Effects of sampling frequency on estimates of dissolved silica export by streams: The role of hydrological variability and concentration-discharge relationships

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Accurate estimates of solute export are critical for mass balance studies of elemental flux. We explored how variation in hydrology (e.g., flashiness) and concentration-discharge relationships modulate the effect of solute sampling frequency on bias and precision associated with estimates of dissolved silica export in rivers. Dissolved silica concentration and discharge data from 14 rivers were used to parameterize a nonlinear concentration-discharge model, which was used to generate simulated data for daily dissolved silica concentration for 20 rivers. We determined how solute sampling at various intervals affects bias, precision, and root-mean-square error of export estimates. Bias and coefficient of variation of dissolved silica export increased with coarser sampling intervals. Flashiness and the coefficient of variation of daily discharge typically explained 90% or more of the variation in bias and precision of dissolved silica export, particularly at finer sampling intervals. Our analysis should be useful to researchers and land managers who are planning or evaluating sampling programs to determine solute flux or who seek error estimates for solute export.


1. Introduction

Changes in atmospheric deposition and land use have dramatically affected the delivery of many nutrients (e.g., nitrate, phosphate) to running surface waters [Likens and Bormann, 1974, 1995; Turner and Rabalais, 2003]. Accurate estimates of nutrient export are necessary for determining nutrient fluxes to receiving ecosystems and for calibrating ecosystem models of elemental cycling [e.g., Wattmough and Dillon, 2004]. As a result, there is a strong interest in the export of a wide variety of nutrients from watersheds across the United States and much of the world.

Annual estimates of nutrient export require measurements of stream discharge (Q) and measurements of nutrient concentration. Usually, Q is measured through the use of recording water level meters (i.e., essentially continuously) but there are many different strategies for sampling nutrient concentrations in rivers. Solutes can be collected (1) at fixed intervals (e.g., samples collected daily, weekly or monthly), (2) at fixed intervals augmented with event sampling (i.e., sampling at or near peak flows), or (3) stratified sampling techniques (i.e., solute samples are collected from regular percentiles of the flow distribution).

Once nutrient concentrations have been measured, there are a variety of methods for calculating nutrient export or load including (1) integration, (2) regression, and (3) ratio estimator approaches [Kronvang and Bruhn, 1996]. With each of these categories there are numerous variations [e.g., see Preston et al., 1989]. To determine the best method for calculating export for a given system, the frequency of measurements (flow and concentration), the length of the study, and the concentration-discharge relationship (described below) should be considered [Preston et al., 1989]. In cases where the relationship between concentration and discharge is well defined, regression or ratio estimator approaches are often used to calculate nutrient export [e.g., Haggard et al., 2003] whereas integration methods are commonly used when the concentration-discharge relationship is not known or weak [e.g., Sickman et al., 2001].

Because nutrient concentrations usually are measured less frequently than stream discharge, the frequency of nutrient concentration measurements can affect the accuracy and precision of estimates of export. Several studies have used records of daily nutrient concentration and flow in rivers and resampling techniques to determine how nutrient sampling frequency affects estimates of nutrient export. A general finding of these studies is that bias of nutrient export increases and precision decreases with decreasing sampling frequency [Dolan et al., 1981; Richards and Holloway, 1987; Guo et al., 2002; Haggard et al., 2003; Robertson, 2003].

Nutrients exhibit different responses to changing streamflow, which impacts how the sampling frequency of nutrients affects estimates of nutrient export. Forms of nutrients that are abundant in soils, and that are carried in
runoff due to soil erosion, tend to increase in concentration with increasing streamflow [Meyer and Likens, 1979; Pacini and Gächter, 1999]. Dissolved forms of nutrients that are prominent in soil water (e.g., dissolved silica) tend to decrease their concentration with increasing streamflow due to dilution by rainwater or snowmelt (Figure 1b) [Johnson et al., 1969; Salmon et al., 2001; Nagorski et al., 2003]. We show in Figure 1a some of the major ways that nutrient concentration in stream water changes with stream flow. A number of models have been used to describe the relationship between concentration and discharge, including simple regression models, models that incorporate seasonal factors [Haggard et al., 2003], and models that describe the mixing of different source water [Johnson et al., 1969]. The Johnson et al. model, described below, is particularly effective at describing how the stream water concentration of solutes prominent in subsurface water, such as dissolved silica, responds to change in stream water flow.

\[
S = \frac{C_6}{(1 + \beta(Q))} + C_\alpha
\]  

Figure 1. (a) Typical responses of solutes to changing discharge in streams. Type I is dilution [Johnson et al., 1969]. \(C_\alpha\) is the solute concentration in stream water during periods of high discharge. \(C_6\) is the difference between the solute concentration of subsurface water and \(C_\alpha\), \(Q\) is discharge, and \(\beta\) is a proportionality parameter. The ratio \(C_6/C_\alpha\) is a measure of the magnitude of change in solute concentration with change in discharge.

Phosphorus, and nitrogen to a lesser extent, have been the focus of many of the previous studies that have addressed how sampling frequency affects estimates of nutrient export, largely because of the availability of data sets that contain daily concentrations of total phosphorus, soluble reactive phosphorus, and nitrate [Dolan et al., 1981; Kronvang and Bruhn, 1996; Haggard et al., 2003]. Total phosphorus, and other constituents of soils that are readily entrained in runoff, tend to increase in concentration with increased stream flow. Less is known about how the export of dissolved nutrients that tend to be abundant in subsurface water (soil water, groundwater) and that tend to decrease in concentration with increasing streamflow, are affected by nutrient sampling frequency. In the current study we use dissolved silica as a model for solutes that are abundant in subsurface water and tend to become diluted with increasing streamflow. Little is known about how sampling frequency affects export estimates of dissolved silica, for which daily records of concentration for a year or more are rare [Bukaveckas et al., 1998]. Dissolved silica flux from rivers is important in the global biogeochemical cycle of silica as about 80% of the net inputs of dissolved silica to the world ocean come from rivers [Treguer et al., 1995]. In addition, anthropogenic activity in watersheds has changed the N:P:Si ratio of inputs to oceans, which has been linked to changes in primary production and phytoplankton community structure [Justic et al., 1995; Jickells, 1998; Turner et al., 1998].

Because most nutrients change in concentration with changing discharge, nutrient concentrations are susceptible to bias and lack of precision at coarse frequencies of sampling. Regardless of the method used to estimate flux (integration or regression), lack of concentration measurements during storm events can lead to considerable errors in estimating export [Robertson and Roerish, 1999]. For nutrients that increase in stream water concentration with increasing discharge, such as total nitrogen, lack of concentration measurements during high-flow events can lead to negatively biased estimates of nutrient export [Kronvang and Bruhn, 1996]. For nutrients that tend to decrease in concentration with increasing discharge, such as dissolved silica, export estimates tend to be positively biased when concentration measurements are lacking during high-flow events. Most past studies of export bias and precision have focused on how solute sampling regime and method of export calculation affect the bias and precision of export estimates [Kronvang and Bruhn, 1996; Robertson, 2003]. Because of the fundamental influence of hydrology on solute flux and concentration-discharge relationships in rivers, hydrology per se may have important
2. Methods

[11] We resampled modeled data of dissolved silica concentration, using the Johnson et al. [1969] model (equation (1) and described below), and used these data and daily records of flow from U.S. streams to calculate dissolved silica export. We determined how dissolved silica sampling frequency and hydrological variation, calculated from daily flow records, affected the bias and precision of export estimates. We also examined how the nature of the concentration-discharge relationship affected estimates of dissolved silica export.

[12] We parameterized the Johnson et al. [1969] model by fitting it to paired measurements of dissolved silica concentration and daily discharge from 14 streams in North America from a United States Geological Survey (USGS) data set [Alexander et al., 1996]. We used the term dissolved silica to refer to dissolved reactive silicate, which may include more than one form [Wels et al., 1991; Wetzel and Likens, 2000]. We used this information (Table 1) to determine realistic ranges for \( C_s \) and \( C_{so} \). The \( C_s:C_{so} \) ratio ranged from about 1 to 7, with a median of 1.6. Discharge did not explain all of the variation in dissolved silica concentration and the amount of variation explained varied among the 14 streams. To reduce computational complexity we did not consider this unexplained variation when applying the parameterized model to other streams (see below). As we discuss later there are other factors (e.g., soil type) that can drive variation in dissolved silica concentration in stream water besides hydrology.

[13] We used the parameterized Johnson et al. model and daily discharge data from 20 streams and rivers in North America [Alexander et al., 1996] to predict daily dissolved silica data for these systems for entire years. The following ratios of \( C_s:C_{so} \) were used to reflect natural variation in the relationship between stream water dissolved silica concentration and discharge: 0.5, 1.5, 2.5, 3.5, and 4.5. Part of this paper will focus on an “average” relationship between discharge and dissolved silica in stream water (\( C_s:C_{so} = 1.5 \)). Beta (\( \beta \)) is a proportionality parameter that tends to normalize the relationship between \( C_s \) and \( C_{so} \). Beta tends to decrease with increasing discharge (Table 1) and also reflects the curvature of the concentration-discharge relationship [Salmon et al., 2001]. Beta was set at 0.44 in all cases because discharge varied modestly (it was scaled from 1 to 100, see below). Dissolved silica concentrations were predicted with Equation 1 because of the rarity of data sets on daily dissolved silica from lotic systems. Streams and rivers were selected to span a range of variability in hydrological flashy and seasonality (Table 2) [Baker et al., 2004]. Discharge data were transformed to a 1 to 100 scale (based on the maximum discharge in the 5-year record of each river) for comparability among rivers of different size. Discharge data from 1979 to 1983 were selected in the interest of locating complete data sets for daily discharge. Thus daily dissolved silica data were generated for a total of 100 stream years.

[14] To determine how sampling frequency affects the bias and precision of dissolved silica export the modeled dissolved silica data were resampled at 1-, 7-, 14-, 28-, 56-, and 91-day frequencies. Resampling was done sequentially. For example, for the 7-day frequency, the data were first resampled on the first day of every week, then the second

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### Table 1. Streams and Rivers in the United States Used to Parameterize the Johnson et al. [1969] Model

<table>
<thead>
<tr>
<th>Ecosystem</th>
<th>Watershed Area, ha</th>
<th>( C_s, \mu M ) SiO(_2)</th>
<th>( C_{so}, \mu M ) SiO(_2)</th>
<th>( C_s:C_{so} )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andrews Cr.</td>
<td>WA</td>
<td>5696</td>
<td>0.0009</td>
<td>83</td>
<td>105</td>
</tr>
<tr>
<td>Beaver R.</td>
<td>UT</td>
<td>78444</td>
<td>0.0009</td>
<td>431</td>
<td>360</td>
</tr>
<tr>
<td>Big Cr.</td>
<td>LA</td>
<td>13203</td>
<td>0.0003</td>
<td>263</td>
<td>106</td>
</tr>
<tr>
<td>Buffalo Bayou</td>
<td>TX</td>
<td>79479</td>
<td>0.0005</td>
<td>558</td>
<td>80</td>
</tr>
<tr>
<td>Cypress Cr.</td>
<td>MS</td>
<td>13721</td>
<td>0.0001</td>
<td>155</td>
<td>40</td>
</tr>
<tr>
<td>Falling Cr.</td>
<td>GA</td>
<td>18640</td>
<td>0.0005</td>
<td>221</td>
<td>167</td>
</tr>
<tr>
<td>Half Moon Cr.</td>
<td>CO</td>
<td>6213</td>
<td>0.0032</td>
<td>88</td>
<td>54</td>
</tr>
<tr>
<td>Minimes R.</td>
<td>NM</td>
<td>47636</td>
<td>0.0010</td>
<td>354</td>
<td>507</td>
</tr>
<tr>
<td>Napa R.</td>
<td>CA</td>
<td>56438</td>
<td>&lt;0.0001</td>
<td>217</td>
<td>272</td>
</tr>
<tr>
<td>Skagway R.</td>
<td>AK</td>
<td>37539</td>
<td>0.0001</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>Sopcherry R.</td>
<td>FL</td>
<td>26407</td>
<td>0.0006</td>
<td>76</td>
<td>46</td>
</tr>
<tr>
<td>Waima R.</td>
<td>HI</td>
<td>15016</td>
<td>0.0009</td>
<td>290</td>
<td>127</td>
</tr>
<tr>
<td>Wet Bottom Cr.</td>
<td>AZ</td>
<td>9320</td>
<td>0.0367</td>
<td>608</td>
<td>250</td>
</tr>
<tr>
<td>W6 of HBEF</td>
<td>NH</td>
<td>13</td>
<td>0.4546</td>
<td>48</td>
<td>52</td>
</tr>
</tbody>
</table>

\*The model was fit to daily discharge and dissolved silica concentration from 1979 to 1981. All data were from Alexander et al. [1996] except watershed 6 (W6) at Hubbard Brook Experimental Forest (HBEF). \( N \) ranged from 17 to 55 among streams.
day, and so forth. Thus, for a single stream in a single year, 7-day sampling frequency generated 7 different sets of dissolved silica data, 14-day frequency generated 14 different combinations, and so forth.

[15] Annual export of dissolved silica was calculated by using the integration method [Bukaveckas et al., 1998; Buso et al., 2000]. Consider a time interval bounded by two measurements of dissolved silica concentration. For each of the two days in which dissolved silica data existed (i.e., modeled resampled data), export was determined by multiplying total daily discharge by dissolved silica concentration. During the intervening period, export was determined by multiplying cumulative discharge by the average dissolved silica concentration of the two samples. Estimates of annual export of dissolved silica were obtained by summing the export from a series of intervals throughout the year. Annual export based on daily sampling was considered the “unbiased” value. The bias in estimates of annual export when sampling (for concentration) was coarser than a daily interval was calculated as follows:

\[
\text{Bias} \% = \left( \frac{E_{\text{daily sampling}} - E_{\text{weekly sampling}}}{E_{\text{daily sampling}}} \right) \times 100
\]

where \( E \) is mean annual export and \( i \) sampling frequencies from 7 to 91 days.

[16] Precision of annual export estimates was determined as the coefficient of variation of annual export estimates for a given year and stream. The \( N \) (the number of export estimates) used to determine the mean bias and the coefficient of variation ranged from 7 (for weekly sampling frequency) to 91 (for seasonal sampling).

[17] Root-mean-square error (RMSE) was used as a composite measure of bias and variance for the export estimates [Preston et al., 1989; Kronvang and Bruhn, 1996; Haggard et al., 2003] and was expressed as a percentage of annual dissolved silica export. Percent bias and percent standard deviation (SD) of each estimate were used to calculate RMSE as follows:

\[
\text{RMSE} = (\text{Bias}^2 + \text{SD}^2)^{0.5}
\]

[18] Several parameters were used to describe variation in discharge during a year.

[19] A flashiness index \( F \), described below, was used to measure the day-to-day variation in discharge (equivalent to the Richards-Baker flashiness index [Baker et al., 2004]).

[20] Streams with high values of \( F \) experience large changes in discharge from one day to the next.

\[
F = \sum \frac{Q_{t-1} - Q_t}{365 Q_{\text{avg}}}
\]

where \( Q \) is total discharge for a day, \( t \) is time in days, and \( Q_{\text{avg}} \) is mean daily discharge for a year.

[21] The coefficient of variation of \( Q \) for a year \( CV_Q \) was used to describe overall variation in \( Q \) within a year [Chetelat and Pick, 2001]. Unlike \( F \), there is no time dependency to \( CV_Q \) such that a stream with a hydrograph that exhibits high flashiness or high seasonality would be expected to have a high \( CV_Q \). Skewness in the distribution of \( Q \) for a year was determined as this would likely indicate whether there was a relatively small number of large flows (positive skewness) due to storm or snowmelt events. Kurtosis of \( Q \) for a year was determined as another measure of overall variation in \( Q \). A negative value of kurtosis (shorter tails than a normal distribution) might be indicative of streams that have relatively stable flows.

[22] Additional parameters were used to describe the seasonality of discharge: \( Q_{\text{spring}}/Q_{\text{avg}} \) (where \( Q_{\text{spring}} \) is the mean daily discharge for spring), \( Q_{\text{summer}}/Q_{\text{avg}} \) (where \( Q_{\text{summer}} \) is the mean daily discharge for summer), \( Q_{\text{fall}}/Q_{\text{avg}} \) (where \( Q_{\text{fall}} \) is the mean daily discharge for fall), and \( Q_{\text{winter}}/Q_{\text{avg}} \) (where \( Q_{\text{winter}} \) is the mean daily discharge for winter). A seasonality index was calculated by dividing the maximum seasonal term by the minimum seasonal term for a given year. Streams with hydrographs that are strongly dominated by spring snowmelt or that reflect seasonal variation in rainfall would be expected to have a high seasonality index.

[23] Bivariate and trivariate plots were used to explore how dissolved silica sampling frequency, flashiness, and the concentration-discharge relationship influenced the bias, precision, and RMSE of estimates of annual silica export. Stepwise multiple regression (with forward selection of variables) was used to explore the influence of the hydrological parameters on modeled annual dissolved silica export, rather than to establish statistical inference. The criteria for inclusion in the models was a \( P \) of 0.15. Because multicollinearity existed between the flashiness index and \( CV_Q \), the residuals of the simple regressions between the flashiness index and \( CV_Q \) were used in the multiple regression models [Graham, 2003]. In addition to flashiness and \( CV_Q \) (or the appropriate residual term for each), variables available for entry into the regression models included the seasonality index, skewness, and kurtosis.

Table 2. Streams and Rivers in the United States Used for Resampling Dissolved Silica Concentration and for Calculation of Bias and Precision of Annual Dissolved Silica Export

<table>
<thead>
<tr>
<th>Ecosystem</th>
<th>State</th>
<th>Watershed Area, ha</th>
<th>Flashiness Index</th>
<th>CVQ</th>
<th>Seasonality Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andrews Cr.</td>
<td>WA</td>
<td>5696</td>
<td>0.102</td>
<td>174</td>
<td>16.6</td>
</tr>
<tr>
<td>Big Cr.</td>
<td>LA</td>
<td>13203</td>
<td>0.609</td>
<td>286</td>
<td>6.5</td>
</tr>
<tr>
<td>Charles R.</td>
<td>MA</td>
<td>47377</td>
<td>0.087</td>
<td>102</td>
<td>6.4</td>
</tr>
<tr>
<td>Cossatot R.</td>
<td>AR</td>
<td>23000</td>
<td>0.630</td>
<td>224</td>
<td>8.1</td>
</tr>
<tr>
<td>Elwha R.</td>
<td>WA</td>
<td>69641</td>
<td>0.217</td>
<td>98</td>
<td>2.3</td>
</tr>
<tr>
<td>Grant R.</td>
<td>WI</td>
<td>69646</td>
<td>0.206</td>
<td>92</td>
<td>1.7</td>
</tr>
<tr>
<td>Half-moon Cr.</td>
<td>CO</td>
<td>6213</td>
<td>0.090</td>
<td>150</td>
<td>20.5</td>
</tr>
<tr>
<td>Kashiwihiv R.</td>
<td>MN</td>
<td>65499</td>
<td>0.037</td>
<td>112</td>
<td>7.7</td>
</tr>
<tr>
<td>Kimichiii R.</td>
<td>OK</td>
<td>10536</td>
<td>0.635</td>
<td>249</td>
<td>34.8</td>
</tr>
<tr>
<td>N. Fork Whitewater R.</td>
<td>MN</td>
<td>26148</td>
<td>0.199</td>
<td>111</td>
<td>2.2</td>
</tr>
<tr>
<td>Narraguagus R.</td>
<td>ME</td>
<td>58768</td>
<td>0.193</td>
<td>103</td>
<td>5.3</td>
</tr>
<tr>
<td>Rio Mora Cr.</td>
<td>NM</td>
<td>13721</td>
<td>0.100</td>
<td>143</td>
<td>16.0</td>
</tr>
<tr>
<td>Sophochuppy R.</td>
<td>FL</td>
<td>26407</td>
<td>0.251</td>
<td>173</td>
<td>10.1</td>
</tr>
<tr>
<td>South Hogan Cr.</td>
<td>IN</td>
<td>9838</td>
<td>0.951</td>
<td>320</td>
<td>65.2</td>
</tr>
<tr>
<td>South Twin R.</td>
<td>NV</td>
<td>5178</td>
<td>0.087</td>
<td>137</td>
<td>8.7</td>
</tr>
<tr>
<td>Tularosa Cr.</td>
<td>NM</td>
<td>31067</td>
<td>0.117</td>
<td>61</td>
<td>1.3</td>
</tr>
<tr>
<td>Upper Twin Cr.</td>
<td>OH</td>
<td>3107</td>
<td>0.564</td>
<td>218</td>
<td>72.4</td>
</tr>
<tr>
<td>Washington Cr.</td>
<td>MI</td>
<td>3366</td>
<td>0.223</td>
<td>179</td>
<td>15.3</td>
</tr>
<tr>
<td>Wet Bottom Cr.</td>
<td>AZ</td>
<td>9320</td>
<td>0.174</td>
<td>452</td>
<td>3647.5</td>
</tr>
<tr>
<td>W6 of HBEF</td>
<td>NH</td>
<td>13</td>
<td>0.594</td>
<td>203</td>
<td>23.7</td>
</tr>
</tbody>
</table>

*Hydrological parameters, defined in section 2, are means of annual values from 1979 to 1983.
Five-year means of the hydrological parameters and error estimates (bias, CV, and root-mean-square error) were used in the multiple regression models, which resulted in one set of observations per stream ($N = 20$).

3. Results

[34] We will first focus on how sampling frequency and hydrologic variability affects estimates of dissolved silica export for an average dissolved silica concentration relationship ($C_d/C_a = 1.5$).

3.1. Accuracy

[35] When sampling frequency was high, estimates of annual dissolved silica export were positively biased by as much as 25% (Figure 2a). As the sampling frequency decreased, dissolved silica export became increasingly positively biased up to 50% and greater. (Figures 2b–2e and Table 3). Hydrological flashiness explained much of the variation in bias of annual dissolved silica export, particularly at high sampling frequencies ($R^2 = 0.94$, Figure 2a). Flashiness explained a decreasing amount of variation in export bias as sampling frequency decreased (91-d frequency, $R^2 = 0.53$, Figure 2e). Inclusion of other hydrological variables increased the amount of variation in export bias that could be explained and more overall variation was explained at higher sampling frequencies than at low sampling frequencies (Table 4). In agreement with the bivariate plots (Figure 2) the multiple regression models indicate that flashiness was a very important driver of variation in export bias at dissolved silica export at high sampling frequencies (note magnitude of standardized coefficients in Table 4) but less important at low sampling frequencies. The CV$_Q$ became the most important predictor of variation in export bias at low sampling frequencies (Table 4).

3.2. Precision

[36] Solute sampling frequency had a smaller effect on the precision of dissolved silica export than on the % bias. Although the mean of the coefficient of variation (CV) increased as dissolved silica sampling frequency decreased (Table 3), the CV ranged from near 0 to about 10 regardless of the frequency of sampling (Figure 3). Systems with flashy hydrographs tended to have decreased precision of export estimates relative to systems with nonflashy hydro-

**Table 3.** Means of Percent Bias and CV for Estimates of Dissolved Silica Annual Export at Different Frequencies of Dissolved Silica Sampling

<table>
<thead>
<tr>
<th>Sampling Frequency, days</th>
<th>Percent Bias</th>
<th>CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>7.12</td>
<td>1.85</td>
</tr>
<tr>
<td>14</td>
<td>10.17</td>
<td>2.29</td>
</tr>
<tr>
<td>28</td>
<td>13.24</td>
<td>3.34</td>
</tr>
<tr>
<td>56</td>
<td>17.56</td>
<td>4.54</td>
</tr>
<tr>
<td>91</td>
<td>21.61</td>
<td>5.62</td>
</tr>
</tbody>
</table>

* $C_d/C_a = 1.5$. $N = 100$.

**Figure 2.** Percent bias in annual export of modeled dissolved silica versus flashiness index. Dissolved silica sampled at (a) 7, (b) 14, (c) 28, (d) 56, and (e) 91 days; $C_d/C_a$ is set at 1.5. Linear regression models were fit to the data.
graphs, particularly at higher sampling frequency (Figure 3). There was little variation in CV among streams with low flashiness when sampling frequency was every 28-d or higher. However, when these streams were sampled at lower frequencies, the variation in CV among streams was considerably higher (Figure 3).

[27] As for bias in dissolved silica export, hydrological flashiness explained considerable variation in the precision of export estimates, especially at high sampling frequency (7-day frequency $R^2 = 0.76$, Figure 3). The ability of flashiness to explain variation in the CV of dissolved silica export decreased sharply as sampling frequency decreased (Figure 3). As with % bias, inclusion of other hydrological variables substantially improved the amount of variation in CV of dissolved silica export that could be explained (Table 4). In addition to hydrological flashiness, CVQ was an important driver of variation in CV of dissolved silica export. The amount of variation in CV of dissolved silica export that could be explained in the multiple regression models decreased at lower sampling frequency.

### 3.3. Root-Mean-Square Error

[28] Flashiness and CVQ also were the most important factors in explaining variation in root-mean-square error (RMSE) of dissolved silica export (Table 4). We considered how sampling frequency, flashiness, and the nature of the concentration-discharge relationship simultaneously affected RMSE of dissolved silica export. The RMSE of annual dissolved silica export is highest in flashy streams that are sampled at coarse intervals (Figure 4). The RMSE increases by about fourfold as $C_c:C_v$ increases from 0.5 to 4.5. For a given $C_c:C_v$, RMSE increases about twofold from 7- to 91-d sampling intervals in flashy streams and tenfold in the least flashy streams. However, in the flashiest streams RMSE of dissolved silica export is highest at every sampling frequency than is the RMSE in the least flashy streams even at a 91-d frequency (Figure 4).

### 4. Discussion

[29] There was a consistent positive bias in most of the streams when estimating the annual export of dissolved silica. Because dissolved silica in stream water tends to become diluted with increasing flow [Johnson et al., 1969; Hornberger et al., 2001; Nagorski et al., 2003], storm events produce relatively large slugs of stream water depleted in dissolved silica. When dissolved silica is sampled at low frequency, these storm events tend to be missed. In cases where integration methods are used to calculate export, dissolved silica concentrations for these storm events tend to be overestimated, leading to overestimation of dissolved silica export. As sampling frequency decreases, the magnitude of export bias increases because on average, a larger amount of stream water, depleted in dissolved silica, is mischaracterized. Other investigators have noted that export estimates for solutes that become diluted with increasing flow are positively biased [Kronvang and Bruhn, 1996; King and Harmel, 2003].

[30] Hydrological variation influenced the relationship between sampling frequency and dissolved silica export. As flashiness increased, bias of dissolved silica export tended to increase. This result occurred because as flashiness increases there is an increasing opportunity for storm events to be missed when sampling for dissolved silica with a standard protocol. Flashiness was a much better predictor of export bias at high sampling frequencies than at low sampling frequencies for a $C_c:C_v$ of 1.5 (Figure 2). At high flashiness (>0.30), bias tended to be high at all sampling frequencies. At low flashiness (<0.30), increasing flashiness predicted bias at high sampling frequencies but not at low sampling frequencies. At very coarse sampling frequencies (56- and 91-d), bias was often 10–20% even at low flashiness (Figure 2). This result primarily reflects the bias that can occur when large predictable discharge peaks, typical of snowmelt-dominated streams with low flashiness, are missed at very coarse sampling frequencies. The gradual changes in dissolved silica concentration in stream water that accompany gradual changes in flow in streams with low flashiness, are sufficiently captured when sampling frequency is high, thus bias is consistently very low. In contrast to our findings, Robertson and Roerish [1999] and Robertson [2003] found that flashiness was only weakly related to errors in estimating export in 8 Wisconsin streams.

[31] The coefficient of variation of discharge (CVQ) does not separate the basic hydrograph types as effectively as the flashiness index, and that is probably why the former is not as good in predicting bias in dissolved silica export.
especially at high sampling frequencies. For example, the flashiness index distinguishes snowmelt-dominated streams with predictable flow from streams with unpredictable flow in warmer climates. However, these two stream types could have similar CVQ values. As CVQ is a measure of overall hydrological variation, but not the timing of the variation, it cannot separate these stream types. However, because CVQ tends to reflect variation regardless of timing, it tends to increase as hydrological variation in streams becomes more seasonal and flashier. Thus CVQ is a better predictor of bias of dissolved silica export than flashiness at low (56- and 91-d) sampling frequencies (Table 4).

[32] Mean coefficient of variation of export (precision) tended to increase with decreasing sampling frequency (Table 3), but unlike bias, the overall range did not change. Other studies showed that decreased sampling frequency tends to increase coefficient of variation (or a similar measure of variation) [Kronvang and Bruhn, 1996; Robertson and Roerish, 1999; Haggard et al., 2003]. The uniformly high CVQ of export for streams with high flashiness (&gt;0.30) suggests that sampling frequency has little impact on precision of estimates of dissolved silica export in flashy streams. However, streams with low flashiness had higher and more variable CVQ of export as sampling frequency decreased. As with bias at low flashiness this increased CVQ of export at low sampling frequency largely reflected seasonal variation in hydrology.

[33] Bias and precision of dissolved silica export are affected by sampling frequency primarily because of the relationship between dissolved silica concentration and discharge. Concentration-discharge relationships in most streams are a function of the mixing of three separate sources of water (groundwater, soil water, and overland flow), and each can have a different solute concentration [e.g., Asano et al., 2003]. Dissolved silica concentration tends to be relatively high in groundwater and soil water [Asano et al., 2003], relatively low in throughfall (e.g., in forests) and overland flow [Asano et al., 2003] and approaches zero in precipitation [Likens and Bormann, 1995; Buttle and Peters, 1997]. Dissolved silica concentration in stream water generally decreases with increasing discharge, because the contributions of precipitation and runoff increase during stormflow.

[34] The slope of the concentration-discharge relationship strongly affects the bias and precision of dissolved silica export (Figure 4). As $C_d$:$C_a$ increases, the bias and coefficient of variation increase, and thus the RMSE of estimates of dissolved silica export increases (Figure 4). This ratio is variable in streams (Table 1), and reflects the difference between the dissolved silica concentration of subsurface water and precipitation. Because precipitation typically has a very low concentration of dissolved silica, the $C_d$:$C_a$ ratio will tend to be highest when the soil water and/or groundwater has high dissolved silica concentration. Chemical weathering and leaching exert a large control on the dissolved silica concentration in groundwater and soil water. Silicate weathering occurs primarily by carbonation reactions [Schlesinger, 1997; Rice and Bricker, 1995]. Organic acids and sulfuric acid, associated with acid rain, can also be important [Rice and Bricker, 1995]. Several factors affect the rates at which silicate minerals are weathered including rock type [White et al., 2001], soil type [Wels et al., 1991],

**Figure 3.** Coefficient of variation of annual export of modeled dissolved silica versus flashiness index. Dissolved silica sampled at (a) 7, (b) 14, (c) 28, (d) 56, and (e) 91 days. $C_d$:$C_a$ is set at 1.5. Linear regression models were fit to the data.
precipitation [Schlesinger, 1997], water table depth [Rice and Bricker, 1995], and temperature [White and Blum, 1995]. Because the contact time between water and silicate rocks and soils can affect if weathering reactions reach equilibrium, water residence time also influences the concentration of dissolved silica in groundwater and soil water [McKeague and Cline, 1963; Rice and Bricker, 1995]. The C_d:C_a ratio would probably be highest, and thus the potential for bias of dissolved silica export to be greatest, in watersheds containing silicate-rich rocks that are rapidly weathered.

Figure 4. The influence of sampling frequency, hydrologic flashiness, and the nature of the concentration-discharge relationship on the root-mean-square error (RMSE) as a percentage of annual export of modeled dissolved silica. Five-year means of flashiness were used to place rivers in flashiness categories (0–0.2, 0.2–0.4, etc.). RMSEs are means of rivers in a particular flashiness category. (a) C_d:C_a = 0.5 (see Johnson et al. [1969] model). (b) C_d:C_a = 1.5. (c) C_d:C_a = 2.5. (d) C_d:C_a = 3.5. (e) C_d:C_a = 4.5.
programs and for those with data in hand who want to estimate the errors associated with their export estimates. If the goal is to keep RMSE below a certain threshold (e.g., <30%), then the acceptable sampling frequency will depend on the concentration-discharge relationship ($C_a:C_r$) and the flashiness of the system (Figure 4). For a stream with low to moderate flashiness and with a $C_a:C_r$ of 1.5 (Figure 4b) sampling at high frequencies may not be worth the added cost and effort, since sampling at moderate to coarse frequencies would probably keep the RMSE below 30%. When more accurate and precise export estimates are necessary (e.g., RMSE < 15%), as are usually needed for detailed mass balance studies of nutrient cycling, then higher sampling frequency would be required for a stream with low to moderate flashiness and with a $C_a:C_r$ ratio of 1.5. If the stream was moderately flashy and with a higher ratio of $C_a:C_r$ (e.g., 2.5, Figure 4c) then weekly, or more frequent, sampling may be necessary to keep RMSE at acceptable levels. 

[30] Our analysis suggests that annual estimates of dissolved silica export can be positively biased depending on the sampling frequency, hydrograph shape, and the concentration-discharge relationship. Estimates of annual export for other solutes in which concentration varies with discharge are also susceptible to bias. There has been an increasing interest in measuring the cycling and flux of nitrogen in rivers. Unlike dissolved silica, the concentration of nitrate and other N species may increase [Johnson et al., 1969; Hill, 1978; Sickman and Melack, 1998; Coats and Goldman, 2001; Guo et al., 2002], decrease [Hill, 1978; Sickman and Melack, 1998; Lewis et al., 1999], or be unrelated or weakly related [e.g., McDowell and Ashby, 1994] with discharge in streams and rivers. Several investigators have found that nitrate concentration in streams draining forest watersheds increases during snowmelt periods [Coats and Goldman, 2001] but stays low during the summer [Likens and Bormann, 1995]. Nitrate concentration increases with discharge regardless of season in agricultural streams [Guo et al., 2002]. Because nitrate concentration in stream water tends to increase during snowmelt, there is the potential for estimates of N export during these periods to be negatively biased when hydrographs are flashy and periods of high discharge, N-rich water are missed during sampling efforts.

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