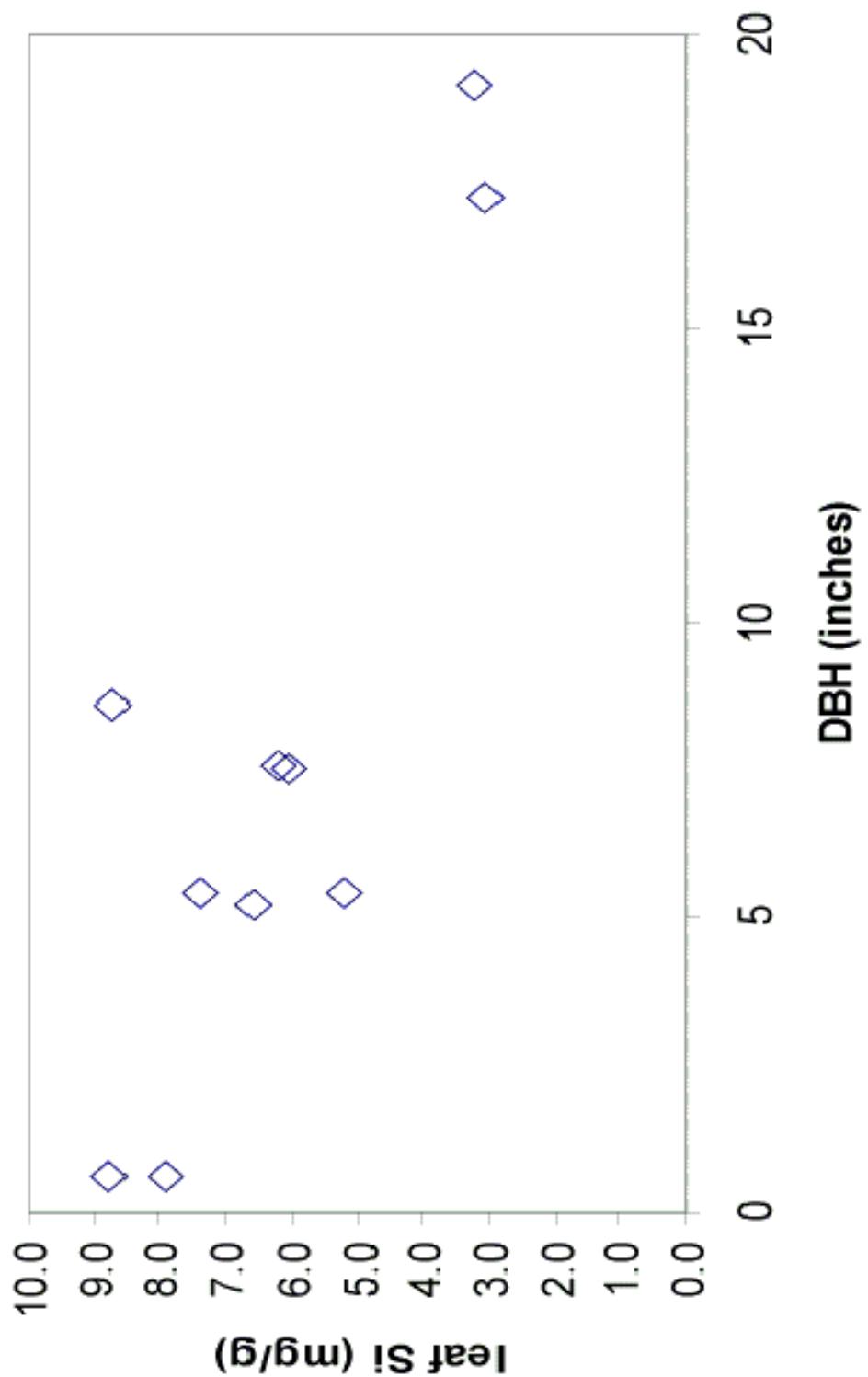
The continuous increase of leaf Si gives rise to a potential issue in our Si cycle model. Annual plant Si uptake, as well as the total Si in plant biomass, is estimated using the measured leaf Si concentrations from samples collected in August (these calculations are detailed later, in the *Sleepers River Si cycle model* section). If, as we propose, plants continuously accumulate Si in their leaves, then the August leaf Si concentration does not reflect the total amount of Si incorporated in leaves during the entire growing season, since the growing season was not yet over at that point. Therefore, by calculating plant Si uptake and the plant Si reservoir using August leaf Si values instead of values from leaves collected closer to senescence, we might have underestimated these values for Sleepers River trees. However, senescence occurs not too long after mid-August in northern Vermont, so we assume that the leaf Si concentrations did not increase significantly from what we measured, and thus our calculated plant uptake rates should not differ greatly from actual plant uptake. Again, in the future, a greater leaf sampling frequency extending beyond mid-August will help resolve this issue and allow us to better estimate plant Si uptake rates and total Si in biomass.

#### *Si versus tree size*

Since sugar maple is the dominant tree species at Sleepers River, it was subject to a greater sampling intensity than the other species. During sampling, an effort was

made to obtain leaves from maples of different sizes for the purpose of examining whether tree size affects leaf Si content. A plot of tree diameter against leaf Si (Figure 4) shows an inverse relationship between the two; the larger trees have a lower percentage of Si in their leaves than do the smaller trees. Unfortunately, this observation is based on only a few data points. A greater number of samples from a wider variety of tree sizes should be obtained in the future to determine the validity of our results. If this trend is real, three possible explanations exist. One is that small, young trees allocate a higher percentage of the Si that they take up to their leaves, a result that has been previously noted for nitrogen (Reich et al., 2004). The second is that the shallow reservoir of water from which these small trees are drawing is more Si-rich than the combined shallow/deep reservoir being utilized by the larger trees. This explanation is plausible since the shallow root systems of small trees usually have access only to shallow soil water, which likely contains a high concentration of Si from dissolved phytoliths. During drought conditions, however, small trees can also take up hydraulically lifted deep water (Dawson, 1993), which might not necessarily have a high Si concentration, and is the same water taken up by larger trees with apparently lower Si concentrations in their leaves. An analysis of stable oxygen isotope ratios from xylem sap in large and small trees in the watershed would give us a better idea of where they are obtaining their water. In such an analysis, the two end members, groundwater (i.e., hydraulically lifted water) and shallow soil water, are usually isotopically distinct because groundwater receives input from many different recharge sources, such as summer rain and winter snowmelt (Dawson, 1993). Unlike Ge/Si ratios, oxygen isotope ratios are not fractionated in water during uptake, so the xylem water can be used to trace the source from which the tree is deriving its water (Dawson, 1996). Quantification by this method of deep and shallow water uptake for small and large trees, combined with Si concentrations in these waters, would allow a

**Figure 4** Maple leaf Si concentration plotted against tree diameter at breast height (DBH). Apparent trend is a decrease in Si with increasing tree size, a possible result of differences in nutrient allocation, uptake sources, or transpiration rates between large and small trees.



determination of the relative amount of Si taken up by the trees. A third possibility is that smaller trees accumulate more Si in their leaves because they have higher transpiration rates per unit area than large trees (Jed Sparks, pers. comm.). If the observed variation in leaf Si between small and large trees does exist, the explanation is probably a combination of differences in nutrient allocation, water uptake source, and transpiration rates between small and large trees.

#### *Coniferous needle Si*

Balsam fir, the dominant conifer at Sleepers River, had very little Si in its needles relative to the concentrations in the deciduous tree leaves (Table 2). The measured Si levels in fir needles were lower even than those measured in conifers at other sites (Hodson and Sangster, 1999; Carnelli, 2001, and references therein) (Table 3). It is therefore expected that conifers in the Sleepers River watershed have little impact on the overall biogeochemical Si budget. In addition, it appears that the balsam fir may be a Si-excluder, as its average Si concentration of 0.07% is well below the 0.25% that usually represents the maximum excluder tissue Si concentration.

#### *Carbon and nitrogen in leaves and cores*

Carbon/nitrogen ratios were measured in ten leaf samples and three core samples taken from trees in the Sleepers River watershed in August 2005 (Table 4). There was little variation in %C among leaf samples (all were between 31 and 37%), thus C/N ratios were controlled mainly by N concentrations. These ratios are indicators of the relative nutrient content of the plant tissue: the higher the C/N ratio, the lower the nutrient levels. Balsam fir needles had the highest C/N ratios (26-27) of all species measured. Sugar maples averaged 19.3, American beech 17.7, and yellow

**Table 3** Leaf Si concentrations from this and other studies. Data in the table are averages for each species. Grass tissue Si concentrations are given below the horizontal line for comparison.

	Si (mg/g)
<i>Acer Saccharum</i> <sup>1</sup>	5.60
<i>Betula alleghaniensis</i> <sup>1</sup>	1.40
<i>Fagus grandifolia</i> <sup>1</sup>	7.24
<i>Abies balsamea</i> <sup>1</sup>	0.07
<i>Betula</i> <sup>2</sup>	1.65
<i>Fagus</i> <sup>2</sup>	6.65
<i>Abies</i> <sup>2</sup>	5.20
<i>Picea</i> <sup>3</sup>	24.3
<i>Larix</i> <sup>3</sup>	22.1
<i>Pseudotsuga</i> <sup>3</sup>	9.90
<i>Abies</i> <sup>3</sup>	5.70
<i>Pinus</i> <sup>3</sup>	2.00
<i>Cedrus</i> <sup>3</sup>	0.90
<i>Taxodium</i> <sup>3</sup>	0.80
<i>Thuja</i> <sup>3</sup>	0.60
<i>Juniperus</i> <sup>3</sup>	0.40
<i>Abies alba</i> <sup>4</sup>	0.60
<i>Juniperus nana</i> <sup>4</sup>	0.70
<i>Larix decidua</i> <sup>4</sup>	10.90
<i>Picea abies</i> <sup>4</sup>	8.50
<i>Pinus cembra</i> <sup>4</sup>	1.10
<i>Pinus mugo</i> <sup>4</sup>	0.90
<i>Festuca halleri</i> <sup>4</sup>	32.7
<i>Nardus stricta</i> <sup>4</sup>	25.6
<i>Carex sempervirens</i> <sup>4</sup>	22.9

1 - This study (in bold); 2 - Bartoli and Souchier (1978); 3 - Hodson and Sangster (1999); 4 - Carnelli et al. (2001)

birch 13.4. Typically, nutrient levels in leaves are significantly higher than in wood (Hobbie, 1992), as was the case in the samples we measured. Core wood samples from Sleepers River had slightly higher carbon (~ 40%), and significantly lower nitrogen, than leaf samples. Thus, core C/N ratios, ranging between 99 and 183, were

greater than leaf C/N ratios and were similar to the vegetation wood C/N average of 160 from the literature (Vitousek et al., 1988).

**Table 4** Weight percent nitrogen, weight percent carbon, and C/N ratios for leaves and cores sampled in August from Sleepers River watershed W-9.

	% N	% C	C:N ratio
American beech	1.875	33.20	17.7
Yellow birch	2.754	34.03	12.4
Yellow birch	2.297	32.75	14.3
Balsam fir	1.338	36.82	27.5
Balsam fir	1.393	36.65	26.3
Sugar maple	1.708	32.54	19.1
Sugar maple	1.443	31.55	21.9
Sugar maple	1.910	36.94	19.3
Sugar maple	2.005	36.71	18.3
Sugar maple	1.849	33.01	17.9
<b>Avg. Sugar Maple</b>	<b>1.783</b>	<b>34.15</b>	<b>19.2</b>
White ash core	0.421	41.83	99.5
Balsam fir core	0.221	40.46	182.9
Sugar maple core	0.276	43.30	156.9

#### *Leaf C/Si*

C/Si ratios were determined for the ten leaf samples on which %C was measured (Table 5). In sugar maples, C/Si was low (38-47) in leaves from the four smaller trees analyzed and high (99) in the leaves from the one large tree measured. C/Si should be inversely correlated to Si concentration, since carbon makes up the bulk of the leaf mass against which Si concentrations are determined. As expected, the four smaller trees each had a higher Si concentration than did the large tree.

American beech leaf C/Si was similar to that of the maple leaf C/Si from the smaller maple trees, and C/Si was higher in yellow birch leaves than in leaves from any other species measured.

**Table 5** Tree leaf chemistry and diameter at breast height (DBH) for trees sampled in August 2005 from the Sleepers River watershed. Abbreviations are for sugar maple (SM), yellow birch (YB), American beech (AB), and balsam fir (BF).

	DBH (in)	Opal Si (mg/g leaf)	Supernatant Si (mg/g leaf)	Total Si (mg/g leaf)	Ge/Si (μmol/mol)	C/Si	N/Si
SM1	7.6	6.23	0.00	6.23	.035	---	---
SM2	19.1	3.19	0.01	3.20	.046	99	5.34
SM3	17.2	2.47	0.56	3.03	0.031	---	---
SM4	0.6	8.79	0.00	8.79	0.023	42	1.64
SM5	0.6	7.41	0.48	7.89	0.023	47	2.42
SM6	8.6	8.71	0.00	8.71	.031	38	2.30
SM7	5.4	4.98	0.23	5.21	0.025	---	---
SM8	5.4	7.10	0.26	7.36	0.038	44	2.51
SM9	7.5	6.03	0.00	6.03	---	---	---
SM10	5.2	6.48	0.11	6.59	---	---	---
YB1	24.8	1.39	0.01	1.40	0.049	243	19.7
YB2	13.1	1.98	0.03	2.01	0.041	167	11.4
YB3	11.6	1.05	0.00	1.05	---	---	---
AB1	11.8	7.17	0.07	7.24	0.053	46	2.59
AB2	15.6	6.03	0.00	6.03	0.080	---	---
AB3	6.1	8.49	0.06	8.55	---	---	---
BF1	7.6	0.00	0.15	0.150	0.34	2440	89.2
BF2	5.1	0.01	0.015	0.025	--	15000	560
BF3	5.1	0.02	0.011	0.031	--	12000	450
<b>SM Avg.</b>	<b>7.7</b>	<b>6.14</b>	<b>0.16</b>	<b>6.30</b>	<b>0.033</b>	<b>54</b>	<b>2.84</b>
<b>YB Avg.</b>	<b>16.5</b>	<b>1.47</b>	<b>0.02</b>	<b>1.49</b>	<b>0.045</b>	<b>205</b>	<b>15.6</b>
<b>AB Avg.</b>	<b>11.2</b>	<b>7.23</b>	<b>0.04</b>	<b>7.27</b>	<b>0.067</b>	<b>46</b>	<b>2.59</b>
<b>BF Avg.</b>	<b>5.9</b>	<b>0.01</b>	<b>0.060</b>	<b>0.070</b>	<b>0.340</b>	<b>9800</b>	<b>366</b>

### *Leaf Ge/Si*

Ge/Si ratios in plant leaf phytoliths from Sleepers River ranged from 0.023 to 0.080  $\mu\text{mol/mol}$  (Table 5). The highest values were for American beech, while sugar maples averaged 0.046. These ratios are on the same order as those observed in Hawaiian phytoliths (Derry et al., 2005) and show the expected fractionation of Ge and Si noted previously (Kurtz and Derry, 2004; Derry et al., 2005). Dissolution of these phytoliths, once integrated into the soil, should provide a low-Ge/Si, high-Si source of water for soil solution and stream water.

### *Leaf N/Si*

Leaf N/Si ratios can be used to compare relative transpiration rates of different trees because Si deposition in leaves is controlled primarily by transpiration, while leaf N concentration has additional controlling mechanisms. Assuming these other controls on N concentration are similar among all species, leaf N/Si ratios should be directly correlated to transpiration rate; low N/Si ratios should be indicative of trees with low transpiration rates, while trees with higher rates of transpiration should have higher N/Si. According to the N/Si data in Table 5, balsam fir likely had the lowest transpiration rates of the dominant species at Sleepers River, while American beech and sugar maple appear to have had the highest rates. Thus, the differences in leaf Si concentration among the dominant species could be caused by transpiration rate variations rather than by Si exclusion or accumulation during uptake.

### *Wood silicon*

Si concentrations in core wood were consistently low, relative to leaf Si, among tree species at Sleepers River. The measured values of 0.1 to 0.2 mg/g are within the range of concentrations measured in trees at other sites (Markewicz and

Richter, 1998; Carnelli, 2001). C/Si ratios in the wood varied from 2000 to 4000. These ratios are dependent mostly upon Si concentrations, as carbon composes roughly 40% of all samples.

## **Soil Chemistry**

### *Water-extractable silicon*

Silicon extracted from soil from the Sleepers River watershed varied with depth. Concentrations were highest in the surface litter and decreased with depth until about 40 cm below the surface. Then, from 40 cm to the bottom of the sampled soil profile (~70 cm), Si increased slightly. This trend compares favorably to unpublished USGS data from Sleepers River (Figure 5). While the amount of Si extracted from the soil differs between the two data sets, the pattern of Si versus depth is similar. These qualitative similarities are more important than the differences in absolute concentration with depth because small variations in water-extraction methodology (e.g., amount of time the soil is in contact with water, amount of water added, intensity of centrifugation, etc.) can create differences in the amount of Si extracted. Therefore, as long as the extraction procedure is consistent for all samples within a study, the differences in relative concentration of those samples are significant, while the differences in absolute concentration between studies using slightly different methodologies may not be.

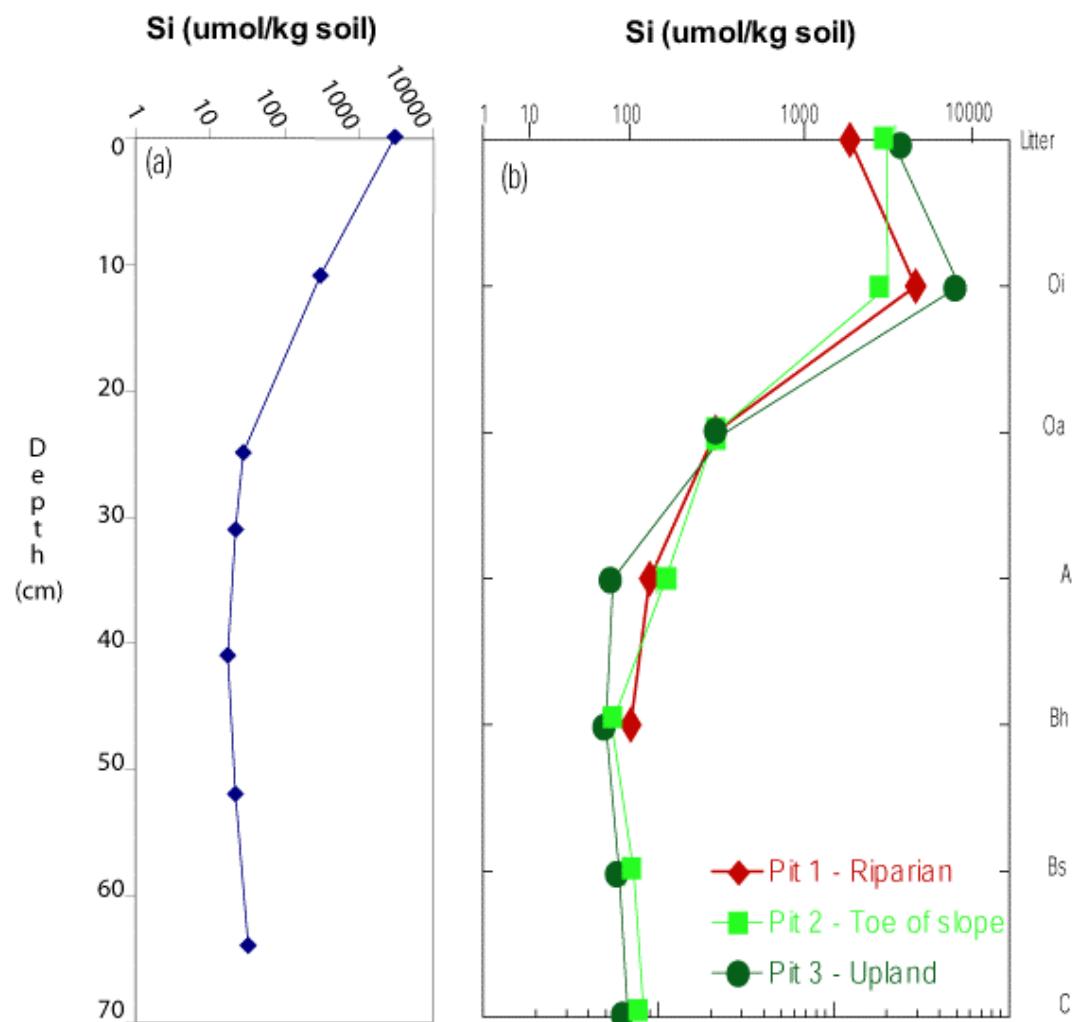
The relatively high levels of water-extractable silicon in the litter and organic horizon indicate the presence of a shallow reservoir of Si. This shallow Si is most likely of biogenic origin, as has been observed in other forest systems (Lucas et al., 1993; Alexandre et al., 1997; Meunier et al., 1999; Derry et al., 2005). A shallow pool such as this is expected because of phytolith input to the upper soil from tree litterfall. In the future, closer observation of soil using an optical microscope or SEM could

verify the presence and quantify the abundance of phytoliths in the shallow horizons (Meunier et al., 1999). Deeper in the soil, biogenic Si becomes less prevalent (Alexandre et al., 1997), and most extractable Si is likely derived from mineral weathering. Primary bedrock minerals contain more Si than secondary soil minerals, so a greater amount of Si is typically present closer to the bedrock than in the more highly weathered soil above it. The observed increase in extractable Si from intermediate-depth soils to deep soils is consistent with this explanation.

#### *Water-extractable Ge/Si*

Ge/Si ratios were lowest in the leaf litter ( $0.04 \mu\text{mol/mol}$ ), increased to 0.43 in the organic soil, increased further to 2.6 at 30 cm, and then dropped slightly to less than 1.0 in the deepest soil (Figure 6). Litter Ge/Si was similar to living leaf tissue Ge/Si and is thus consistent with a biogenic input of Si. Organic soil Ge/Si probably represents a mixture of biogenic- and mineral weathering-derived Ge/Si, as some of the phytoliths in the litter would likely have already been dissolved at this depth. The variation in Ge/Si between the deep mineral soil ( $>40 \text{ cm}$ ) and the shallow mineral soil (20-40 cm) is most likely related to the different minerals being weathered at each depth. In the deep soil, Ge and Si are derived from primary mineral weathering, which typically produces waters with low Ge/Si ratios, a result of the preferential incorporation of primary mineral-derived Ge into secondary clay minerals (Murnane and Stallard, 1990). Hence, during weathering of secondary minerals in shallow soils, solutions with higher Ge/Si ratios are generated. Such a scenario could explain the Ge/Si pattern seen in the Sleepers River soil profile.

**Figure 5** Si concentration from water-extracted soil solution plotted vs. soil depth in the W-9 watershed at Sleepers River from (a) this study and (b) previous work by the USGS (Shanley, unpublished data). These trends likely reflect a high-Si phytolith source near the surface, a low-Si source of secondary mineral weathering at intermediate depth, and an increasingly higher Si source as more primary minerals are weathered in the deep soil.



### *Soil carbon and nitrogen*

As anticipated, soil C and N concentrations (Table 6) were highest in the litter and upper soil, where organic matter is prevalent. Nitrogen in these layers is mineralized during decomposition by soil microbes (Hobbie, 1992). As a result, less nitrogen than carbon is present in the soil below this, and the measured C/N ratio in the mineral soil was higher than in the litter or organic horizon, though concentrations of both elements were considerably lower.

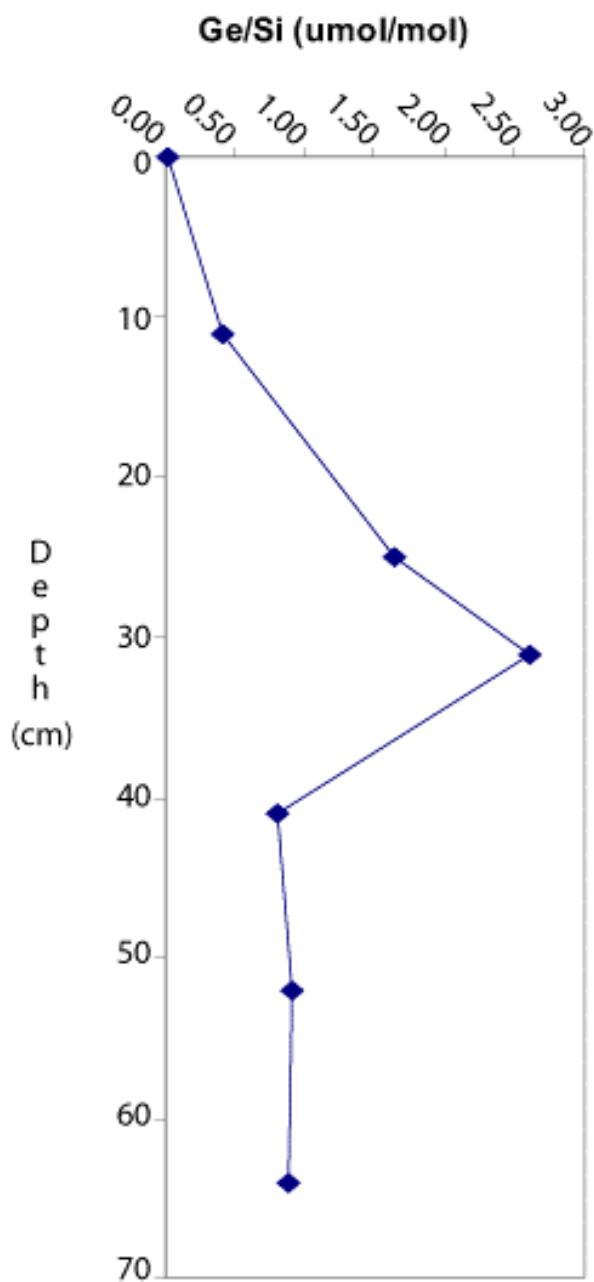
**Table 6** Percent nitrogen, percent carbon, and C/N ratio for soil samples measured on an elemental analyzer. Samples were collected in August 2005.

	% N	% C	C/N ratio
Litter	1.851	28.63	15.5
0-22 cm (organic)	1.195	10.73	9.0
22-27 cm	0.024	0.55	23.3
27-34 cm	0.016	0.51	32.8
34-47 cm	0.020	0.58	28.9
47-57 cm	0.022	0.94	42.7
57-70 cm	0.038	0.78	20.8

### **Sap Chemistry**

There have been few studies published on the chemistry of sugar maple sap. Instead, research has focused mostly on identifying the organic molecules present in the sap (Mollica and Morselli, 1984; Kermasha et al., 1995), or on the effect of heavy metals (Robinson et al., 1989; St. Clair et al., 2003) and soil pH (Perkins et al., 2004) on tree health and sap production. As such, there are no published data on Si levels in maple sap water. Our measurements, on sap sampled in April 2005, showed high Si concentrations in sugar maple sap from Sleepers River trees (Table 7). In fact, Si was up to seven times more concentrated in the sap than in the groundwater. While this might appear to indicate that sugar maples can act as Si accumulators (i.e., taking up

**Figure 6** Ge/Si ratios in water-extracted soil solution from a range of depths in the W-9 watershed at Sleepers River. The observed pattern is characteristic of phytolith dissolution near the surface, secondary mineral dissolution at intermediate depth, and primary mineral dissolution in the deepest soil.



Si at a greater rate than water), xylem and phloem water are known to contain Si levels many times that of the soil solution, regardless of plant species (Hull, 2004). The apparent increased concentration of Si in the sap may instead be related to the transpiration of water from the tree, concentrating the chemical species dissolved in the remaining sap.

Sugar maple sap water Ge/Si ratios averaged 0.076  $\mu\text{mol/mol}$  and ranged from 0.043 to 0.123 (Table 7). Ge/Si ratios have not previously been measured on maple sap water, so there is no data from other studies to which these results can be compared. However, the sap Ge/Si ratios were of the same magnitude as sugar maple leaf phytolith Ge/Si (0.076 and 0.046, respectively) and were 1-2 orders of magnitude lower than soil water Ge/Si, and had thus already been fractionated. The mechanism of plant Ge/Si fractionation is currently under debate and has been argued to occur either during plant uptake of water, during opal phytolith formation, or at some point in between. Evidence from the Sleepers River sap supports plant Ge/Si fractionation during uptake, or soon after uptake, rather than during phytolith formation, since Ge and Si in the sap had already been fractionated and had not yet been incorporated into phytoliths.

Also included in Table 7 are data for other elements measured in the sap, including Sr, Ca, K, and Mg, the latter three of which are considered important nutrients for sugar maple health (Horsely et al., 2002). Like Si, all three of these elements were significantly more concentrated in the sap than they typically are in soil water (Johnson et al., 1999). Ca, K, and Mg were all present at concentrations comparable to Si, while Sr was two orders of magnitude less concentrated. Two of the tapped trees are located on calcium-rich soil (RHW 2063A and 2063B), while two others are located on calcium-poor soil (PHW 5143 and 5126). Not surprisingly, there was a distinct difference in Ca in the sap water from these trees (average of 2.57

**Table 7** Sugar maple sap water chemistry for samples obtained in April 2005 from the Sleepers River watershed.

Tree ID	Si mM	Ge/Si $\times 10^{-6}$	Ca mM	Mg mM	K mM	Sr $\mu\text{M}$	Ca/Sr $\times 10^3$	Ca/Mg
RHW 2063A	0.72	0.066	2.75	0.39	3.34	3.82	0.20	7.01
RHW 2063B	0.68	0.123	2.39	0.39	3.20	3.63	0.58	6.18
New MR #1	0.62	0.079	1.17	0.19	1.94	1.59	0.36	6.06
New MR #2	0.52	0.085	3.09	0.45	3.56	4.35	0.10	6.81
PHW 5143	0.61	0.059	1.58	0.34	1.92	3.07	0.52	4.63
PHW 5126	0.63	0.087	1.41	0.23	2.21	2.87	0.49	6.24
TH 5970	0.62	0.067	1.22	0.28	2.28	2.22	0.55	4.44
TH 5784	0.72	0.043	1.70	0.28	2.41	3.06	0.56	6.14
<i>Average</i>	<b>0.64</b>	<b>0.076</b>	<b>1.91</b>	<b>0.32</b>	<b>2.61</b>	<b>3.08</b>	<b>0.62</b>	<b>6.90</b>

versus 1.50 mol/L for the RHW and PHW, respectively). Interestingly, Sr, which acts as pseudo-isotope of Ca (a relationship analogous to that of Ge and Si), varied relatively less between the two sites than did Ca. The average Ca/Sr ratios of the two sites were  $0.69 \times 10^3$  and  $0.50 \times 10^3$  for RHW and PHW, respectively. It is worth noting that Ca/Sr ratios, like Ge/Si, appear to be fractionated during plant uptake, with discrimination against Sr relative to Ca (Poszwa et al., 2000; 2004). However, while this indicates that Ca/Sr ratios are probably lower in the soil than in the sap at both sites, it does not, by itself, explain the discrepancy in ratios between the two sites. Perhaps Ca cycling by vegetation (and therefore Ca/Sr fractionation) is more rapid in the PHW site than in the RHW site, leading to a lower Ca/Sr ratio in the PHW soil. Ca/Si ratios in the water taken up by trees at PHW would thus be lower than ratios in water from RHW, and the fractionated values in the sap water would also be lower. Ca/Mg ratios were constant between six and seven for most trees. The ratio, though, dropped to 4.63 in PHW 5143, suggesting that this tree has access to a source of Mg -- perhaps the weathering products of dolomite -- that is not available to the other trees. Finally, K varied similarly to Ca between the RHW and PHW sites.

## Water Chemistry

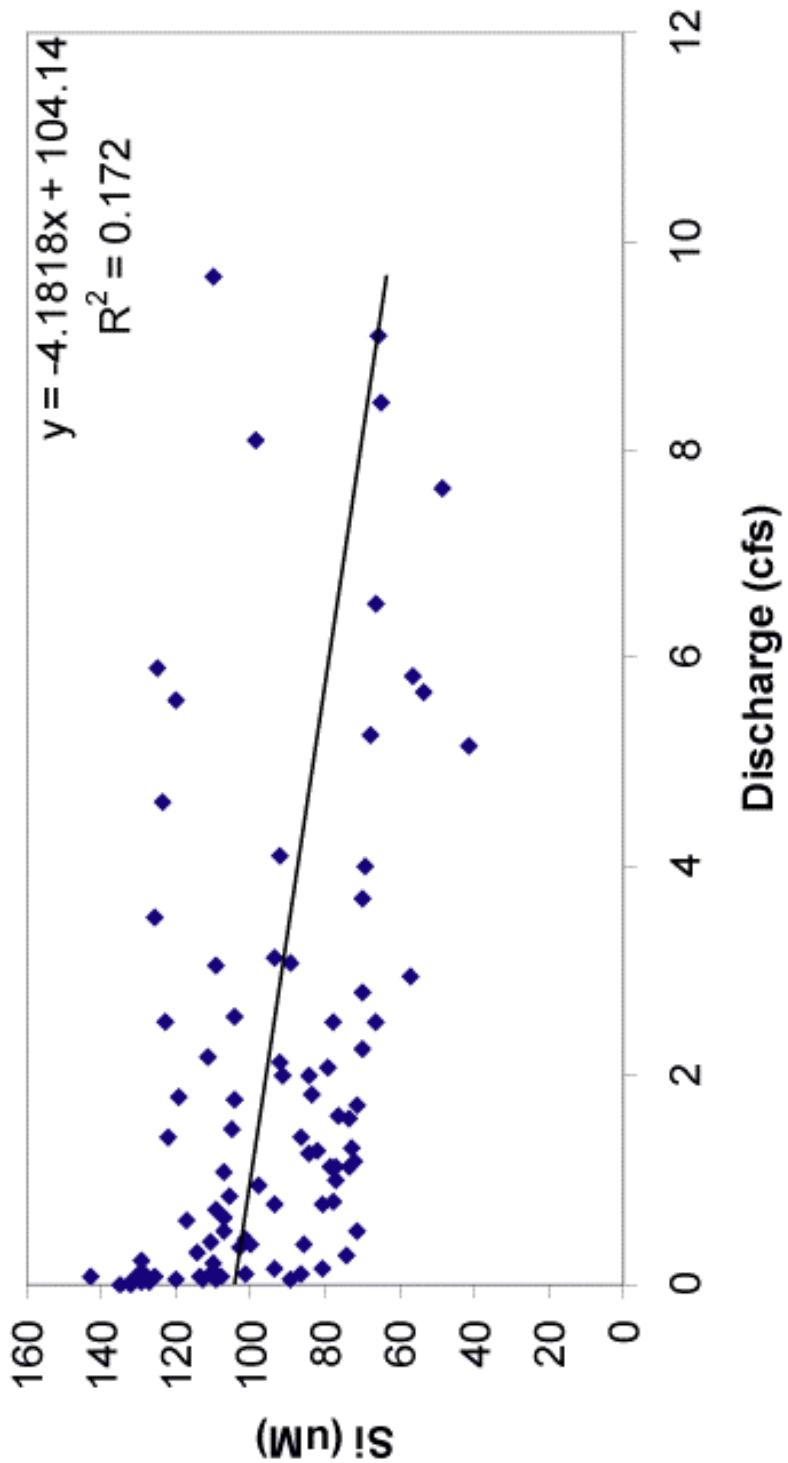
### *Stream water silicon*

Measured stream water Si concentrations ranged from 40 to 140  $\mu\text{M}$ . The general pattern observed in stream Si was a decrease in concentration with increasing discharge (Figure 7), which was at least partly due to dilution effects. The trend is more significant when only data points of samples taken following dry periods were included (Figure 8). This plot excludes samples taken at high discharge with high Si concentrations. Most stream flow at high discharge comes from one of three sources: overland flow, direct channel precipitation, or soil water that is flushed into the stream by infiltrating rainwater. The first two are typically low in Si, while the latter can contain significant amounts of Si (Buttle and Peters, 1997; Scanlon et al., 2001). Therefore, following wet intervals, soil water input to Sleepers River appears to be significant and results in stream flow with high discharge and relatively high Si, as we observed. For storm events preceded by dry periods, either soil water did not contribute as significantly to high discharge stream flow, or the soil water that did contribute had lower Si concentrations due to a shorter residence time in the soil (i.e., the soil water originated as precipitation during that particular storm instead of during a previous storm, as would be the case for events preceded by wet periods). During dry periods at Sleepers River, groundwater is the primary source of water to stream flow (Shanley, 2002). We saw generally high Si in samples collected during low flow, consistent with this predicted groundwater-dominated input. However, past research at Sleepers River has not examined the impact of phytolith-derived Si on stream water chemistry, and thus we cannot rule out the possibility that the dissolution of phytoliths also contributed to the high Si we measured at low flow.

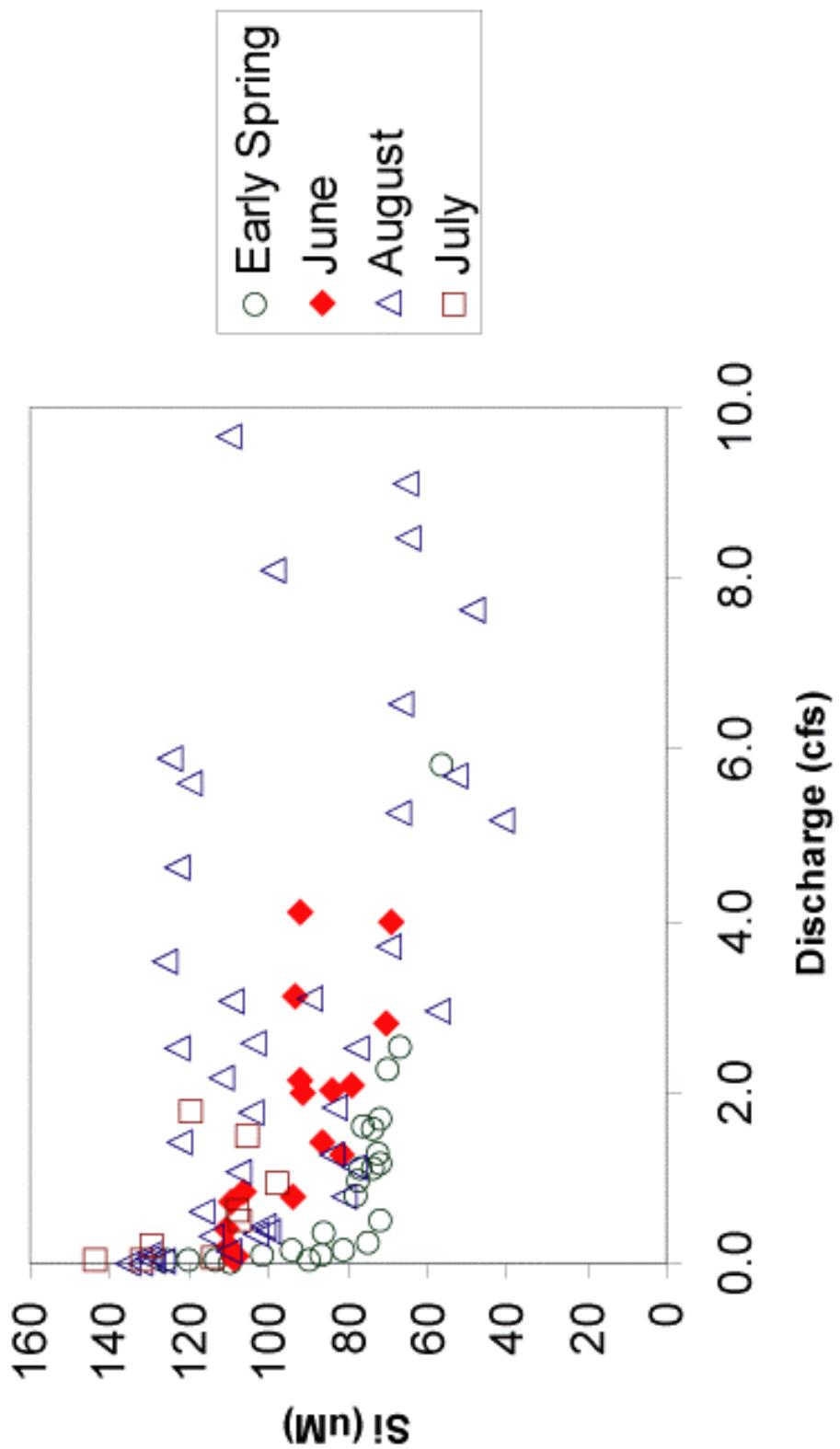
*Stream water Ge/Si*

In general, stream water Ge/Si ratios increased with increasing discharge (Figure 9). The high Ge/Si ratios at high discharge are consistent with Ge/Si ratios in soil water obtained from the weathering of secondary clay minerals in other studies (Mortlock and Froelich, 1987; Murnane and Stallard, 1990; Kurtz et al., 2002). Data from rivers tend to form arrays on Ge/Si vs. Si (or 1/Si) plots, which have been interpreted to represent a mixture of sources, usually between primary and secondary mineral weathering or between mineral weathering and phytolith dissolution (Froelich et al., 1985; Evans et al., 2004; Derry et al., 2005). A plot of Ge/Si against Si from Sleepers River (Figures 10 and 11) reveals a more complex mixing relationship, suggesting that the Si in Sleepers River water has more than two source areas. There are several possible explanations for this observation; the two most plausible will now be discussed. One is that the stream water is a three-component mixture of shallow soil water carrying dissolved biogenic Si, intermediate soil water carrying dissolved Si from secondary mineral weathering, and groundwater carrying dissolved Si from primary mineral weathering. Examination of water-extractable Ge/Si from the soil at Sleepers River (Figure 6) shows the probable depth of these three Si source areas in this watershed. At the time of data collection, the high Ge/Si component was ~30 cm below the surface, the low Ge/Si component was at the surface, and the intermediate Ge/Si component was in the deepest soil. The high Ge/Si at high discharge could have then been due to the flushing of high-Ge/Si soil water, while the low Ge/Si at low discharge might have been caused by some combination of biogenic Si dissolution and base flow bedrock weathering. However, more data on the Ge/Si ratios of phytoliths in the soil, soil minerals, and bedrock minerals are needed to better constrain the source area chemistry and determine the likelihood of this scenario. Another possible explanation is that soil water Ge/Si differs throughout the watershed

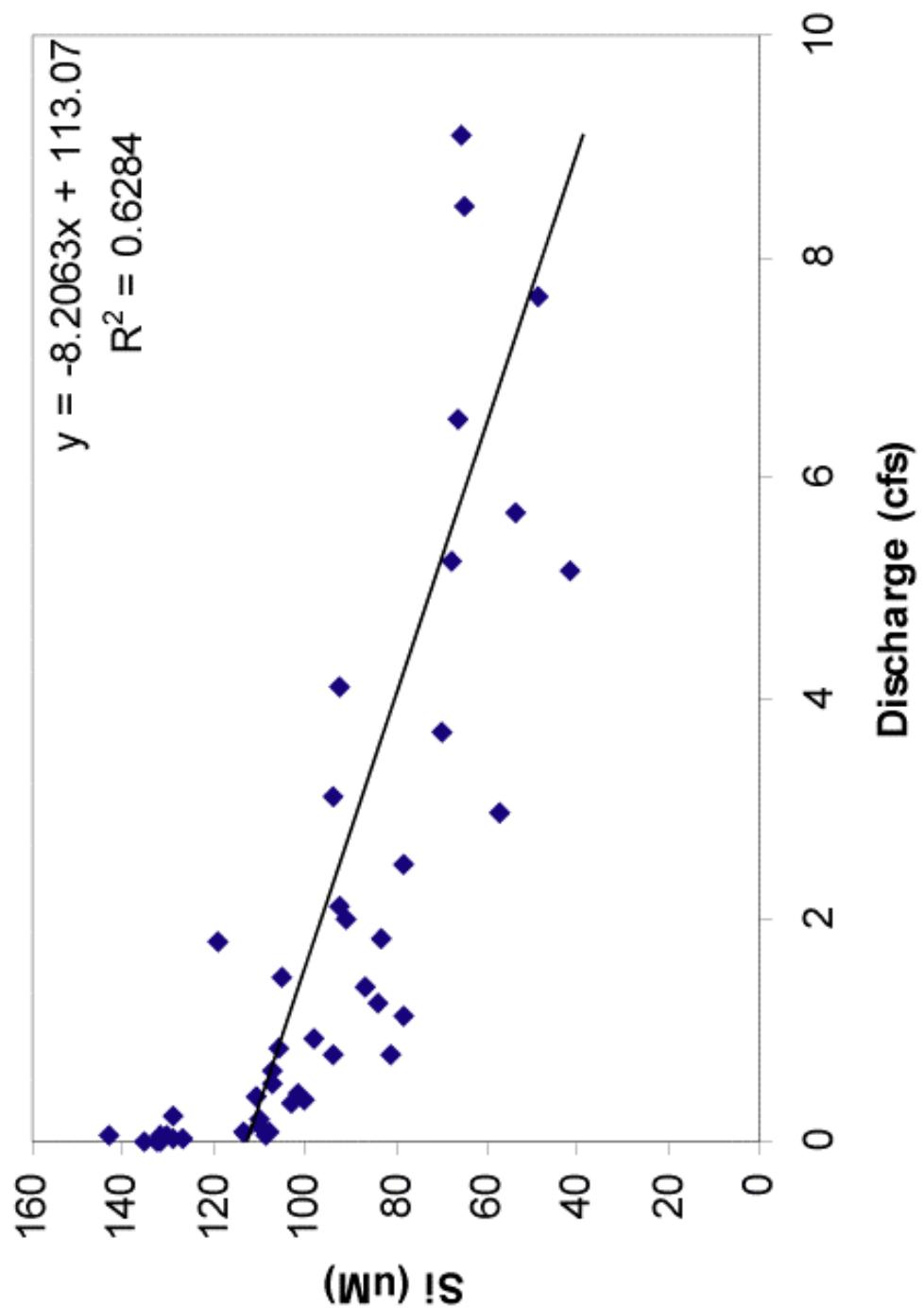
**Figure 7** Si concentration of stream water plotted against stream discharge for samples collected from the W-9 weir at Sleepers River during the 2005 growing season. Si concentrations in the stream water decrease as discharge increases ( $P < 0.01$ ).



**Figure 8** Data from Figure 7 separated by collection date. Si concentrations decrease with increasing discharge in samples from all dates, though concentrations are lowest early in the spring and are highest in July and August. June sample concentrations are intermediate.



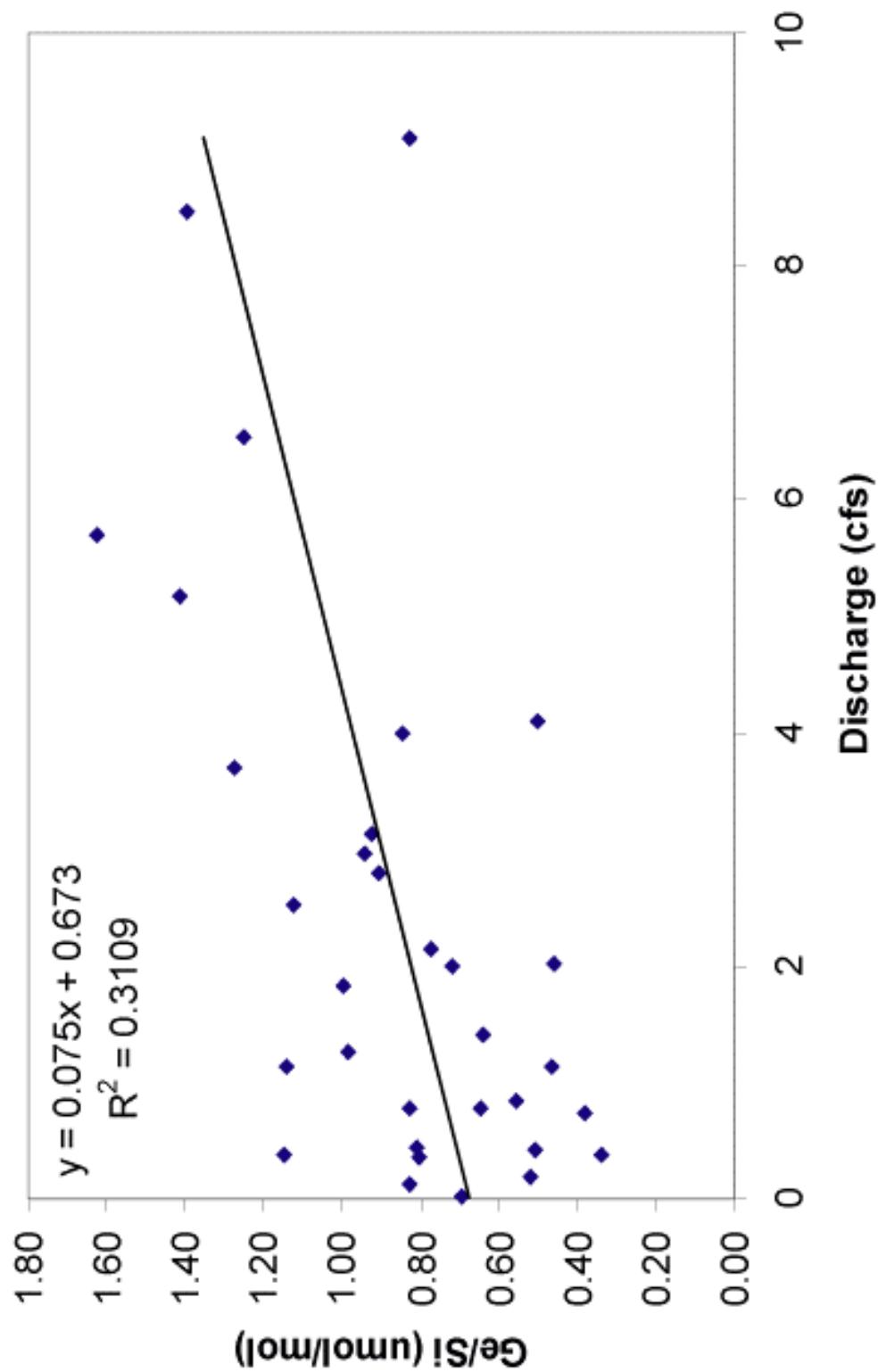
**Figure 9** Si concentration of stream water plotted against stream discharge for samples collected following dry periods (defined as less than 0.1 inches of rain in the previous five days). Samples obtained during rainstorms after dry periods were included in the plot. This plot exhibits a better-defined trend of decreasing Si at higher discharges than in Figure 7 ( $P < 0.01$ ). Note that the trend is logarithmic, rather than linear, as Si concentrations drop rapidly with small increases in discharge at lower discharge rates and drop more slowly with large increases in discharge at higher discharge rates.



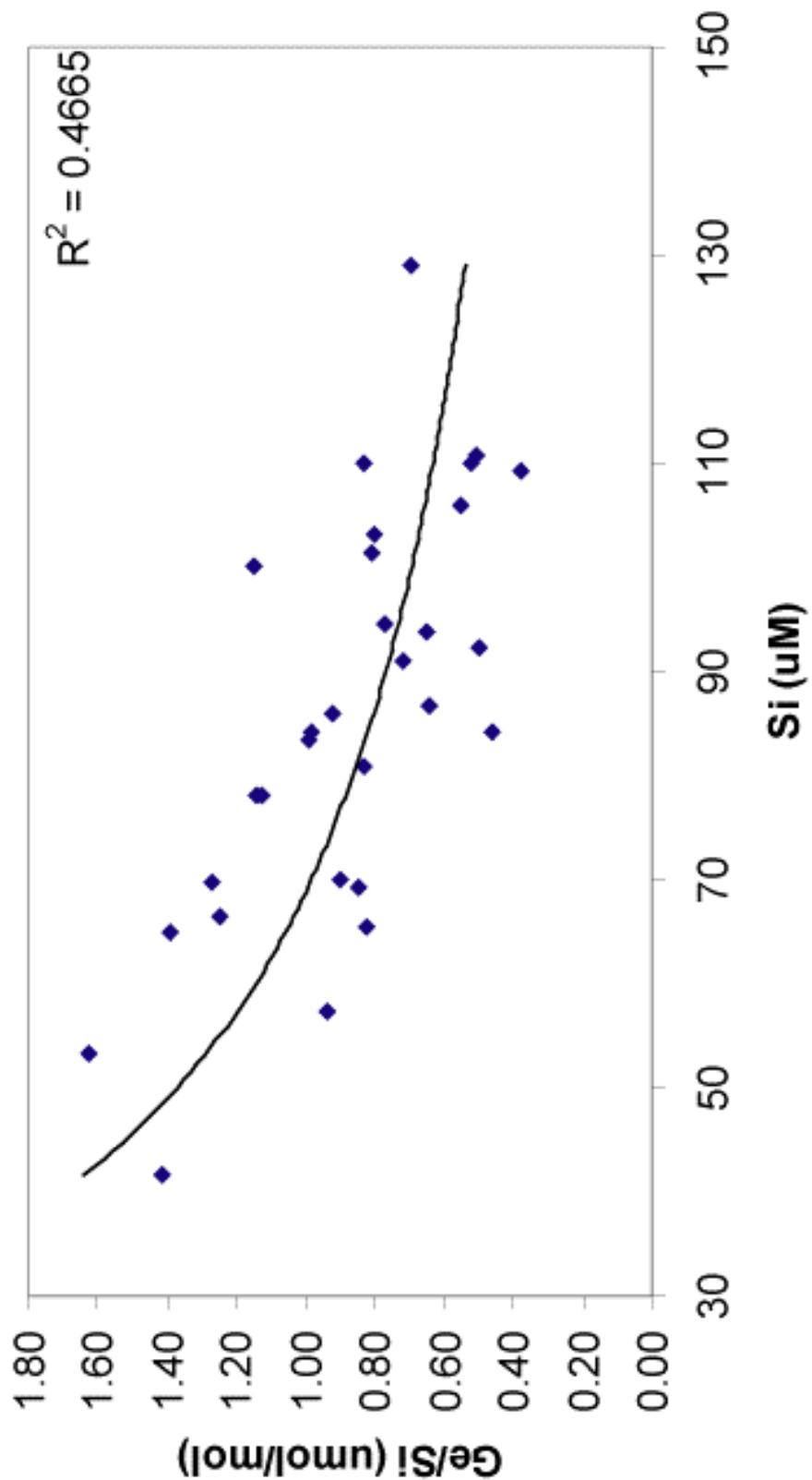
due to spatial variations in soil mineralogy. This situation could arise as a result of the soil at Sleepers River forming partly from the weathering of heterogeneous metamorphic bedrock (for comparison, Hawaiian soil forms from a homogeneous basalt). Consequently, soil chemistry and mineralogy could differ from what was due more to seasonal effects than to stream water source area. A similar (but more pronounced) shift was seen in the shallow lowland lysimeter water, in which Ge/Si increased from a ratio of ~0.4 in June to ~1.2 in August. The observed temporal trend of Ge/Si in the stream water might be related to a change in the amount of phytolith-derived Si in stream water between June and August. Based on water-extractable Ge/Si from the soil (Figure 6), only the phytolith-rich surface soil had Ge/Si low enough to produce the observed Ge/Si in the stream water in June. In August, however, there appeared to be a larger contribution of mineral-derived Si to the stream water, and little, if any, contribution from phytolith dissolution. The shift away from a biogenic Si source might be associated with a large-scale seasonal trend, such as the change from a wet spring to a dry summer. The typically high levels of precipitation in the spring could increase phytolith dissolution in the shallow soil, with the resulting low-Ge/Si water contributing to stream flow. Later in the summer, when precipitation decreases, less water infiltrates the shallow phytolith-rich soil, so less biogenic Si enters the stream water. An analysis of stable oxygen and hydrogen isotopes, which would help define the stream water source area and age (Kendall et al., 1995), should strengthen these claims regarding the seasonal water cycle at Sleepers River.

A second possible cause of the seasonal increase in Ge/Si is the continuous fractionation of Ge/Si ratios by plant uptake throughout the growing season. If plants preferentially take up Si over Ge, then the Ge/Si ratio in the soil solution should gradually increase during the year. Thus, we would expect Ge/Si ratios to be higher in

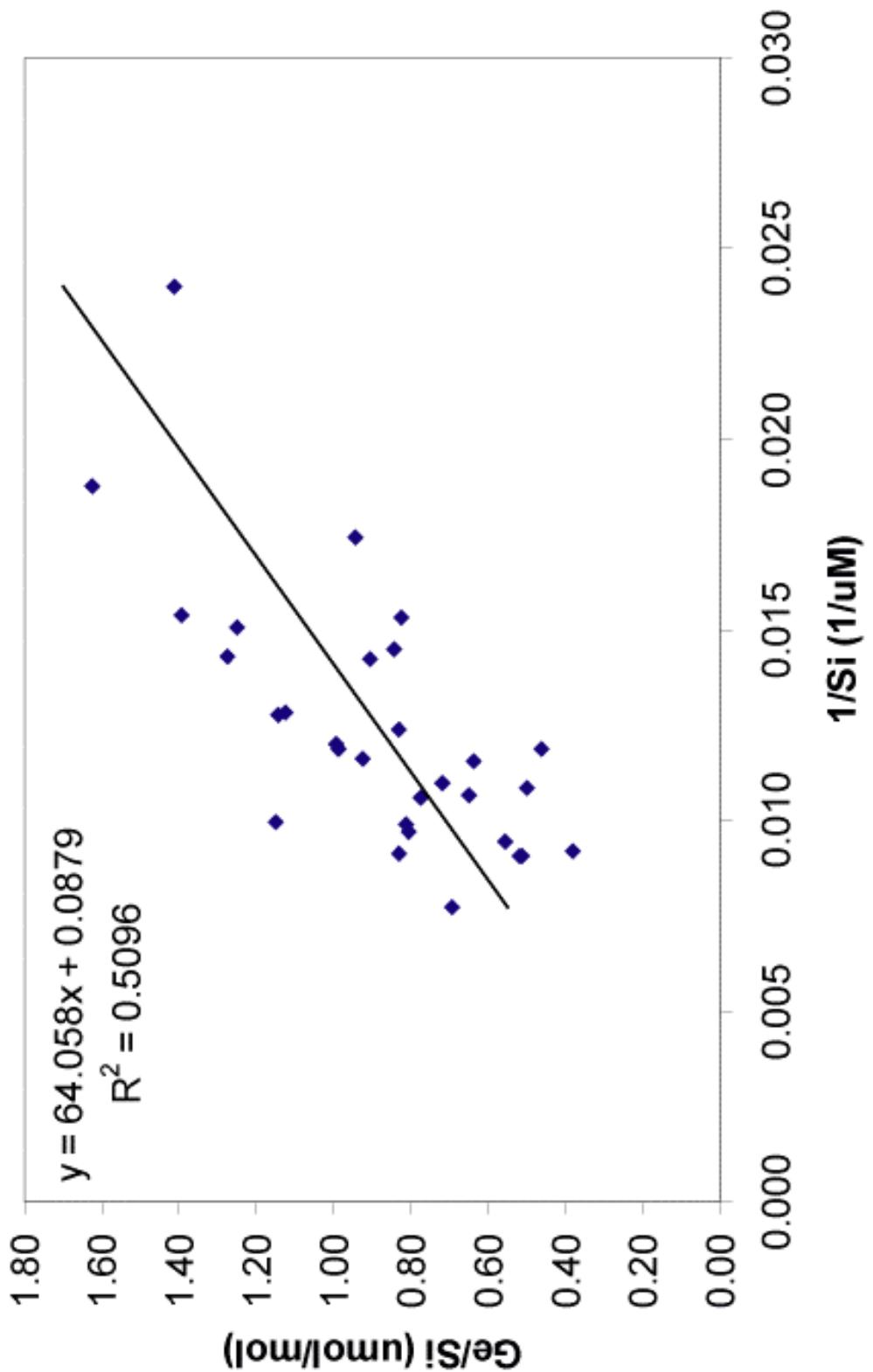
**Figure 10** Stream water Ge/Si plotted against discharge from the W-9 weir at Sleepers River in 2005. Ge/Si is positively correlated with discharge ( $P < 0.01$ ), indicating a switch in source from biogenic Si and groundwater to soil water during high discharge.



**Figure 11** Ge/Si vs. Si concentration for stream water from the W-9 weir in Sleepers River in 2005. The data represent a complex mixture of sources, as they do not fit along a common curve.



**Figure 12** Stream water Ge/Si plotted against 1/Si, which linearizes the relationship in Figure 10. Assuming a phytolith solution Si concentration equal to the phytolith solubility Si concentration of 1800  $\mu\text{M}$  (Fraysse et al., 2004) gives a phytolith solution Ge/Si of 0.125. This value is 2-3 times higher than the measured phytolith Ge/Si in Sleepers River leaves, indicating that either the trend line does not closely enough represent the data (i.e., the mixture of sources in complex), or that phytolith dissolution is not a primary control on stream Ge/Si.

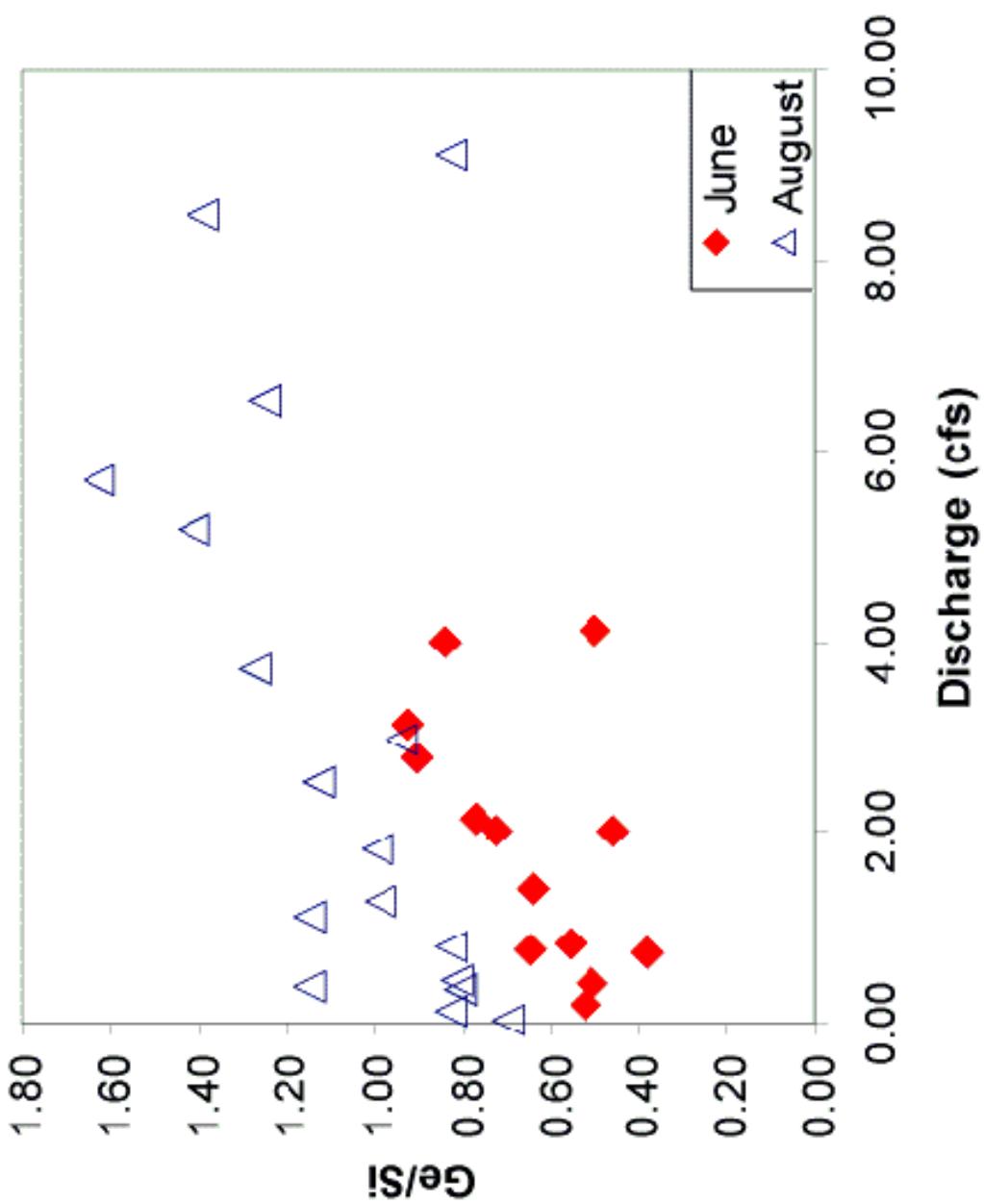


the soil water and stream water in August than in June, which is what we observed in the Sleepers River samples. However, the extent to which this fractionation affects Ge/Si ratios depends on the degree of fractionation and the size of the pool of Si and Ge from which the trees are drawing. The plausibility of this scenario is discussed later.

#### *Stream water hysteresis*

Stream water source areas can also be derived using geochemical hydrograph separations (Swistock et al., 1989; Wels et al., 1991), using the principle that water from different sources has different chemical signatures. Variations in stream water chemistry often display a cyclical relationship with discharge (Evans and Davies, 1998). This cyclical pattern, known as hysteresis, occurs when the concentration of a chemical tracer at a particular discharge on the rising limb of the hydrograph differs from the concentration at the same discharge on the falling limb. A line connecting the data points on a concentration-discharge plot would therefore form a loop, and the path of this loop (e.g., clockwise or counterclockwise) can be used to determine the changes in stream water source with varying discharge. Si has been used as a tracer of stream water source area in numerous studies (Wels et al., 1991; Buttle and Peters, 1997; Scanlon et al., 2001; Fulweiler and Nixon, 2005). In these, a typical sequence of stream water source, beginning immediately before a storm event, is as follows: base flow (groundwater source, high Si), followed by overland flow (rainwater source, low Si), then shallow subsurface storm flow (soil water source, intermediate Si), and back again to base flow (Buttle and Peters, 1997; Scanlon et al., 2001). Such a sequence produces a counter-clockwise hysteresis loop (higher Si concentration on the falling limb than on the rising limb). Different conditions would, of course, lead to different hysteresis loops. For example, wet antecedent conditions might cause

**Figure 13** Ge/Si versus stream discharge for the Sleepers River W-9 watershed in 2005. Data are separated based on collection date. Samples collected in August have higher Ge/Si than samples collected at the same discharge in June. This might be related to a decrease in the flux of biogenic Si to the stream in August, when precipitation rates are lower.



overland flow to become active earlier during the rising limb of the hydrograph, accentuating the hysteresis effect. Wet antecedent conditions can also result in a larger percentage of soil water contributing to stream discharge (Swistock et al., 1989).

There are many assumptions made when using hydrograph separations. One of the most critical is that the chemical concentrations assigned to the source areas remain constant over the analytical period (Scanlon et al., 2001). Using a tracer also requires that the chemical signatures of each source area be distinct, and that the tracer behave conservatively during mixing of the compartments (Wels et al., 1991). Furthermore, it is important that the tracer concentration be independent of the residence time of the water (Wels et al., 1991). Si has been shown to violate some of the above assumptions. For example, Buttle and Peters (1997) demonstrated that Si concentrations in the different source areas are not necessarily distinct from one another: overland flow is sometimes indistinguishable from subsurface water, and water from all source areas displays some amount of spatial variability. Additionally, seasonal Si variations can occur, as water residence time in different soil zones can vary, and short-term fluctuations in permanent water table levels can lead to fluctuation in the groundwater dissolved Si signature (Scanlon et al., 2001). For these reasons, using Ge/Si ratios (which do not violate the aforementioned assumptions), in conjunction with Si concentrations, is a better way of analyzing hysteresis patterns in stream flow.

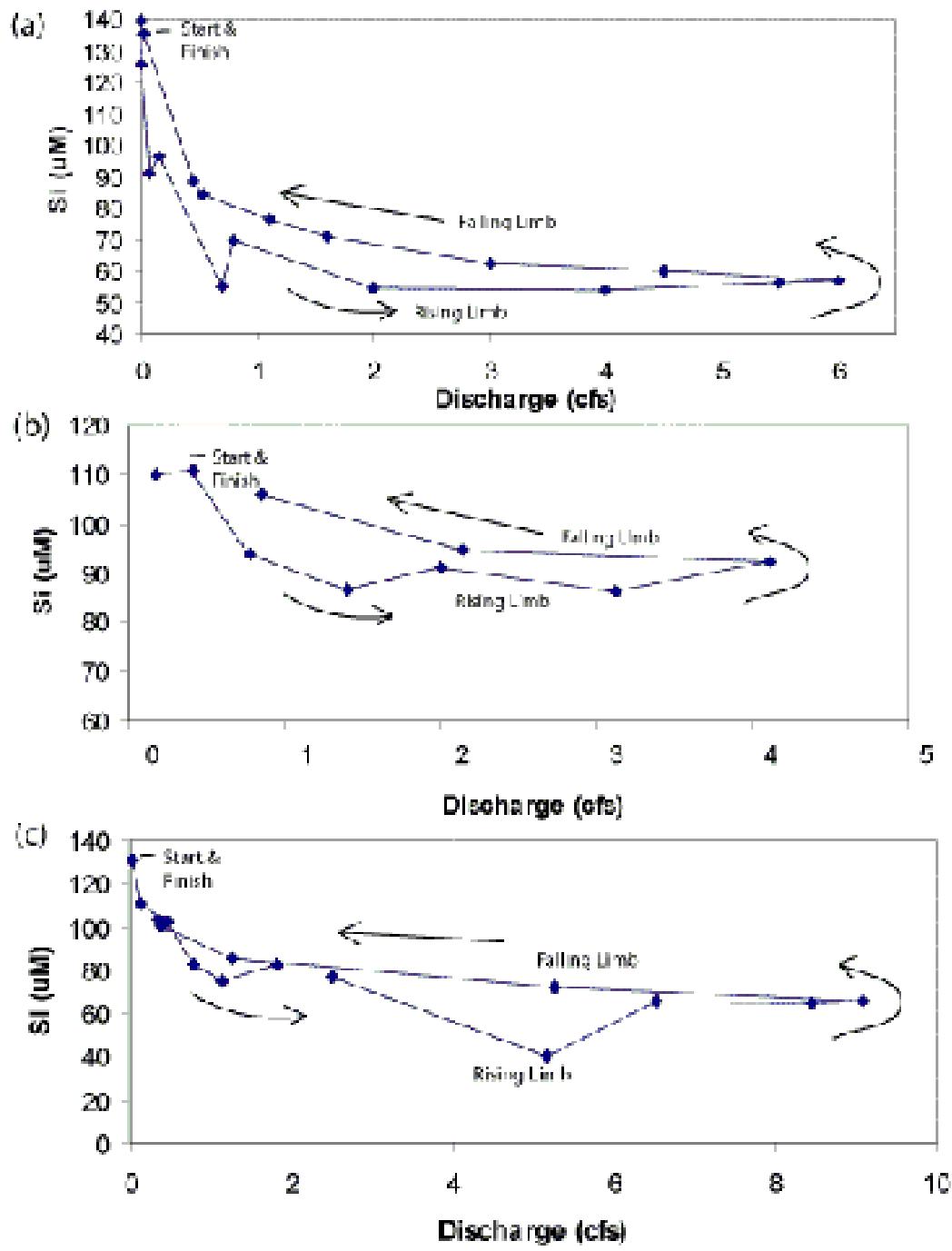
Hydrograph separations for three storm events at Sleepers River all show counterclockwise hysteresis in the Si versus discharge plots (Figure 13) and clockwise hysteresis in the Ge/Si versus discharge plots (Figure 14). Similar patterns were observed at storm events in Puerto Rico (Kurtz and Derry, 2004). We offer two scenarios as possible explanations for the observed patterns. In the first, as suggested

by Buttle and Peters (1989), groundwater (low Ge/Si and high Si) is the only source of water to the stream during base flow. In the early stages of a storm event, overland flow (high Ge/Si (?), low Si) begins to contribute to the stream discharge. As the storm continues, there is input to the stream from soil water (intermediate Ge/Si and Si) that has been flushed out of the soil and replaced by new rainwater. After the storm ends, groundwater input again dominates stream flow. The other scenario begins with combined base flow input from groundwater (low Ge/Si, high Si) and dissolved phytoliths (lower Ge/Si, higher Si), followed this time by input dominated by soil water (high Ge/Si, low Si) flushed out of the soil by infiltrating precipitation, and then by input dominated by shallow soil water and overland flow carrying the dissolved products of phytoliths, once again concluding with base flow input of groundwater and dissolved phytoliths. The second scenario is probably more accurate, as it takes into account the impact of phytolith-derived Si, which has only been considered in one previous hydrograph separation (Kurtz and Derry, 2004). In the future, when Sleepers River source area Ge/Si has been better defined, we will be able to derive more meaning from the hydrograph separations. Also of note is that the June hysteresis loop has a lower overall Ge/Si than the August hysteresis loop (Figure 14), again showing that dissolved phytoliths might contribute more significantly to stream chemistry in June than in August.

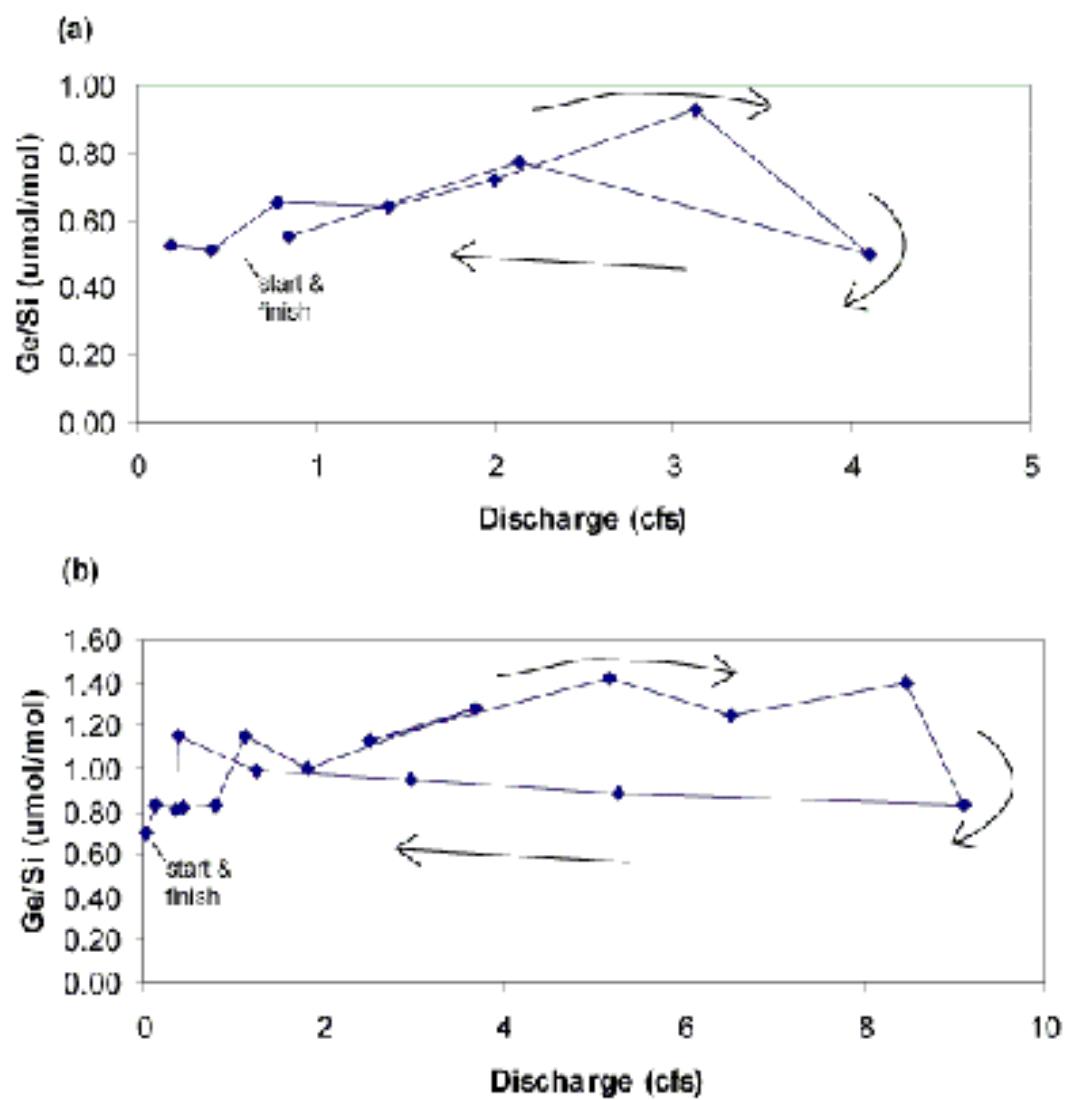
#### *Soil water and groundwater silicon*

Lysimeters and wells can be used to gather data on nutrient dynamics within the soil profile (Bormann and Likens, 1967). We obtained water samples from five soil lysimeters and four wells at Sleepers River (Table 8) and analyzed them for Si. The lysimeters are located at various elevations on a hill slope and are split into three groups: lowland, midland, and upland. Each group contains lysimeters at different

**Figure 14** Counterclockwise hysteresis observed during three storms -- (a) 9/15/2002; (b) 6/14/2005; (c) 8/21/2005 -- at the Sleepers River W-9 weir. At any given discharge on the rising limb of the hydrograph, Si concentration is lower than at the same discharge on the falling limb. Such a pattern is typical of sites in which groundwater Si concentration is greater than soil water Si concentration, which is, in turn, greater than surface event flow Si concentration.



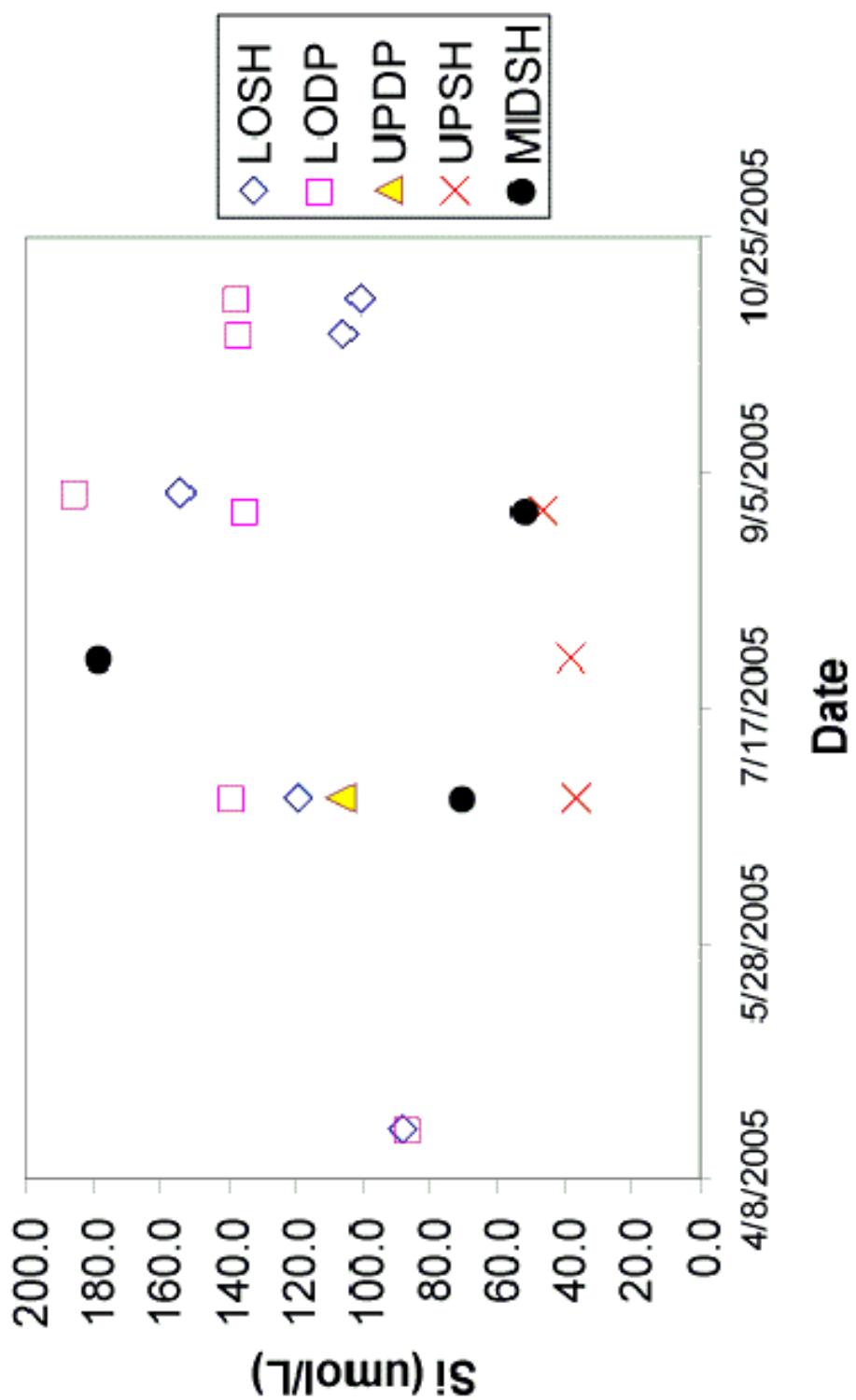
**Figure 15** Clockwise hysteresis in Ge/Si versus discharge plots for two 2005 storms -  
- (a) 6/14/2005; (b) 8/21/2005 -- at Sleepers River. Stream water Ge/Si is higher  
during the rising limb of the hydrograph than during the falling limb, possibly  
indicating a higher flux of soil water early in the storm, followed by an increased flux  
of biogenic silica.



depths. Wells are located at various depths and elevations throughout the watershed. Lysimeter water Si varied unpredictably throughout the growing season (Figure 15). On two of the dates the lowland lysimeters were sampled, the Si concentration in LOSH water was lower than in the LODP water. However, in the April samples, Si was approximately equal at both depths. Concentrations in water from both lysimeters increased throughout the summer. Of the two upland lysimeters sampled, the UPSH water had extremely low Si throughout the summer, with the UPDP water containing about three times the Si present in the UPSH water in June, the only date the deep one was sampled. However, the silicon concentration in the UPDP water was still lower than either of the lowland lysimeter waters on that date. The one midland lysimeter sampled (MIDSH) contained water with intermediate levels of Si compared to the upland and lowland lysimeters in June and August. In July, however, its Si was among the highest levels measured in the soil water on any date.

Si was measured in water from four wells at Sleepers River (Figure 16). Only one of these wells, BW 39A, was sampled on more than one occasion, and, much like the lysimeter water, Si concentrations in the water from this well increased throughout the summer. The Si concentrations in this water were higher than those in water from any other lysimeter or well, probably because it had been in contact with glacial till, where weathering of primary minerals typically leads to high levels of dissolved Si. The other three wells were all sampled on the same day in July, and Si concentration was inversely proportional to sampling depth. This trend is presumably due to subtle variations in mineralogy at each depth, such that weathering of the deeper minerals produced less Si.

**Figure 16** Variation in Si concentration in lysimeters throughout 2005 at the W-9 watershed. While there is no apparent consistent trend among all the lysimeters sampled, Si concentrations do increase in water from both lowland lysimeters (LOSH and LODP) from spring to fall.



**Table 8** Lysimeter and well depths. The following are abbreviations: LYS = lysimeter; BW = well; LO = lowland; MID = midland; UP = upland; SH = shallow; DP = deep; 39A, T-1, T-2, and T-3 are well ID numbers (see Figure 1b for locations).

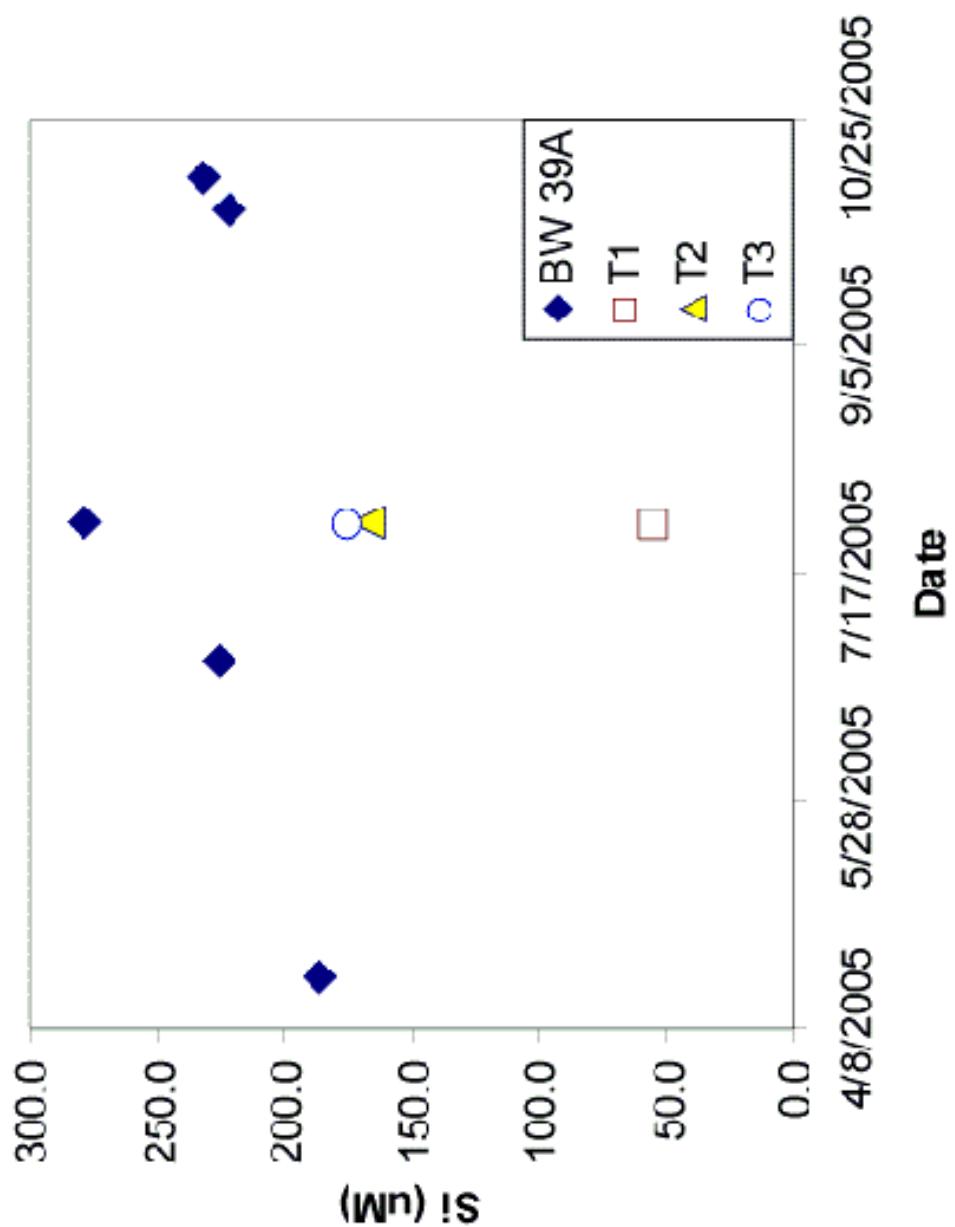
Lysimeter/Well ID	Depth (m)
LYS LOSH	0.10
LYS LODP	0.33
LYS MIDSH	0.08
LYS UPSH	0.10
LYS UPDP	1.12
BW 39A	3.12
BW T-1	2.50
BW T-2	1.77
BW T-3	1.01

*Soil water and groundwater Ge/Si*

Ge/Si ratios were measured in water from the two lowland lysimeters (LOSH and LODP) and the deepest well (BW 39A), as these were sampled more frequently than the other lysimeters and wells. The well contains deep soil water, at 3.30 meters below the surface, in direct contact with glacial till. Because the well water contained the dissolved products of primary minerals from the till, Ge/Si ratios were low, averaging 0.14 (Figure 17). Ge/Si ratios in the lowland lysimeters were more variable, ranging from 0.40 to 1.60 in the shallow lysimeter and from 0.30 to 1.10 in the deep one (Figure 17). Further examination of the lysimeter data reveals that Ge/Si ratios increased during the growing season in both LOSH and LODP water (Figure 18), complementing the seasonal trend observed in the stream water.

It is difficult to draw conclusions about seasonal changes in soil water and groundwater from the lysimeter and well data presented here. Clearly, samples need to be taken more frequently to identify significant trends. However, it does appear

**Figure 17** Well water Si concentrations throughout 2005 at Sleepers River. Si increased during the growing season in BW 39A, before dropping in the fall. In the other three wells, Si concentration was inversely proportional to depth.



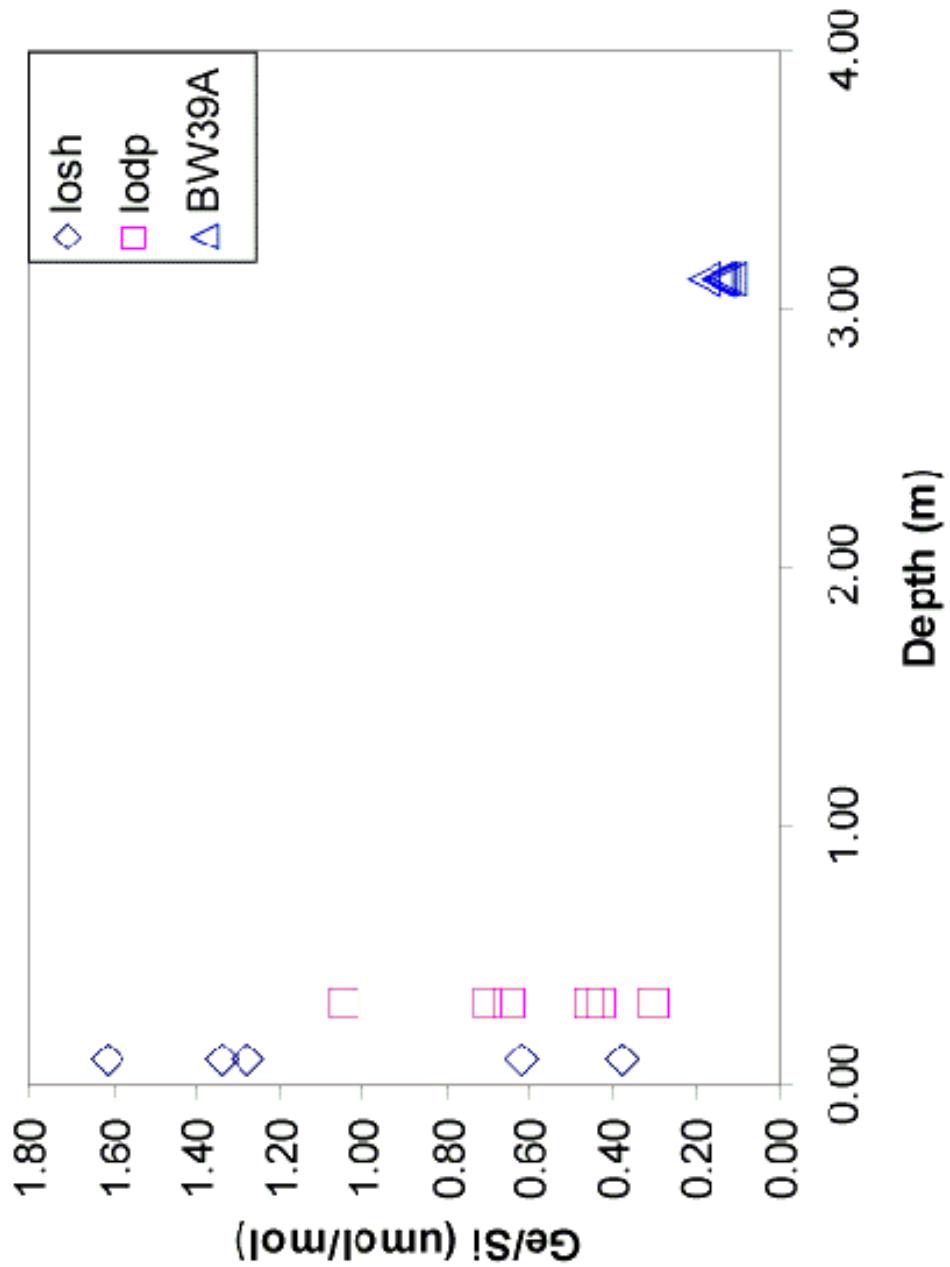
that there is some variation in Si and Ge/Si with depth and with time in the waters that we analyzed.

#### *Chemistry summary*

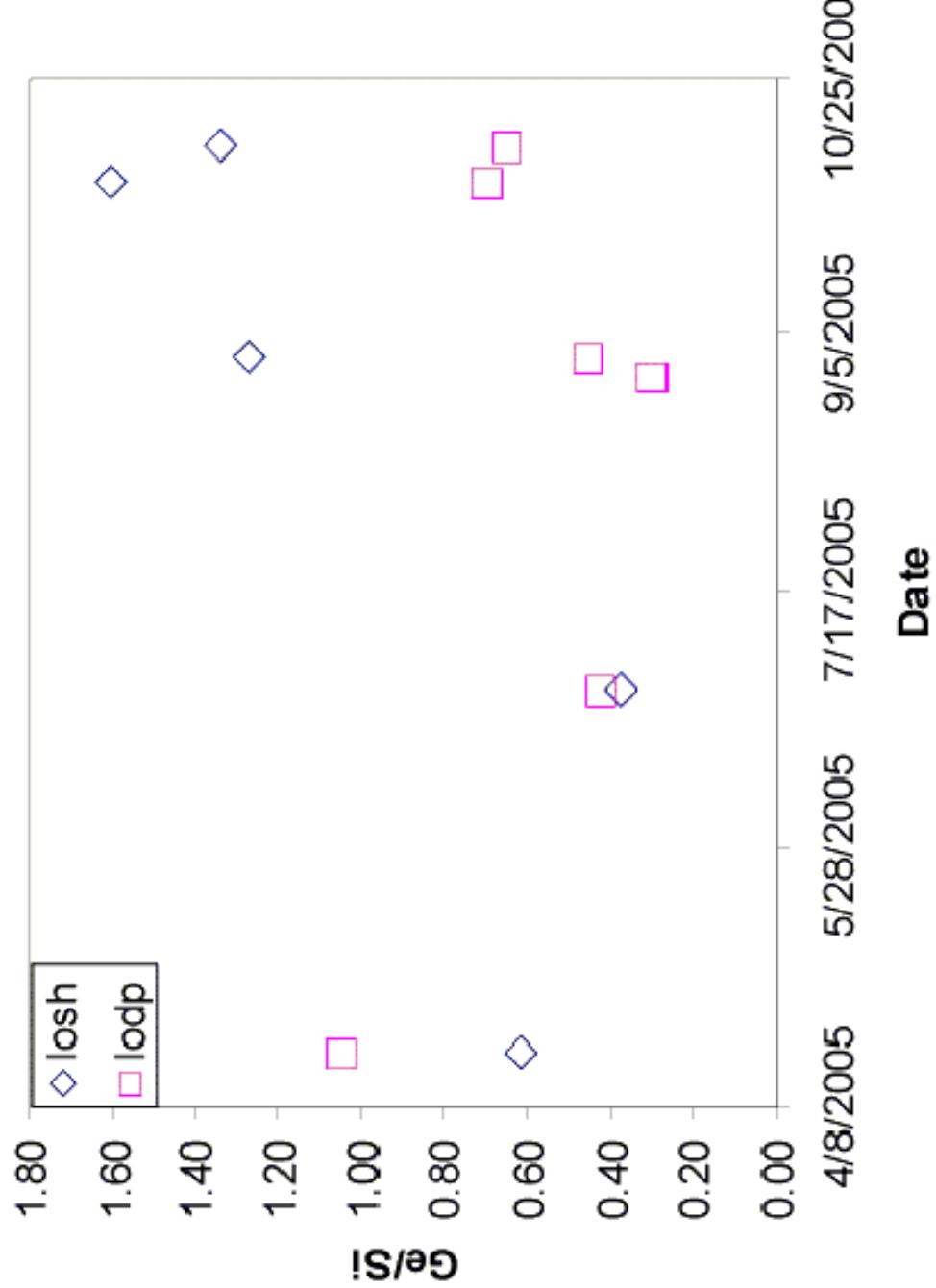
Of the data gathered through our chemical analyses of plant tissue, soil, water, and sap, perhaps the most meaningful result is the significant level of Si measured in deciduous tree leaves, particularly those of the sugar maple and American beech. It verifies our prediction that vegetation plays an important role in the Si cycle at Sleepers River and indicates that the same is probably true of most northern temperate forests. Conversely, Si measured in balsam fir needles was unequivocally low, thus balsam fir trees do not significantly affect the Si cycle at Sleepers River. Furthermore, this suggests that vegetation in balsam fir-dominated forests may not have as large a role in the Si cycle as vegetation in deciduous forests. We also found low levels of Si in the tree cores from all species, indicating that, despite the large amount of woody production in trees at Sleepers River, the wood is not a major reservoir of Si in aboveground biomass.

There was variation in both water-extractable Si and Ge/Si with soil depth. Consistent with this finding, stream water Si and Ge/Si fluctuated with discharge, presumably due to varying contributions of water carrying dissolved products from different soil depths. Additionally, hydrograph separations based on Ge/Si and Si concentrations gave clues about the order in which water from each depth was seen in stream water before and during storm events. The shallow soil water, with the highest Si and lowest Ge/Si (due to phytolith dissolution, most likely), seemed to contribute most significantly during low flow, particularly early in the growing season, and may have also contributed to the receding stream flow following a storm event (i.e., during

**Figure 18** Ge/Si ratios in lysimeter and well water plotted against collection depth. Samples were collected between June and October 2005. LYSLOSS is the shallow lowland lysimeter, LYSLODP is the deep lowland lysimeter, and BW39A is a deep well. We interpret the low Ge/Si of the well water as reflecting the dissolution of primary minerals. Ge/Si in the two lysimeters is much more variable, suggesting a fluctuating source of water to each. Higher Ge/Si is likely derived mostly from dissolution of secondary minerals, while lower Ge/Si is the result of a more significant input of biogenic silica.



**Figure 19** Ge/Si ratio of water from the two lowland lysimeters plotted against the sample collection date in 2005. The Ge/Si pattern is consistent between the two lysimeters during the growing season; both show an increase that might be due to either higher phytolith dissolution early in the year or continuous fractionation by plants.



the falling limb of the hydrograph). Deep soil water and groundwater, with high Si and low Ge/Si (possibly from weathering of primary minerals), also contributed during base flow. Intermediate soil water, however, with low Si and high Ge/Si (from weathering of secondary clay minerals), appeared to contribute mostly to the rising waters early in a storm event (i.e., during the rising limb of the hydrograph).

Similarly, we conclude from plots of Ge/Si versus Si that stream water is derived from a complex mixture of sources that requires a more detailed analysis to fully elucidate. The simplest such combination is a three-part mixture of groundwater, soil water, and phytolith dissolution. A much more complicated combination could arise due to the heterogeneity of the soil in the Sleepers River watershed, which would create myriad source areas producing water with a wide spectrum of Si and Ge/Si values depending on which minerals are present in that area.

Several temporal trends became apparent during data analysis. One was an increase in leaf Si concentration between mid-June and mid-August. We suspect this Si accumulation actually occurs throughout the entire growing season, since water containing dissolved Si is continuously transported to the leaves via the transpiration stream during this time. In addition, the high concentration of Si in tree leaves means that there is a significant flux of Si to the soil every autumn during leaf fall. At this time, it is unclear how the concentrated seasonal input of Si affects the overall Si cycle, though, for the temperate forest Si cycle, it undoubtedly represents a major point of departure from the tropical forest Si cycle.

Another observed seasonal trend was the upward shift in Ge/Si in the stream water and shallow lysimeter water between June and August. This increase was more pronounced in the lysimeter water than in the stream water, which is expected, since the stream water is integrating multiple sources, some of which are likely not exhibiting a similar increase. We suggest that the shift in Ge/Si is caused by one of

two scenarios. The first is a seasonal change in the source of dissolved Si to stream and lysimeter water, with phytolith dissolution contributing more heavily in June than in August. This could result from a greater flux of water (due to greater rainfall totals) through the shallow, phytolith-rich soil in the late spring than in the late summer, causing an increase in phytolith dissolution in the late spring. The second scenario that would result in increasing Ge/Si is the continuous fractionation of Ge and Si by plant uptake throughout the growing season, leaving behind water with a progressively higher Ge/Si ratio. We tested the plausibility of this second scenario by examining whether the actual fractionation during uptake could have a measurable impact on the Ge/Si of the soil solution. The size of the soil solution Si pool is small (0.071-3.63 kg Si ha<sup>-1</sup> -- see *Soil solution Si reservoir* below), while the plant uptake rate is comparatively high (10.8-32.3 kg Si ha<sup>-1</sup> yr<sup>-1</sup> -- see *Si flux from soil solution to plant*), resulting in a Si residence time in the soil solution, relative to plant uptake, of ~1-150 days. We estimate the plant fractionation factor to be about 3.5 [the rate of Si uptake is 3.5 times faster than that of Ge (Steve Blecker, unpublished data)]. This fractionation factor, combined with the short residence time of Si, suggests that the observed increase in soil solution Ge/Si as measured in the lysimeter water could be caused by plant uptake during the growing season.

The seasonal rise in soil solution Ge/Si indicates the potential for a similar increase in the Ge/Si of the extractable soil pool. These two reservoirs are linked through equilibration of Si between its solid and dissolved form, suggesting that chemical variations in one pool would also occur to some extent in the other. However, the details of the relationship between the two pools are unclear at this point, and little is known about the rate at which the extractable pool turns over or how it contributes to stream water. We nonetheless attempted to determine whether plant

uptake has the potential to cause seasonal variation in Ge/Si in the extractable pool. To test this hypothesis, we estimated the size of this pool from soil dry bulk density values (ranging from 100 kg/m<sup>3</sup> for the litter/organic soil to 1600 kg/m<sup>3</sup> for the mineral soil), the thickness of each layer, and the measured extractable Si concentrations, scaled up to the size of the watershed. The resulting mass of the extractable Si pool was 14.0-25.2 kg Si ha<sup>-1</sup>, a Si reservoir significantly larger than the soil solution Si reservoir. Because of its larger size, the extractable Si reservoir had a greater residence time relative to plant uptake, as well. The calculated residence time of 0.3 to 2.3 years suggests that this pool would probably not show a seasonal increase in Ge/Si due to plant uptake fractionation, unless the actual residence time was at the low end of the calculated range and the actual uptake rate was at the high end of the determined uptake range. In future work, extractable Ge/Si should be measured throughout the growing season as a check on whether it varies seasonally, and if so, how that variation compares to soil solution Ge/Si shift.

Finally, Si and Ge/Si in water from all lysimeters and wells varied throughout the growing season, though not in a predictable manner for most. To determine the cause of these soil and groundwater chemical fluctuations, as well as the other apparent seasonal trends, a greater number of measurements need to be taken throughout the year.

Analysis of sugar maple sap water chemistry revealed three additional results. One was the increased concentration of elements in the sap compared to soil water concentrations. The second was the variation in element concentrations between trees on different soils, as well as some variation among trees on the same soil. The third was the fractionation of Ge and Si by the time they reached the sap, showing that this fractionation occurs before phytolith formation in sugar maples, which could have broader implications for the use of Ge/Si ratios as a tracer of Si.

### Sleepers River Si cycle model

We used the chemistry data we collected to create a model of the Si cycle in the Sleepers River watershed. The validity of this model is contingent upon several underlying assumptions. One is that the system is in steady state. This assumption is supported by research at the nearby Hubbard Brook forest, which is ten years older than the Sleepers River forest, showing that biomass accrual had ceased by 1994 (Johnson et al., 2000). By analogy, the Sleepers River forest, located in a similar climate and containing the same tree species, should have stopped accruing biomass by the time of this study. A second assumption is that, of all the vegetation in the watershed, only trees with a diameter at breast height (dbh) of greater than 2 cm have a significant impact on the Si cycle. This assumption is also backed by work at Hubbard Brook showing that the elemental content of trees with  $\text{dbh} > 2$  represents more than 98% of the total vegetation pool (Whittaker et al., 1979). A third assumption used in this model is that the forest is made up entirely of sugar maple trees. Because sugar maple is the dominant tree species at Sleepers River, and also because the American beech - another common tree in the forest - has similar Si content, this assumption is not expected to significantly affect the model results. Our model has one input - chemical weathering of soil and bedrock silicate minerals - and two outputs - stream export and phytolith preservation. Si can also move within the system in various ways: it can be taken up from soil solution by plants and redistributed to the soil as opal phytoliths during litterfall; the opal phytoliths can, in turn, be dissolved so that their Si re-enters the soil solution. The fluxes and reservoirs of Si in this system are detailed below. While the model is an oversimplification of the biogeochemical Si cycle at Sleepers River, it will hopefully provide a framework on which later work can build.

*Si flux from soil solution to plant*

Net primary productivity (NPP) at Sleepers River is assumed to be 2600-3000 kg C ha<sup>-1</sup> yr<sup>-1</sup>, an approximated range based on measured maple NPP from Hubbard Brook (Whittaker et al., 1974). Furthermore, leaf NPP in sugar maple is ~31% of total plant NPP (Johnson et al., 2000), or 800-930 kg C ha<sup>-1</sup> yr<sup>-1</sup> at Sleepers River. Using our measured range of maple leaf C/Si ratios of ~40-100, and assuming that forest production and forest uptake are similar, we obtain a leaf Si uptake rate of 8.0 to 23.3 kg Si ha<sup>-1</sup> yr<sup>-1</sup>. To estimate the flux of Si to the woody parts of trees in the Sleepers River watershed, we use the Si concentrations we measured in the tree cores combined with allometric equations determined for sugar maples at Hubbard Brook (Whittaker et al., 1974), a forest that, as already noted, is similar in many ways to Sleepers River. We also assume that Si concentrations are similar in all woody components. In the future, Si in each woody component from Sleepers River trees should be measured to ensure an accurate rate calculation. The allometric equations use tree diameter to determine the productivity rates. The average DBH of the maples sampled at Sleepers River was 22.6 cm, yielding a production rate of ~16.4 kg yr<sup>-1</sup> per tree. Assuming a tree density of 2500-4000 trees per hectare and subtracting the amount of production by leaves, the total woody production is 28000-44800 kg ha<sup>-1</sup> yr<sup>-1</sup>. Multiplying by our measured Si concentrations of 0.1-0.2 mg/g gives a woody uptake rate of 2.8-9.0 kg Si ha<sup>-1</sup> yr<sup>-1</sup>. This, combined with the leaf uptake rate, produces a total plant uptake rate of 10.8 to 32.3 kg Si ha<sup>-1</sup> yr<sup>-1</sup>. This range of rates is similar to Si uptake rates calculated in other temperate Si cycle studies (Bartoli, 1983; Markewicz and Richter, 1998; Fulweiler and Nixon, 2005).

As a check on our estimated uptake rate, we used transpiration rates to calculate plant Si uptake, as well. We determined an average sugar maple transpiration rate of 0.79-2.45 mm water per day per tree from data given by Dawson

(1993). This rate is equivalent to  $2.9 \times 10^6$ - $8.9 \times 10^6$  L ha $^{-1}$  yr $^{-1}$ . Multiplying by the concentration of Si in the soil water ( $\sim 40$ - $140$   $\mu$ M) and converting to kilograms gives a range of uptake between 3.2 and 35 kg Si ha $^{-1}$  yr $^{-1}$ , encompassing the rates calculated above.

#### *Si flux from plant to soil phytolith reservoir*

Because the system is assumed to be in a steady state, Si in plant litterfall is considered equal to Si in plant uptake, as each is the only input and output, respectively, of the plant biomass reservoir. Therefore, the plant litterfall rate, like plant uptake, is 10.8-32.3 kg Si ha $^{-1}$  yr $^{-1}$ . The Si in litterfall is transferred to the soil as opal phytoliths as the dead plant tissue in which it was contained decomposes. In the soil, the phytoliths become part of one of two pools (Alexandre et al., 1993). The first is a pool of young phytoliths that are rapidly dissolved and recycled by vegetation. The size of this pool decreases with soil depth. The second pool consists of more stable phytoliths and remains constant with depth. This bicompartamental model of phytolith distribution in the soil is analogous to that of soil carbon (Anderson, 1992; Alexandre et al., 1997).

#### *Si flux from soil phytolith reservoir to soil solution*

Most of the phytoliths integrated into the soil are labile and become part of the first pool described above. The Si resulting from the dissolution of these labile phytoliths enters the soil solution reservoir, where it is either taken back up and recycled by the plant reservoir or lost from the system in the stream water. In a tropical forest, Alexandre et al. (1997) determined that 92.5% of phytoliths in litterfall enter the labile pool and are recycled by the vegetation. No such estimates exist for temperate forests, so we are forced to rely on the tropical forest values to develop our

model. Taking 92.5% of Si in plant litterfall at Sleepers River gives a phytolith Si recycling rate of 10.0 to 29.9 kg Si ha<sup>-1</sup> yr<sup>-1</sup>. Since weathering rates are higher in tropical climates than in temperate climates, it is possible that the percentage of phytoliths recycled at Sleepers River is lower than 92.5%, but other factors likely contribute to the recycling rate (e.g., phytolith morphotypes in litter, burial rates, soil acidity, etc.). It is therefore difficult to predict the actual rate of recycling at Sleepers River without having a better understanding of the dynamics of the system.

#### *Long-term phytolith burial*

The second pool of soil phytoliths is more stable and remains in the soil in its solid form, unavailable to plants. Phytoliths in this stable pool can persist for thousands of years and have been used to reconstruct vegetation histories for the sites in which they are found (Fredlund and Tieszen, 1997). In a tropical forest, the stable pool was found to consist mainly of a specific morphotype (circular rugose), as these phytoliths were more resistant to dissolution (Alexandre et al., 1997). Because the Si in the stable phytolith pool cannot be used by plants or exported by the stream, it is considered an output of Si from the watershed. Assuming that ~7.5 % of phytoliths in litterfall are stable and are not redissolved (Alexandre et al., 1997), we determine the flux of phytolith Si to the stable pool at Sleepers River to be 7.5% of litterfall Si, or 0.8 to 2.4 kg Si ha<sup>-1</sup> yr<sup>-1</sup>.

#### *Si flux from soil solution to stream water*

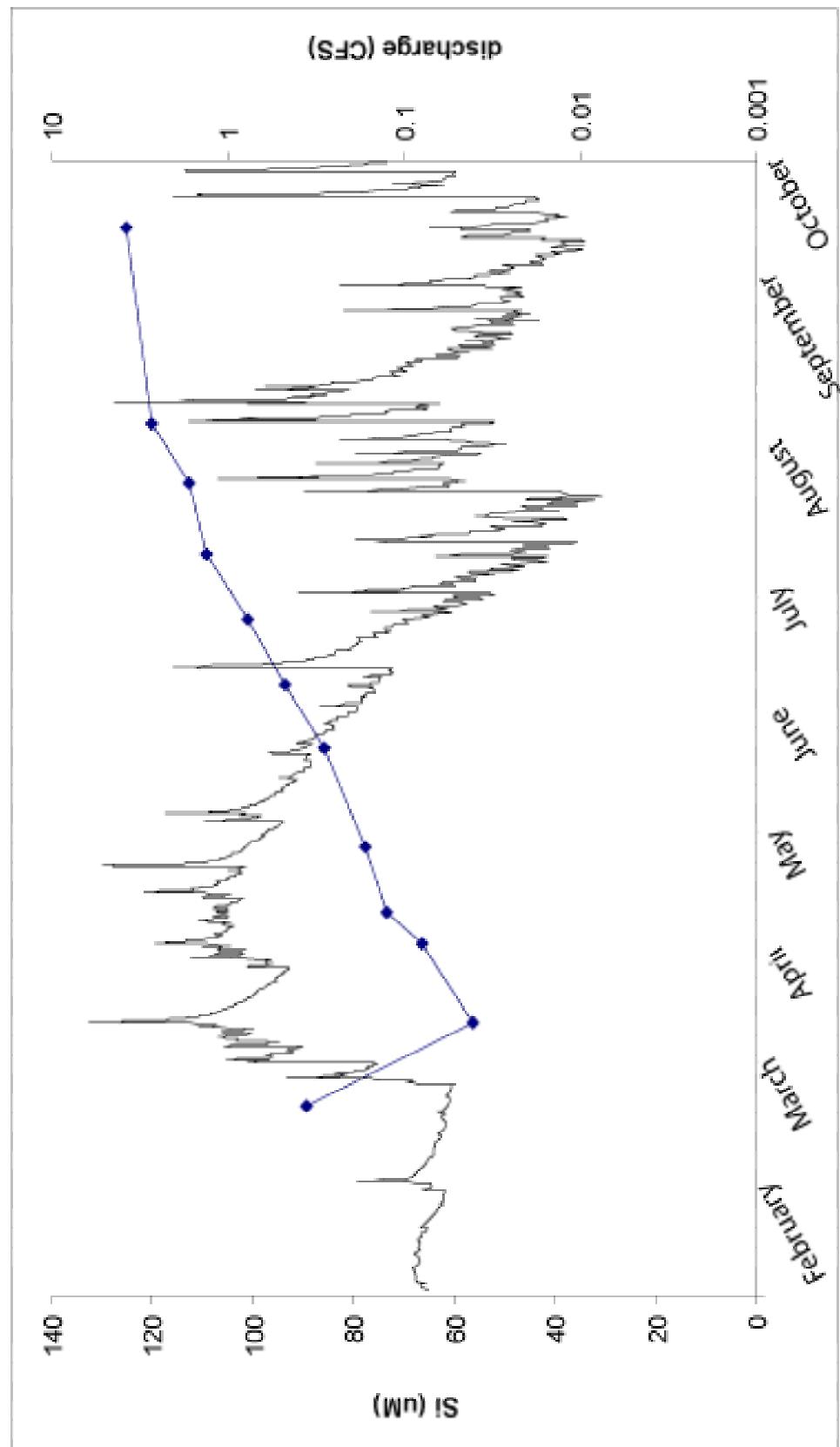
The main route by which Si leaves the Sleepers River watershed is stream flow. Dissolved Si, derived from phytolith dissolution or mineral weathering, enters stream flow via groundwater or soil water. For this model, geometric means of Sleepers River stream water Si concentrations and discharge from 2003 (Figure 19)

are used to generate an annual export flux of Si from the watershed. The resulting mean discharge of 0.27 cfs and mean Si concentration of 90  $\mu\text{M}$ , scaled up to the Sleepers River watershed area of 40.5 ha, give an annual export flux of 620 mol Si  $\text{ha}^{-1} \text{yr}^{-1}$ , or 15.0 kg Si  $\text{ha}^{-1} \text{yr}^{-1}$ . The accuracy of this number is dependent upon two assumptions. One is that the annual flux of Si from the watershed can be approximated from the January-September Si flux, as this was the extent of the available 2003 data. The other is that the 2003 stream data gives an export flux representative of an average year at Sleepers River. The validity of these assumptions is examined below.

In 2003, stream flow data were continuously collected by the USGS at the W-5 weir on Sleepers River, downstream from the W-9 weir. From January through September 2003, at W-5, the mean stream discharge was 18% lower than the 14-year January-September mean (57.23 cfs versus 70.20 cfs). Similarly, at nearby Pope Brook, in North Danville, Vermont, the January-September flow was 14% lower than normal. However, the lower discharge in 2003 should not have significantly affected the Si export rate. This is because low discharge results from low levels of precipitation, which also cause watershed NPP to decline (Schlesinger, 1997). Lower NPP means that less Si is taken up by plants, and thus more dissolved Si in the soil is available for export in stream flow. Therefore, while stream flow was lower than average in 2003, the concentration of Si in the water was probably higher than average, a combination that should have resulted in a Si export rate similar to “normal” years. If this was indeed the case, the first assumption (that the 2003 data result in an export rate equal to what would be observed in an average year) is valid.

The January-September 2003 discharge did not differ greatly from the 14-year October-December mean discharge. At the W-5 weir on Sleepers River, January-September 2003 discharge was 8.7% lower than the October-December 14-year

**Figure 20** Silicon concentration and stream discharge plots from January through September 2003 at the W-9 weir in the Sleepers River watershed. Data were obtained from Jamie Shanley of the USGS. Si was analyzed 1-2 times per month, while discharge was measured continuously.



average (57.23 cfs versus 62.7 cfs). At Pope Brook, January-September 2003 discharge was 6.0% *greater* than the October-December average. It is therefore likely that the discharge at W-9 from January-September 2003 was close to the long-term October-December average and that the second assumption (using the January-September 2003 mean discharge to represent the 2003 annual discharge) is acceptable.

#### *Si flux from mineral weathering to soil solution*

There are two sources of Si to a watershed: atmospheric deposition (i.e., precipitation and dust) and mineral weathering. However, dissolved Si in precipitation is present in insignificant quantities and can be ignored as an input to the system (Bartoli, 1983). Furthermore, in dust, Si exists in its mineral form and would have to undergo chemical weathering before entering the soil solution. Therefore, any dissolved Si in the system originating from dust is considered a weathering input. As a result, in our model, mineral weathering is the only input of Si to the watershed.

The contribution of mineral weathering to Si in soil solution can vary depending upon the bedrock and soil characteristics of a watershed. Watersheds underlain by silicate rocks, like Sleepers River, have a greater weathering input rate of Si compared to watersheds with carbonate bedrock. Another important factor to consider when determining the weathering input of Si to a watershed is the relative contributions of bedrock-mineral weathering and soil-mineral weathering. The weathering of primary bedrock minerals results in a solution with high Si and low Ge/Si, while the weathering of secondary soil minerals produces a solution with low Si and high Ge/Si. Future research will focus more on the mineralogy of the soil and bedrock at Sleepers River, as knowledge of Ge/Si of common minerals in the watershed will allow for an estimate of the weathering flux from bedrock and soil minerals, separately. For the purposes of building the Si cycle model for the

watershed, an estimate of the overall contribution of mineral weathering (primary and secondary mineral weathering together) is used.

A common method for determining the weathering input of an element to a watershed in steady state is to subtract the inputs to the system from the outputs. Usually, this means measuring the flux of the element exported in stream water and subtracting the flux entering via atmospheric deposition (Likens et al., 1977; Johnson et al., 2000). In the case of Si, atmospheric input is zero, and long-term burial of phytoliths is considered an additional output from the watershed. Taking these alterations into account gives the following equation for estimating weathering flux:

$$\text{weathering input} = \text{stream output} + \text{phytolith burial} \quad (3)$$

The calculated weathering input is only accurate, though, if the system is in steady state. If, instead, the aboveground plant reservoir is accruing biomass, less Si is exported from the watershed than is produced in chemical weathering reactions, and weathering inputs cannot be estimated by equation 3. For this reason, our assumption that the Sleepers River watershed is in steady state is critical to determining the weathering Si flux. Since the stream export flux is approximately  $15.0 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$  and phytolith burial is  $0.8\text{-}2.4 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ , we estimate the weathering input to be  $15.8\text{-}17.4 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ .

#### *Plant Si reservoir*

The total amount of Si in sugar maple biomass is estimated for the Sleepers River watershed in the same way that plant Si uptake is estimated: allometric equations for sugar maples from nearby Hubbard Brook are used in conjunction with measured Si concentrations from leaves and cores are Sleepers River. Hubbard Brook allometric equations (from Whittaker et al., (1974)) are used because similar formulae for Sleepers River have not yet been determined, and the two watersheds share many

of the same characteristics (see *Soil to plant*, above). The leaf Si reservoir is calculated by multiplying the annual Sleepers River maple leaf Si accumulation rate ( $8.0\text{-}23.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) by the leaf residence time ( $\sim 1$  year), yielding a leaf mass of  $8.0\text{-}23.3 \text{ kg Si ha}^{-1}$ . The mass of Si in the remainder of the tree is determined by plugging the average DBH (22.6 cm) for sugar maples at Sleepers River into allometric equations for average dry weight per tree (Whittaker et al., 1974), yielding a mass of 330.4 kg per tree. Multiplying by the number of trees per hectare ( $\sim 2500\text{-}4000$ ) and subtracting the leaf mass gives a wood mass of  $\sim 8.5 \times 10^5\text{-}13.6 \times 10^5 \text{ kg ha}^{-1}$ . Multiplying by the woody concentration of Si (0.1-0.2 mg/g) we measured in Sleepers River maples results in a woody Si mass of 84.8-272.0 kg Si ha $^{-1}$ . Adding together the two calculated masses results in a total plant Si reservoir at Sleepers River of 92.8-295.3 kg Si ha $^{-1}$ . These values fall mostly within the range estimated for temperate deciduous forests by Bartoli (1983) of  $180 \pm 100 \text{ kg Si ha}^{-1}$ .

#### *Soil solution Si reservoir*

Si can enter soil solution through the dissolution of either minerals or phytoliths. Once in solution, Si can be taken up by plant roots, enter the stream water, or revert back to a solid form in the soil. We define the soil solution Si reservoir as the total amount of dissolved Si in the soil water and groundwater in the watershed, at any given time, that exits soil solution by plant uptake or stream flow. This definition excludes from our soil solution reservoir the dissolved Si in dynamic equilibrium with the solid phases, since that process has little effect on the overall Si cycle at Sleepers River. It is important to note that the soil solution reservoir contains only Si that is in solution (i.e., Si that could be measured in lysimeter water) and not all Si in the soil that could potentially enter solution (i.e., water-extractable Si). We define the reservoir in this way so that it includes only the Si that we know is available for uptake

or export at any given time and are not speculating on how much Si might eventually become available. A possible limitation of defining the reservoir in this way is that its size is highly dependent upon the amount of water in the soil. During wet periods, water occupies a greater number of soil pores, resulting in more dissolved Si in the soil water. During dry periods, conversely, only a small amount of water is present, and thus only a fraction of the dissolved Si present during wet periods is in solution. The result is that soil solution Si reservoir mass can fluctuate significantly over relatively short periods of time. As long as we can numerically constrain this fluctuation, then its existence should not be a concern. One might argue that dissolved Si in dynamic equilibrium with its solid phase is also available for uptake or export before it is reincorporated into a solid. While this is probably true, we have no data from Sleepers River with which to constrain this flux, so we have chosen to ignore the process for the purposes of this model. However, with more research in the future on Si dynamics in the soil solution at Sleepers River, we should be able to quantify mineral neoformation in the soil and include it as an export from soil solution.

We can estimate the mass of the soil solution Si reservoir by multiplying the flux to and from the reservoir ([weathering + phytolith dissolution] or [plant uptake + stream export]) by the residence time of Si in solution. We define the residence time as beginning the moment an individual atom of Si is first derived from mineral or phytolith dissolution and ending the instant it is taken up by a plant root or exported by the stream. Again, this only includes atoms of Si that are taken up by plant or exported by stream flow and not those that re-enter solid state.

Now that the soil solution Si residence time has been defined, we must try to quantify it. We know it has to be less than the residence time of the water in which it is dissolved, since the Si enters solution after the water has entered the watershed, and leaves the soil solution at the same time as the water, at latest, and possibly much

earlier if it is taken up by plant roots. Soil water residence time in forested watersheds similar in size to Sleepers River has been measured at between two months and one year (DeWalle et al., 1997; McGuire et al., 2002). However, we have also noted the short-term variability of Si measured in lysimeter water at Sleepers River throughout 2005 (see *Soil and groundwater Si*, above), which suggests that soil solution Si residence time is significantly less than one year and is probably more on the order of days-to-weeks. Based on our measurements, we estimate the upper limit of soil solution Si residence time to be four weeks, though it is likely even shorter than that. The minimum is set at one day, assuming Si can be taken up by plants immediately after entering soil solution. This range of residence times, multiplied by the flux of Si into and out of soil solution ( $25.8\text{-}47.3 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$ ), gives a reservoir size of  $0.071\text{-}3.63 \text{ kg Si ha}^{-1}$ . Admittedly, there is a large difference between the minimum and maximum reservoir sizes, reflecting the uncertainty involved in this estimate. The actual mass likely fluctuates daily due to changes in the water cycle and variations in weathering intensity and would therefore be difficult to accurately quantify.

#### *Soil phytolith Si reservoir*

We did not sample phytoliths from the soil at Sleepers River, so we again must rely on data from another study to estimate the mass of soil phytolith Si. As before, we use the numbers from the study of a tropical forest by Alexandre et al. (1997), which are likely to differ from the actual values at Sleepers River. However, as a first approximation, the resulting values should be adequate.

Alexandre et al. (1997) estimate the residence time of the labile phytoliths in the soil to be 280 to 370 years. Assuming a similar residence time for this pool at Sleepers River, and multiplying by the flux to the labile pool of  $10.0\text{-}29.9 \text{ kg Si ha}^{-1} \text{ yr}^{-1}$  determined earlier, we obtain a labile phytolith Si mass of  $2800\text{-}11050 \text{ kg ha}^{-1}$ . If

the labile pool is fully contained within the 20-cm thick litter/organic layer (Alexandre et al., 1997), and we assume this soil has a dry bulk density of  $\sim 0.5\text{-}1.0 \text{ g cm}^{-3}$  (Miller and Donahue, 1995), then Si in the labile phytolith pool would make up  $\sim 0.01\text{-}0.06\%$  of the soil by weight, a reasonable figure considering the amount of Si we extracted from the litter and organic layers. In the tropical system studied by Alexandre et al. (1997), the labile pool makes up 74% of the total soil phytolith pool. If the same is true of the soil phytoliths at Sleepers River, then the total mass of Si in soil phytoliths is  $3780\text{-}15000 \text{ kg ha}^{-1}$ . The size of the pool of stable phytoliths is the difference between the total mass and the labile mass, or  $980\text{-}3950 \text{ kg ha}^{-1}$ , and should be distributed evenly throughout the soil profile (Alexandre et al., 1997).

Our estimated mass of soil phytoliths is large regardless of how much we vary many of our assumptions. However, the mass is significantly affected by the validity of our assumption of the labile phytolith residence time, which we took from a study of a tropical forest. Using this residence time creates a potential source of significant error in the overall Si cycle model for Sleepers River. It is important that future work at Sleepers River aims to determine the size of the soil phytolith reservoir more accurately. Following Alexandre et al. (1997), this can be accomplished by multiplying the percent Si derived from phytoliths (as determined by soil mineralogical and chemical analyses) for a particular soil layer by the bulk density and the thickness of that layer. Summing the resulting values for all layers gives the total stock of phytolith Si in the soil. Furthermore, an SEM analysis of the soil should reveal the particular phytolith morphotypes present at various depths throughout the profile. Some morphotypes are more stable in the soil than others, so this analysis should help determine the percentage of soil phytoliths belonging to the stable and labile pools.

### *Si model summary*

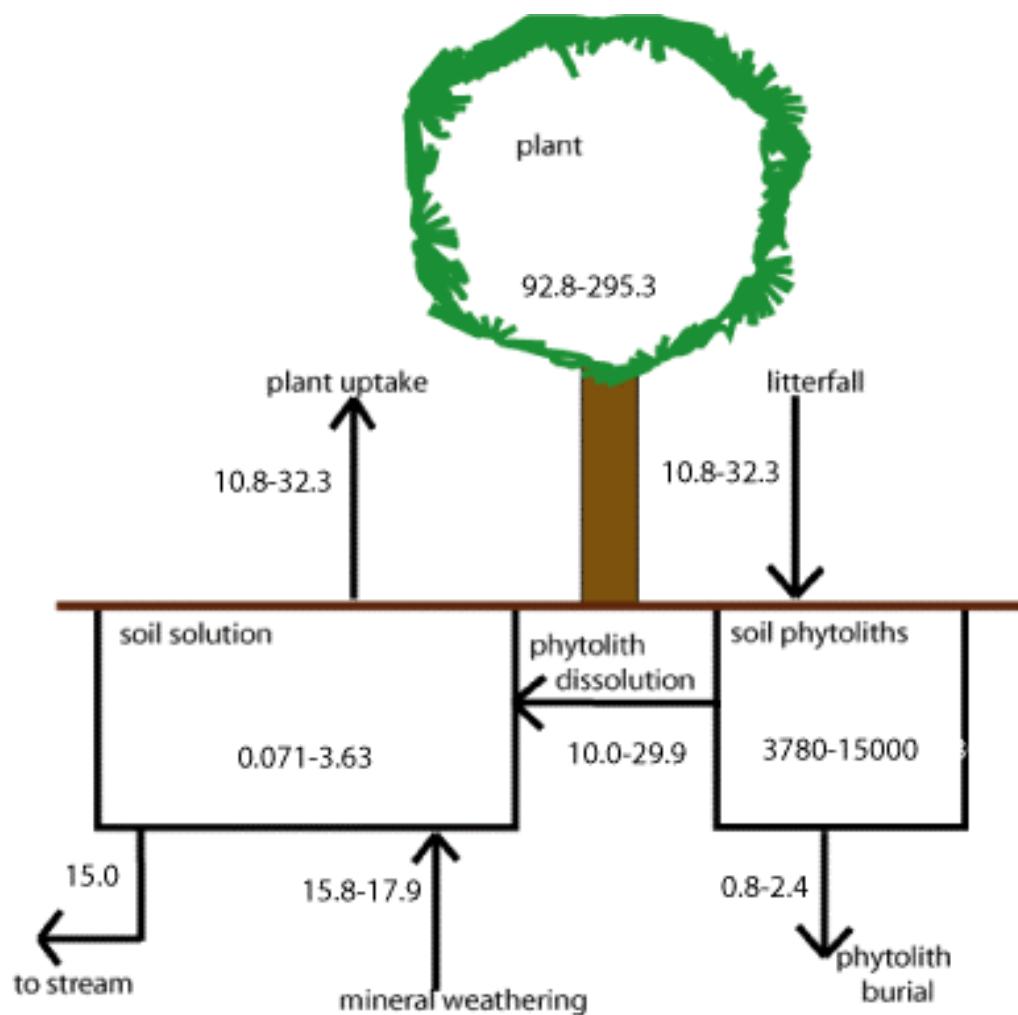
The Si cycle at Sleepers River is modeled in Figure 20, using the fluxes and reservoirs described above. We acknowledge that many of the numbers used in the model are estimates and will probably be modified as more data are collected.

However, we believe the model is qualitatively accurate and shows the major trends of the Si cycle at Sleepers River. Of these, perhaps the most noteworthy is the evidence for significant storage of Si as phytoliths in the biomass and the soil. In the absence of vegetation, and thus the absence of phytoliths, the Si produced by mineral weathering would be lost from the watershed through stream flow at a much greater rate than is currently observed at Sleepers River. Therefore, the storage of biogenic silica in the soil at Sleepers River significantly lowers the output of Si from the watershed.

Similarly, we found that plant uptake and litterfall are on the same order as mineral weathering and stream export, again demonstrating the importance of vegetation in the Si cycle in the watershed. Additionally, Si release to the soil solution due to phytolith dissolution is of the same magnitude as Si release from silicate mineral weathering, the results of which can be seen in stream water Si and Ge/Si.

The biological turnover of Si we estimated for Sleepers River is similar to estimates for other temperate watersheds (Bartoli, 1983; Fulweiler and Nixon, 2005) and significantly lower than the rates seen in tropical forests (Lucas et al., 1993; Alexandre et al., 1997; Meunier et al., 1999; Lucas, 2001, and references therein). This is most likely because of the higher rates of NPP in the tropics and not because species in the tropics have a greater need for Si. Additionally, it appears that the amount of Si in stream water at Sleepers River that had passed through the biogenic pool was not as great as was observed in Hawaiian streams (Derry et al., 2005). This could be due to the relative amount of available non-biogenic Si in the soils at each

**Figure 21** Schematic model of the Si cycle at the W-9 watershed of Sleepers River. All units are  $\text{kg Si ha}^{-1} \text{ yr}^{-1}$  for the fluxes and  $\text{kg Si ha}^{-1}$  for the reservoirs. Boxes represent reservoirs, and arrows represent fluxes into and out of the reservoirs. Note the similarity in fluxes



site. In Hawaii, as in most tropical environments, the soil has been extensively weathered, leaving little Si available for uptake by plants. As a result, plants rely heavily upon recycled biogenic Si to supplement the weathering-derived Si they take up. Thus, most Si in stream water has already passed through the biologic cycle. In temperate forests, like the Sleepers River watershed, soils are young and contain an abundance of non-biogenic Si. While the vegetation takes up some of this Si, the rest is likely lost to the stream, resulting in a stream water Si signal less representative of a biogenic source.

In the future, this model could be altered to include Ge/Si of each component, allowing us to better understand contributions of different sources to stream flow. Furthermore, this would help quantify Si contributions from the weathering of specific soil and bedrock minerals. With this simple model, we have provided many ideas and needs for future research, the completion of which will advance our knowledge of the temperate Si cycle.

## Conclusions

The goal of this study was to create a framework of data and ideas on which future studies could build to eventually develop a well-constrained model of the terrestrial Si cycle in a temperate forest setting. Along the way, more questions arose than were answered, providing proof of the many opportunities available for research in this area. The results of this study, and the Si cycle model we created, should be considered preliminary in the grand scale of research at Sleepers River, but we hope they will act as a starting point from which other studies can be initiated. Some of the important points to be taken from this study are summarized in the following paragraphs.

Our model results demonstrate the importance of the biological cycle on the Si budget at Sleepers River. The flux of Si cycled between the vegetation and the soil is similar to the amount of Si exported in the stream water. Storage of Si in living biomass and in soil phytoliths is significant and slows the release of Si from the watershed. Additionally, the weathering release of biogenic Si stored in the soil is as great, or greater than, the weathering release of Si from soil and bedrock minerals. At this time, the fraction of Si cycled by the vegetation and exported in the stream that comes from phytolith dissolution versus mineral weathering is unclear. We do know, however, that the Si cycle at Sleepers River most likely falls between the following two end-members:

- (1) All of the Si released by mineral weathering is taken up by plants and incorporated into plant phytoliths before being released to the stream.
- (2) All of the Si released by mineral weathering is lost to the stream without passing through the biological cycle. All of the Si in the biological cycle is continually recycled and is never released to the stream.

The actual cycle is probably a combination of these two end-members. However, to make a definitive conclusion, it is necessary to better constrain the Ge/Si ratios of the source areas (phytoliths, minerals, etc.) and of the stream water.

The stream water data show the possibility of a seasonal shift in stream water source. The contribution of biogenic Si appears to be more significant in stream water samples taken in June than those taken in August. We propose that this change is due to a higher amount of water (from precipitation) moving through the shallow soil in the spring than in the summer.

This study also provides the first data set on Si and Ge/Si in sugar maple sap water. An important point suggested by these data is that plant fractionation of Ge/Si occurs prior to phytolith formation, as the Ge/Si ratios in the sap had already been

fractionated. This finding has potential implications for the use of Ge/Si as a tracer of Si in vegetated watersheds and deserves more attention in the future.

## APPENDIX I

### PROCEDURAL DETAILS

#### *Phytolith Separation and Dissolution*

Phytoliths were extracted from solution following a variation of the method described by Parr et al. (2001). 9 ml nitric acid and 1 ml hydrogen peroxide were added to 0.2-0.5 g of powdered leaf samples inside microwave reaction vessels. Vessels were then left uncovered ~10 minutes (until bubbles from the reaction had subsided). After covering, the vessels were placed in a Milestone Ethos laboratory microwave, which aids in the digestion of plant tissue by increasing the acid solution temperature in a controlled and carefully monitored environment. The microwave was programmed to ramp up the solution temperature within each vessel over five minutes to 180° C, where it remained for another ten minutes. The hot acid dissolved all plant material except opal phytoliths. After cooling overnight, the acid solutions were poured into acid-washed plastic centrifuge tubes and centrifuged at 3000 rpm for 20 minutes, which separated the undissolved opal phytoliths from the acid. The acid was decanted and saved for analysis (to ensure that no Si was accidentally decanted). 10 ml of QD water was then added to the opal, and this mixture was centrifuged at 3000 rpm for 10 minutes. The water was discarded and this step repeated twice more to ensure that all acid had been removed from the opal. After decanting the water a final time, 3-5 ml of 2M NaOH was added to dissolve the remaining opal, and this mixture was diluted five times with QD water (Mortlock and Froelich, 1989; Parr et al., 2001).

#### *Si Analysis*

Dissolved Si concentrations were determined by molybdate-blue spectrophotometry (Strickland and Parsons, 1968; Fanning and Pilson, 1973; Mortlock

and Froelich, 1989). This technique is based on the reaction of dissolved silica with molybdate under acidic conditions to form a silicomolybdate complex. After a prescribed amount of time, this complex is reduced to a blue heteropoly acid, the absorbance of which is measured with a spectrophotometer.

Two reagents, A and B, were made for use in this procedure. Reagent A was a 1:1 mixture of ammonium paramolybdate solution and metol-sulfite solution. Reagent B was a mixture of equal parts oxalic acid, sulfuric acid (30%) and hydrochloric acid (0.6 N). We made Si standards by dissolving Na<sub>2</sub>SiF<sub>6</sub> in either QD water (Si concentrations ranging from 0.0-1.0 for use with water samples) or NaOH (concentrations from 0.0-8.0 for use with phytolith samples).

After the reagents and standards were prepared, we began the sample preparation. To acid-washed plastic vials, we added 1.0 ml of reagent A and 2.3 ml of QD water. Then, at even intervals (usually 20 or 30 seconds), we added 200 µl of the sample or standard to each vial. Typically, we prepared 5 standards and 15 samples, each in duplicate, for a total of 40 analytes. 20 minutes after adding the first sample to the first vial, we added 1.5 ml of reagent B to that vial. Reagent B was then added to each subsequent vial at the same time-interval (20 or 30 seconds) used earlier in the procedure. After this, the vials were capped and swirled, and then placed in a dark drawer to allow the reaction to proceed.

After 12-24 hours in the drawer, the solutions were analyzed for Si by a Hewlett-Packard diode array spectrophotometer. This machine pumps each sample through a sipper tube and into a transparent cell for twenty seconds before it measures the absorbance at 812 nm. The standards were measured first, and from these a standard concentration-absorbance curve was generated. Then, samples were run and

their absorbances compared to the standard curve to determine the concentration of Si in each. Reagent blanks were less than 5  $\mu\text{M}$  Si and reproducibility better than 2%.

### *Ge Analysis*

Germanium concentrations were determined by continuous flow isotope-dilution hydride generation (Mortlock and Froelich, 1996; Haffer et al., 1997; Klaue and Blum, 1999; Kurtz, 2000; Carerro et al., 2001) on a Finnigan Element II ICP-MS (inductively coupled plasma-mass spectrometer) at Cornell University. To prepare samples for analysis, they were equilibrated overnight at room temperature with a  $^{70}\text{Ge}$ -enriched spike. The Ge isotope spike we used was prepared as described by Kurtz et al. (2002). The amount of spike added to each sample varied, based on how much germanium was estimated to be present (Ge was calculated from concentrations of Si in the sample and typical Ge/Si ratios). In spiking, we aimed for a  $^{70}\text{Ge}/^{74}\text{Ge}$  ratio of 3-4, which has been found to be an optimal target in practice (Mortlock and Froelich, 1996). Water samples with low Ge (<100 pM), after spiking, were evaporatively concentrated 2-5 times to ensure an adequate Ge signal-to-noise ratio when measured on the ICP. 2-3 ml of each sample was placed in an auto-sampler vial. Samples were interspersed with 100 ppt Ge standards and 2% nitric acid blanks. From the vials, samples were pumped, individually, through the continuous flow apparatus (Figure 3) (see Klaue and Blum (1999) for additional setup details). Pumped simultaneously through separate tubes were a 1M Tris-HCl solution and 2% sodium borohydride. (We also used 5% sodium borohydride during a test run, but did not find a significant change in the Ge standard signal.) At the point when the three tubes combined into one, a reaction occurred in which each sample was buffered to pH 6 by the Tris-HCl solution and reduced to germanium hydride ( $\text{GeH}_4$ ), a volatile gas, by the sodium borohydride. The  $\text{GeH}_4$  was stripped from solution by an inert Ar gas stream

(from the Add 1 gas port on the ICP) and swept through a teflon filter membrane, at which point another Ar gas stream (from the Sample gas port) carried it into the ICP torch, producing a Ge signal on which the  $^{70}\text{Ge}/^{74}\text{Ge}$  ratio was measured. We found the optimal gas flow rates (the ones that produced the strongest, most stable signal while running a 100 ppt Ge standard) to be  $1.180 \text{ L min}^{-1}$  for the sample gas and  $0.085 \text{ L min}^{-1}$  for the add gas.

The measured  $^{70}\text{Ge}/^{74}\text{Ge}$  ratio of each sample was adjusted based on a mass bias correction factor determined from  $^{70}\text{Ge}/^{74}\text{Ge}$  ratios measured on the standards and blanks within a run (see Kurtz, 2000, for details). The corrected ratio was then used to determine the actual Ge concentration of the sample by the following equation (Mortlock and Froelich, 1996; Kurtz, 2000):

$$\text{Moles Ge} = (74_s)/(74_n) * (T) * [R_c - R_s] / [R_n/R_c] \quad (3)$$

where  $74_s$  is the abundance of  $^{74}\text{Ge}$  in the spike (0.61%),  $74_n$  is the natural abundance of  $^{74}\text{Ge}$  (36.54%),  $T$  is the moles of spike added,  $R_c$  is the mass bias corrected measured  $^{70}\text{Ge}/^{74}\text{Ge}$  ratio in the sample,  $R_s$  is the  $^{70}\text{Ge}/^{74}\text{Ge}$  ratio in the spike (161.4), and  $R_n$  is the  $^{70}\text{Ge}/^{74}\text{Ge}$  natural abundance ratio (0.0562).

The precision and accuracy of isotope dilution are limited by uncertainties in natural isotopic abundances of Ge (Green et al., 1986), isotopic spike calibration (Wasserburg et al., 1986), and in determinations of isotope ratios of individual spiked samples. Reproducibility on multiple runs of the same sample with varying dilutions and spike amounts is typically better than 3% (Evans and Derry, 2002), and reagent blanks were ~0.5 ppt Ge.

APPENDIX II  
DATA TABLES

**Table 9** Stream water Si and Ge data collected from Sleepers River throughout 2005.

Data in this table were used to produce the stream water chemistry figures in this paper. Ge/Si ratios have the units  $\mu\text{mol/mol}$ . n/m indicates that Ge and Ge/Si were not in the corresponding sample.

Sample ID	Date	Si (umol/L)	Ge (pmol/L)	Ge/Si	Discharge (cfs)
6_13_1	6/13/2005	108.7	n/m	n/m	0.0898
6_13_2	6/13/2005	109.8	n/m	n/m	0.0683
8_14_1	8/14/2005	132.8	n/m	n/m	0.0059
8_14_2	8/14/2005	132.5	n/m	n/m	0.0083
8_14_3	8/14/2005	132.1	n/m	n/m	0.0113
11074	6/14/2005	110.0	57.36	0.52	0.194
11075	6/14/2005	110.7	56.43	0.51	0.414
11076	6/14/2005	93.9	60.89	0.65	0.779
11077	6/14/2005	86.8	55.47	0.64	1.405
11078	6/14/2005	91.1	65.68	0.72	2.002
11079	6/14/2005	93.5	79.51	0.92	3.123
11080	6/14/2005	92.3	46.17	0.5	4.107
11081	6/14/2005	92.0	73.22	0.77	2.139
11082	6/14/2005	106.0	58.64	0.55	0.847
11083	6/17/2005	109.2	41.58	0.38	0.731
11084	6/17/2005	81.8	n/m	n/m	1.276
11085	6/17/2005	84.3	38.94	0.46	2.010
11086	6/18/2005	70.1	63.37	0.9	2.792
11087	6/18/2005	69.1	58.32	0.84	3.997
11088	6/18/2005	79.0	n/m	n/m	2.074
11113	7/9/2005	100.6	n/m	n/m	n/m
11114	7/9/2005	92.0	n/m	n/m	n/m
11115	7/9/2005	91.0	n/m	n/m	n/m
11116	7/9/2005	90.6	n/m	n/m	n/m
11117	7/9/2005	105.0	n/m	n/m	n/m
11127	7/26/2005	131.8	n/m	n/m	0.055
11128	7/27/2005	143.2	n/m	n/m	0.068
11129	7/27/2005	128.9	n/m	n/m	0.223
11130	7/27/2005	106.9	n/m	n/m	0.520
11131	7/27/2005	97.7	n/m	n/m	0.943
11132	7/27/2005	104.8	n/m	n/m	1.496

Table 9 (Continued)

11133	7/27/2005	119.3	n/m	n/m	1.796
11175	7/28/2005	113.7	n/m	n/m	0.089
11134	7/28/2005	107.2	n/m	n/m	0.649
11159	8/21/2005	129.0	89.59	0.69	0.031
11160	8/21/2005	109.9	91.15	0.83	0.135
11161	8/21/2005	101.3	82.2	0.81	0.445
11162	8/21/2005	80.8	66.94	0.83	0.783
11163	8/21/2005	78.2	89.46	1.14	1.132
11164	8/21/2005	83.5	83.01	0.99	1.826
11165	8/21/2005	78.0	87.85	1.13	2.511
11166	8/21/2005	69.8	88.89	1.27	3.691
11167	8/21/2005	41.6	58.81	1.41	5.162
11168	8/21/2005	66.4	82.91	1.25	6.532
11169	8/21/2005	65.0	90.53	1.39	8.465
11170	8/21/2005	65.4	54.04	0.83	9.092
11171	8/21/2005	67.6	n/m	n/m	5.262
11172	8/21/2005	57.3	53.93	0.94	2.959
11173	8/21/2005	48.6	n/m	n/m	7.630
11174	8/21/2005	53.3	86.6	1.63	5.687
11178	8/21/2005	84.1	82.92	0.99	1.264
11179	8/21/2005	100.2	115.12	1.15	0.385
11180	8/21/2005	103.2	83.09	0.81	0.349
11181	8/28/2005	46.2	n/m	n/m	0.022
11182	8/28/2005	51.5	n/m	n/m	0.022
11183	8/28/2005	134.9	n/m	n/m	0.022
11184	8/23/2005	8.4	n/m	n/m	0.073
11186	8/28/2005	126.9	n/m	n/m	0.022
11192	8/30/2005	130.2	n/m	n/m	0.051
11196	8/31/2005	89.6	n/m	n/m	3.092
11197	8/31/2005	129.6	n/m	n/m	0.122
11198	8/31/2005	114.3	n/m	n/m	0.305
11199	8/31/2005	116.9	n/m	n/m	0.618
11200	8/31/2005	107.3	n/m	n/m	1.077
11201	8/31/2005	104.3	n/m	n/m	1.774
11202	8/31/2005	104.0	n/m	n/m	2.565
11203	8/31/2005	109.3	n/m	n/m	3.061
11204	8/31/2005	122.1	n/m	n/m	1.412
11205	8/31/2005	111.8	n/m	n/m	2.172
11206	8/31/2005	122.7	n/m	n/m	2.520
11207	8/31/2005	125.8	n/m	n/m	3.521
11208	8/31/2005	123.2	n/m	n/m	4.616
11209	8/31/2005	125.0	n/m	n/m	5.899
11210	8/31/2005	98.7	n/m	n/m	8.106
11211	8/31/2005	110.1	n/m	n/m	9.663
11212	8/31/2005	120.1	n/m	n/m	5.597

**Table 10** Lysimeter and well water Si and Ge/Si collected throughout 2005 from the Sleepers River watershed. Data in the table were used to create figures presented in this paper. Ge/Si has units  $\mu\text{mol/mol}$ .

Sample ID	Date	Si ( $\mu\text{mol/L}$ )	Ge/Si
LYS LO SH	4/19/2005	90.0	0.62
LYS LO SH	6/28/2005	119.9	0.37
LYS LO SH	9/1/2005	158.1	1.27
LYS LO SH	10/5/2005	105.3	1.61
LYS LO SH	10/12/2005	101.2	1.34
LYS LO DP	4/19/2005	85.9	1.04
LYS LO DP	6/28/2005	142.8	0.42
LYS LO DP	8/28/2005	134.9	0.30
LYS LO DP	9/1/2005	186.2	0.45
LYS LO DP	10/5/2005	136.2	0.70
LYS LO DP	10/12/2005	136.8	0.65
LYS UP DP	6/28/2005	110.3	n/m
LYS UP SH	6/28/2005	37.4	n/m
LYS UP SH	7/28/2005	37.6	n/m
LYS UP SH	8/28/2005	46.2	n/m
LYS MI SH	6/28/2005	70.7	n/m
LYS MID SH	7/28/2005	178.4	n/m
LYS MID SH	8/28/2005	51.5	n/m
BW 39A	4/19/2005	186.4	0.18
BW-39A	6/28/2005	227.6	0.13
BW-39A	7/28/2005	262.3	0.11
BW-39A	10/5/2005	220.4	0.15
BW-39A	10/12/2005	233.2	0.14
T-1 (well)	7/28/2005	54.8	n/m
T-2 (well)	7/28/2005	167.1	n/m
T-3 (well)	7/28/2005	175.9	n/m

**Table 11** Water-extractable Si and Ge/Si data that was used to create soil solution chemistry profiles.

Depth (cm)	Si ( $\mu\text{mol/L}$ )	Ge/Si ( $\mu\text{mol/mol}$ )
Litter	34.21	0.04
0-22	22.19	0.45
22-27	17.56	1.52
27-34	22.89	2.51
37-47	28.30	0.69
47-57	305.71	0.81
57-70	3128.98	0.76

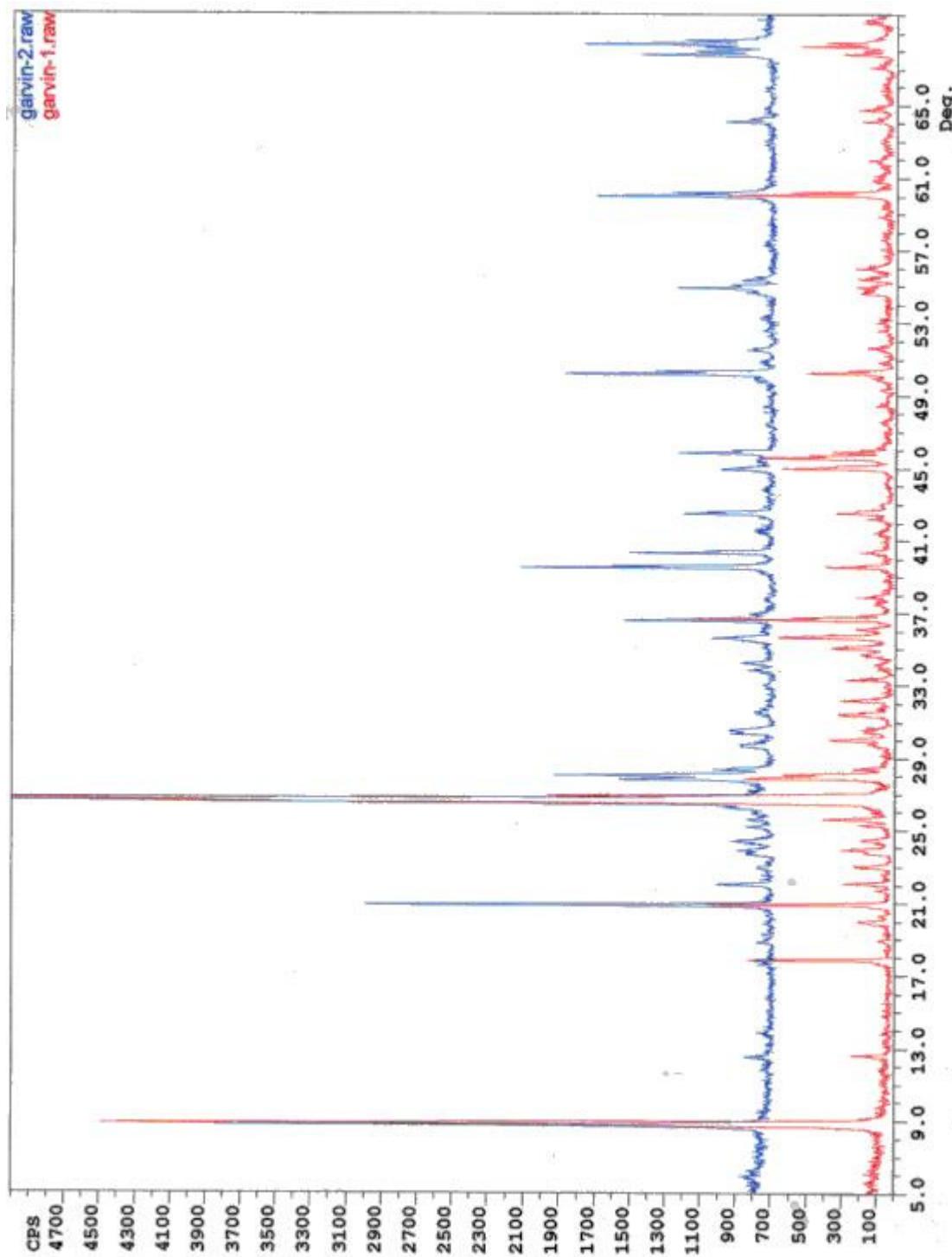
## APPENDIX III

### BEDROCK MINERALOGY

Sleepers River watershed W-9 is underlain by two bedrock units: the Waits River formation and the Gile Mountain formation. The point of contact of the two formations is at the high elevations of the W-9 watershed. Both formations consist of interbedded gray phyllite and calcareous granulite, though the Gile Mountain formation also contains beds of non-calcareous granulite (Newell, 1970). Phyllite is more prevalent than granulite, making up 50-80% of the bedrock in the watershed. Minerals found in the phyllite include quartz, muscovite, biotite, chlorite, plagioclase, and garnet, with some local sulfide inclusions. The calcareous granulite contains quartz, calcite, epidote group minerals, and diopside (Stewart Clark, pers. comm.). X-ray diffraction patterns were generated for two bedrock samples (Figure 21). Both signals were dominated by quartz and, to a lesser extent, albite.

Glacial till, which lies above the bedrock in nearly all parts of the watershed, is mineralogically similar to the underlying bedrock (Newell, 1970). However, the till also contains granitic cobbles transported by glaciers from northern Vermont and Canada. The cobbles are completely disaggregated in the till, and their constituent minerals include feldspar, quartz, biotite, and muscovite.

**Figure 22** Plot of XRD pattern for two bedrock samples from the Sleepers River watershed. Quartz and albite are the two dominant minerals present, though garnet was visible in the hand sample.



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