A Study of High Frequency Water Quality Observations
in the Little Bear River Utah, USA

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Abstract

Process-based understanding of short and longer-term behavior of catchments is becoming increasingly important to our ability to predict hydrologic system response. The time scale of many processes is on the order of minutes to hours, not weeks to months, and understanding the linkages between catchment hydrology and hydrochemistry requires measurements on a time scale consistent with these processes. These are motivating factors in the recent push toward establishment of environmental observatories within the hydrologic and environmental engineering communities that has seen creation of a network of observatory test beds. In this paper we present a study of high frequency water quality observations that have served as the basis for establishing the Little Bear River Test Bed (LBRTB) as one of these test beds with the overarching goal of improving understanding of water quality constituent fluxes and the observing infrastructure and cyberinfrastructure needed to quantify these fluxes. We describe our sensor network design, cyberinfrastructure, and data collection procedures and provide results from four analyses that demonstrate how the scope and resolution of sensor network data enable identification of trends and analysis of hydrologic and hydrochemical behavior that could not be observed by traditional water quality monitoring. Using high-frequency data, we demonstrate the importance of early spring snowmelt in contributing to annual loads of total phosphorus and total suspended solids, the effect of sampling frequency on estimates of annual loading, the relative magnitudes and timing of baseflow versus quickflow as the dominant flow pathways, and differences in ecological responses across sites.
1. Introduction

As water resource managers are faced with growing pressure on limited water resources, process-based understanding of short and longer-term behavior of catchments is becoming increasingly important. Our ability to predict hydrologic system response is dependent on our understanding of catchment behavior and the interacting processes that drive that response. In relatively small catchments, the time scale of many important hydrologic and hydrochemical processes is on the order of minutes to hours, not weeks to months, and understanding the process linkages between catchment hydrology and stream water chemistry, which is necessary for incorporating these processes into predictive models, requires measurements on a time scale that is consistent with these processes [Kirchner et al., 2004].

Many believe that advancing the science of hydrology will require new measurements and hydrologic measurement techniques, and that data generated by coordinated, extensive field studies will be required to enable these advances [Woods et al., 2001; Kirchner, 2006; Hart and Martinez, 2006]. This belief is primarily responsible for the recent push toward establishment of large-scale environmental observatories within the hydrologic and environmental engineering communities. The driver behind environmental observatories is that knowledge of the physical, chemical, and biological mechanisms controlling water quantity and quality is limited by lack of observations at the necessary spatial density and temporal frequency needed to infer the controlling processes [Montgomery et al., 2007]. Within observatories, environmental sensor networks have been proposed as part of the cyberinfrastructure that will be required to generate data of both high spatial and temporal frequency and enable scientific discovery. Sensor network technologies offer several advantages over traditional monitoring techniques by streamlining the data collection process, reducing human errors and time delays, reducing overall
cost of data collection, and increasing the quantity and quality of data on temporal and spatial scales [Glasgow et al., 2004].

Continuous, high-frequency monitoring records generated using in-situ sensors can reveal detail in short-term variability in water quantity and quality that is not well captured by conventional monthly, weekly, or even daily grab sampling programs [Jarvie et al., 2001; Kirchner et al., 2004; Tetzlaff et al., 2007; Tomlinson and De Carlo, 2003]. Continuous records can be critical in capturing and characterizing both regular and transient events and are becoming increasingly common as sensor technology improves. Observable short-term hydrologic and water quality signals include fluctuations in discharge related to precipitation, snowmelt, and agricultural diversions and return flows. Diurnal fluctuations in pH and dissolved oxygen concentration related to in-stream biological activity are evident in many systems [Wang et al., 2003; Mulholland et al., 2005; Chapra, 1997]. Spikes in turbidity related to sediment pulses occurring during spring snowmelt and storm events [Stubblefield et al., 2007; Uhrich and Bragg, 2003], and changes in specific conductance related to variability in the sources of water that make up streamflow are also commonly observed [Covino and McGlynn, 2007; Stewart et al., 2007]. In addition to characterizing short-term variability, high-frequency measurements made over long periods enable us to examine how short-term variability changes across hydrologic regimes and maximizes the chances for serendipitous discoveries [Kirchner et al., 2004].

Despite advances in technology, however, and in some cases because of them, many challenges associated with establishing sensor networks for scientific research remain. Developing and deploying sensor networks can be an onerous task that requires a great deal of expertise, and domain scientists must step outside of their primary knowledge area to gain the skills necessary for designing and deploying field experiments that employ sensor networks.
The sheer volume of data generated by sensor networks presents challenges associated with data processing, quality control, archiving, and analysis that are much different than those encountered with more traditional data. Additionally, logistical challenges, such as obtaining site access, hardening deployments against environmental conditions, and overcoming communication limitations, are inherent in sensor network design and deployment [Lundquist et al., 2003]. In many cases, sensor technology does not yet exist to measure important variables, which has driven research into new sensor technologies and the use of existing sensor measurements as surrogates for variables that cannot be measured continuously [Christensen et al., 2002; Stubblefield et al., 2007; Uhrich and Bragg, 2003]. If sensor networks are to reach their potential as standard research tools, there is a need to simplify and standardize aspects of the design, setup, configuration, programming, deployment, and maintenance of sensor network components.

In 2006, recognizing the challenges associated with establishing sensor networks, and, on a broader scale, the entire infrastructure to support large-scale environmental observatories, a network of 11 environmental observatory test bed projects was created across the United States. These test beds are part of the WATERS (WATer and Environmental Research Systems) network (http://www.watersnet.org/), and each was selected to demonstrate techniques and technologies that could be used in the design and implementation of a national network of large-scale environmental observatories. Technologies investigated within the test beds range from innovative application of environmental sensors to achieve a better understanding of the stores and fluxes of environmental constituents to development of software components for publishing observations data in common formats that can be accessed by investigators throughout the
scientific community [Minsker et al., 2006; Moore et al., 2007; Welty et al., 2007; Stevens et al., 2007; Fisher et al., 2007].

The Little Bear River test bed (LBRTB) was established primarily to test the hypothesis that high-frequency sensor data collected at multiple sites can improve hydrologic and hydrochemical process understanding. We are examining turbidity as a surrogate for concentrations of total suspended solids (TSS) and total phosphorus (TP) to provide a means for better quantifying patterns in constituent fluxes within the watershed. Turbidity can be measured with high-frequency relatively inexpensively, whereas there are currently no reliable continuous in-situ sensors for TP and TSS. We are also examining specific conductance as a tracer that can be measured with high-frequency for investigating flow pathways and dissolved oxygen as an indicator of ecosystem function and dynamic diurnal processes. Secondary research goals within the LBRTB include investigating the effects of sampling frequency on estimates of annual TP and TSS loads and advancing available cyberinfrastructure for storing, archiving, accessing, visualizing, and analyzing observatory data.

In this paper we present findings from our analyses of high-frequency data collected using in-situ sensors to date that include: 1) high-frequency synthetic time series of TSS and TP generated from surrogate turbidity data that reveal concentrated periods of high TSS and TP loading that dominate the annual load and occur primarily during early spring snowmelt; 2) annual TP and TSS load estimates calculated from daily, weekly, and monthly subsets of the high-frequency data that show how annual loads calculated from infrequent samples are only order of magnitude estimates that tend to underestimate the true annual loading in the majority of cases; 3) a two component hydrograph separation based on specific conductance that shows quickflow (i.e., new water) dominating the spring snowmelt hydrograph and baseflow (i.e., old
water) remaining relatively constant throughout the year; and 4) estimates of photosynthesis and
respiration rates calculated based on diurnal dissolved oxygen curves that are very different from
site to site and provide metrics for comparing instream metabolism.

These examples demonstrate how the scope and resolution of data generated by sensor
networks enable identification of trends and analysis of behavior that could not be observed by
traditional water quality monitoring or short-term field campaigns. We also discuss how our
methods, data collection, and analyses can support the design and implementation of large-scale
environmental observatories. It is expected that these analyses will be expanded as the LBRTB
datasets mature.

In Section 2, we describe the physical setting of the Little Bear River watershed. In
Section 3 we describe the experimental and sensor network design, data collection procedures,
and methods that have been implemented to support our analyses. We also provide a brief
description of the data management and publication procedures and cyberinfrastructure that have
been implemented to support the LBRTB. Following these descriptions, in Sections 4 and 5 we
present our results and discuss how the cyberinfrastructure that we have implemented enabled
our analyses. Finally, in Section 6 we summarize our results.

2. Site Description

The Little Bear River in northern Utah, United States (Figure 1) drains an area of
approximately 740 km$^2$ and is typical of many semi-arid watersheds in the western United States
where streamflow is dominated by spring snowmelt and where extensive hydrologic
modification for agricultural diversion has taken place. The Little Bear River drains into Cutler
Reservoir, a shallow, eutrophic reservoir on the mainstem of the Bear River, which ultimately
drains to the Great Salt Lake. The Little Bear River watershed encompasses primarily lower
elevation agricultural, mid-elevation range, and higher elevation forested lands. Approximately 70% of the watershed area is grazing land and forest, 19% is irrigated cropland and, 7% is dry cropland. The area is experiencing rapid population growth, with a 32% increase in population between 1990 and 2000 [U.S. Census Bureau, 2000].

The headwaters of the Little Bear River are located in the Bear River Mountain Range, which consists, in large part, of a thick sequence of carbonate (limestone and dolomite) rocks that range in age from Cambrian to Mississippian [Dover, 1987; Schaefer et al., 2006]. In general, this leads to waters with relatively high and well buffered pH, as well as relatively high specific conductance and dissolved solids concentrations. Elevations in the watershed range from 1,340 m to over 2,700 m. Most of the annual precipitation falls as snow at higher elevations and can exceed 900 mm yr\(^{-1}\), as recorded at the Little Bear River Snowpack Telemetry (SNOTEL) site, with occasional summer storms. Precipitation near the outlet is on the order of 450 mm yr\(^{-1}\), demonstrating the variability in annual precipitation with elevation.

The Little Bear has two principal subdrainages, the East Fork and the South Fork. The South Fork and its major tributary, Davenport Creek, flow northward through forest and range land before the confluence with the East Fork. The East Fork originates in higher elevation, forested land, and flows northwest until it is contained by Porcupine Reservoir, which is used to store water for summer agricultural irrigation. A few miles downstream of Porcupine dam, the East Fork is diverted for irrigation purposes, and for several months of the year, portions of the natural channel are dry. The confluence of the two forks is near the town of Avon, after which the river flows northward through the towns of Paradise and Hyrum. Most of the land adjacent to this stretch of the river is agricultural, including crops and livestock grazing. At Hyrum, the river is contained in Hyrum Reservoir, which is also operated to supply water for irrigation of
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agricultural areas below the reservoir. Below Hyrum dam, the river flows northwest through lower gradient agricultural land, passing through the towns of Wellsville and Mendon before draining into an arm of Cutler Reservoir.

3. Methods

3.1. Monitoring Sites

Seven stream monitoring sites have been established along the Little Bear River, two during the summer of 2005 and five more during the summer of 2007. Sites were selected to characterize the major hydrologic conditions in the watershed and to represent the range of land use conditions, with preference given to locations that would provide the most information given our limited resources. In addition to considering hydrology and land use, site selection was dependent on the presence of a bridge or other permanent structure to which the sensors could be mounted, our ability to obtain permission to access the site, our ability to establish a stream cross section suitable for development of a stage-discharge relationship, and our ability to establish communications with the site to retrieve the data. Two sites were located in the unregulated South Fork (Upper South Fork and Lower South Fork), two sites were located where they would be highly influenced by releases from the two reservoirs in the system (East Fork and Wellsville), two sites were located in intermediate locations that would represent the combination of unregulated flows plus reservoir releases (Confluence and Paradise), and the last site was located near the terminus of the river just upstream of Cutler Reservoir (Mendon).

Two continuous weather stations were also installed during the summer of 2007, one near the boundary of the lower watershed and one near the confluence of the East and South Forks. Weather station locations were selected to characterize the upper and lower watershed and were constrained by similar site access and communication limitations. Two USDA NRCS SNOTEL
sites provide additional continuous weather and snowpack data for the Little Bear. The Little Bear SNOTEL site is located near the headwaters of the South Fork of the Little Bear at an elevation of approximately 1,994 m, and the Dry Bread Pond SNOTEL site is located in the headwaters of the East Fork at an elevation of approximately 2,545 m. Figure 1 shows the location of each of the monitoring sites, which are described in Table 1.

3.2. Continuous Measurements

At each stream monitoring site, a suite of sensors was permanently installed to provide in-situ discharge and water quality records. Data from each of the stream sensors is recorded electronically at 30-minute resolution, with recorded values representing the average over the 30-minute period. At the two weather station sites, data are collected and recorded electronically at hourly resolution (i.e., hourly average/total values) using tripod mounted sensors. Table 2 lists the variables measured at each site, the sensors that are being used, and the manufacturers’ reported accuracy and resolution where available.

Continuous discharge is calculated from the stage records according to stage-discharge rating curves that have been developed for each monitoring site. Periodic discharge measurements and water surface elevations are collected at each site for the purpose of establishing and maintaining stage-discharge relationships. Discharge measurements have been made using the area-velocity method [Buchanan and Somers, 1969] over a range of different discharges to ensure that the derived relationships are representative of the range of hydrologic conditions at each site. Stream velocities are measured using a Marsh McBirney Flo-Mate Model 2000 velocity meter and depths are measured using a top-setting wading rod.

Stream sensors were installed in the main flow of the river and were enclosed inside PVC pipe housings to protect them from debris and vandalism. The PVC sensor housings were fitted
with metal pump screens into which the sensors extend to ensure adequate water flow-through and to protect the sample space around each of the sensors. All sensors are removed and cleaned in the field at least once every two weeks. During each site visit, calibration of the Hydrolab sensors is checked, and recalibration is performed onsite as necessary. The pH sensors are calibrated using both pH 7 and pH 10 buffer solutions, and conductivity sensors are calibrated using a 718 µS cm⁻¹ potassium chloride standard. Dissolved oxygen is calibrated to water saturated air using barometric pressure measurements made onsite using a Hydrolab Surveyor (Hach Environmental, Inc.) equipped with a barometric pressure sensor. The turbidity sensors and pressure transducers do not require regular calibration (per the manufacturer’s specifications), although the sensors are checked and cleaned every two weeks along with the Hydrolabs.

The continuous measurements are passed through two levels of quality control. First, the data are plotted and examined for out of range and obviously erroneous data values. Where possible, spurious values are replaced using linear interpolation. In the second level of quality control, data are adjusted for sensor drift using linear drift corrections between the calibration dates as recorded in field notes. All corrections and edits are performed on a copy of the raw data to ensure that the original data are preserved.

3.3. Chemistry Sampling

From April 2005 to October 2007, storm event samples and sporadic grab samples from prior studies were available at the Mendon and Paradise sites. Beginning in October of 2007 (at which time in-situ instruments had been installed at all but one site), we began regularly collecting water quality grab samples at all seven sites. Sampling occurs once per week during the spring snowmelt season (March through July) and once every two weeks during the rest of
the year. The order in which sites are visited and the day of the week on which sampling occurs are varied in an effort to minimize potential bias due to sampling time of day and day of the week.

In addition to the grab samples, storm event and spring snowmelt event samples have been collected using ISCO 3700 Portable Automated Samplers (Teledyne ISCO, Inc.). These samplers operate by pumping water from the river through tubing into sample bottles held within the sampler, allowing for the collection of multiple samples during an event such as a storm or a period of snowmelt. In general, deployment of the automated samplers has occurred either when precipitation is expected or when a significant snowmelt event is expected.

Phosphorus samples are collected in acid washed 250-mL HDPE bottles, and TSS samples are collected in 500-mL HDPE bottles. Each water quality sample is split for total suspended solids (TSS) and total phosphorus (TP) analysis, with a portion of the sample filtered using a 0.45 µm filter for the analysis of dissolved total phosphorus (DTP). Particulate phosphorus (PP) concentrations are determined by subtracting DTP concentrations from TP concentrations. Laboratory analyses have been performed by labs affiliated with Utah State University and with the State of Utah Division of Water Quality. For TP and DTP analyses, samples are analyzed using USEPA Method 200.8 (Determination of Trace Elements in Water and Waste by Inductively Coupled Mass Spectroscopy) or using USEPA Method 365.2 (Orthophosphate Ascorbic Acid Manual Single Reagent) preceded by an acid digestion of the sample. The analytical method used depends upon the laboratory performing the analysis. For TSS, samples are analyzed using USEPA Method 340.2 (Total Suspended Solids by Mass Balance) or USEPA Method 160.2 (Residue Nonfilterable Total Suspended Solids). Again, the analytical method used depends on the laboratory performing the analysis. In addition to regular
laboratory quality assurance and quality control (QA/QC) procedures, a phosphorus field blank, duplicate, and matrix spike sample are collected at one of the seven sites during each sampling trip, and the site at which QA/QC samples are collected is rotated.

3.4. Cyberinfrastructure

The in-situ sensors at each monitoring site are connected to a Campbell Scientific, Inc. datalogger (both CR206 and CR800 dataloggers are used), and the logged data are transmitted via a Campbell Scientific 900-MHz spread spectrum radio telemetry network to the Utah Water Research Laboratory. The data are then automatically loaded into an Observations Data Model (ODM) [Horsburgh et al., 2008a] database using the ODM Streaming Data Loader (http://his.cuahsi.org/odmsdl.html). Laboratory results for water quality samples are entered into the database by hand as they are received from the analytical labs. QA/QC editing to remove obvious errors and correct for instrument drift in the sensor data is performed using the ODM Tools application (http://his.cuahsi.org/odmtools.html) on copies of the raw data series to ensure that the raw data streams are preserved. Derived data series, including discharge and synthetic phosphorus and TSS concentration time series are also stored in the central database to ease data querying, manipulation, and analysis.

The LBRTB data are published using components of the Consortium of Universities for the Advancement of Hydrologic Science, Inc.’s (CUAHSI) Hydrologic Information System (HIS) (http://his.cuahsi.org). Horsburgh et al. [2008b] describe details of the HIS data publication system. In short, web services have been implemented on top of the central observations database to provide low-level, programmatic access to the data over the Internet, and the LBRTB website (http://littlebearchriver.usu.edu) provides near real time access to the latest
observations at each monitoring site as well as data visualization and analysis capability through Internet browser-based interfaces.

3.5. Generation of Synthetic Time Series From Surrogate Measures

Despite recent developments in sensor technology, there are still water quality constituents such as phosphorus and TSS that cannot be measured continuously using in-situ sensors. However, many studies have demonstrated the potential for using turbidity as a surrogate for predicting TSS and phosphorus concentrations [Uhrich, 2003; Christensen et al., 2002; Stubblefield et al., 2007; and others]. At the Mendon and Paradise sites, the period of sensor deployment and sample collection is longer than at the other sites, and approximately 150 grab and storm event samples were available at each site to support calculation of synthetic time series of TP and TSS concentrations using turbidity as a surrogate. Linear regression was used to develop relationships between turbidity and TSS and turbidity and TP for both sites. A number of additional explanatory variables were considered in the regression equations, including discharge, day of the year, hour of the day, whether samples occurred during a storm or not, and whether samples occurred during spring snowmelt versus baseflow conditions. For TP, regression with maximum likelihood estimation (MLE) was performed using techniques described by Helsel [2005] to account for censored (i.e., below detection limit) observations. Spackman Jones et al. [2008b] describe in more detail the analyses that were used to derive empirical surrogate relationships for the two sites.

For TSS at both sites, the final regression equations used only turbidity as an explanatory variable. Equation (1) shows the model for TSS at the Paradise site, and equation (2) shows the model for TSS at the Mendon site:

\[ TSS = 3.58 + 1.31 \times Turb \]  

(1)
\[ TSS = 0.341 + 1.41 \times Turb \]  

where \( TSS \) is the total suspended solids concentration (mg L\(^{-1}\)) and \( Turb \) is the turbidity (NTU).

For TP, the final regression equations at both sites contained turbidity and an additional categorical variable indicating baseflow versus spring snowmelt conditions. Differentiation between baseflow and snowmelt was done visually by noting the onset and conclusion of the spring snowmelt hydrograph. Additionally, at Mendon the final regression equation contained a variable distinguishing between low (less than 10 NTU) and high (greater than 10 NTU) values of turbidity, which indicates that the relationship between turbidity and TP at Mendon is different at low versus high turbidity. Equation (3) gives the model for TP at the Paradise site, and equation (4) gives the model for TP at the Mendon site:

\[ TP = 0.0209 + 0.000798 \times Turb + 0.0386 \times Z \]  

\[ TP = -0.0341 + 0.0053 \times Turb + 0.0949 \times Z - 0.00404 \times Turb \times Z + 0.0832 \times Y - 0.00871 \times Y \times Turb \]  

where \( TP \) is the total phosphorus concentration (mg L\(^{-1}\)), \( Turb \) is the turbidity (NTU), \( Z \) is a categorical variable for snowmelt \((Z = 1)\) versus baseflow \((Z = 0)\), and \( Y \) is a categorical variable for turbidity less than 10 NTU \((Y = 1)\) versus turbidity greater than 10 NTU \((Y = 0)\). P-values indicating the significance of predictive terms in equations (1) – (4) were all within the 95% significance level, and the final selected model equations were based on the minimum values of the root mean squared error (RMSE). RMSE values ranged from one third to one half of the means of the observed datasets.

Using the derived relationships, synthetic high-frequency (30-minute resolution) time series of TSS and TP concentrations were calculated from turbidity. The synthetic concentration time series were then used along with the high-frequency discharge data to calculate TSS and TP.
loads for each half-hour time period within the 2006 and 2007 water years so that we could examine the total loading and temporal patterns in loading for each water year.

### 3.6. Examining Effects of Sampling Frequency on Estimates of Constituent Fluxes

Water quality constituent loadings are commonly determined through collection and analysis of concentration grab samples paired with instantaneous estimates of discharge [Phillips et al., 1999; Johnes, 2007]. Several studies have examined how the frequency with which grab samples are collected and the equation used in the calculation affects resulting load estimates [e.g., Johnes, 2007; Coynel et al., 2004]. Using the synthetic high-frequency time series of TSS and TP generated at the Paradise site, we investigated the effect of sample frequency on estimates of annual TP and TSS loads. We compared annual load estimates for the 2006 water year at the Paradise site calculated using the high-frequency synthetic time series to annual load estimates calculated from subsets of data created by artificially decimating the synthetic time series. Sub sampling of the synthetic time series was done to simulate hourly, daily, weekly, and monthly sampling frequencies. Excepting the hourly results, sub sampling was done randomly. For example, to simulate daily sampling, we randomly selected one discharge and concentration pair per day for each day of the year and used those values to create an estimate of the annual load. A total of 10,000 annual load estimates were generated for each of the simulated sampling frequencies so that we could examine the resulting distribution of the annual load estimates.

### 3.7. Investigating Hydrologic Pathways and Hydrochemical Response

Assessing water balances, flow paths, and rates is another goal of environmental observatories [Montgomery et al., 2007] that can be supported using continuous high-frequency data. Hydrograph separations based on conservative tracers can be powerful tools for determining contributions to stream discharge from different sources [Covino and McGlynn,
If multiple sources contributing to stream discharge are unique and their signatures are known, end-member mixing analysis can be used to separate the contribution from each source [Burns et al., 2001]. Separation techniques generally use isotope or chemical tracers to define the signatures of each of the end-members. However, laboratory analyses of isotope and chemical tracer concentrations can be expensive, and these constituents cannot be measured with high-frequency over long periods of time. Because of this, many separation studies have focused on individual storm events, leaving longer term catchment behavior uncharacterized.

Our current conceptual model of discharge in the South Fork of the Little Bear is that there is little surface runoff, and that stream discharge is primarily made up of two flow components: 1) slow subsurface flow, or baseflow, which is made up of older water that has a longer residence time in the system; and 2) relatively fast surface and subsurface flows, resulting from spring snowmelt and other storm events throughout the year, which in this paper we refer to as quickflow. Using the high-frequency discharge and specific conductance data collected at the two monitoring sites in the South Fork, we developed continuous, two-component streamflow separations for the two major catchments that make up the South Fork of the Little Bear River (i.e., the Upper South Fork and Davenport Creek). Several previous studies have used specific conductance, which is easily measured with high-frequency using existing sensor technology, as a tracer for hydrograph separation [Covino and McGlynn, 2007; Tetzlaff et al., 2007; Stewart et al., 2007]. A two-component separation of the form given in equations (5) – (7) [e.g., Pinder and Jones, 1969; Jarvie et al., 2001; Stewart et al., 2007; Covino and McGlynn, 2007] was used to quantify the contribution to stream discharge from two end members:

\[ Q_t = Q_1 + Q_2 \] (5)
\[ \frac{Q_1}{Q_t} = \frac{(C_t - C_2)}{(C_1 - C_2)} \]  

(6)

\[ \frac{Q_2}{Q_t} = \frac{(C_t - C_1)}{(C_2 - C_1)} \]  

(7)

where \( Q_t \) is the total discharge of the two components, \( Q_1 \) and \( Q_2 \) represent the discharge of each of the two components, \( C_t \) is the tracer concentration within the combined flow (in this case the tracer is specific conductance), and \( C_1 \) and \( C_2 \) are the tracer concentrations in each of the two flow components. These equations can be solved simultaneously to get the contribution to the total stream discharge from each source.

We were unable to monitor Davenport Creek directly. Instead, continuous time series of discharge and specific conductance were calculated for Davenport Creek (using equations (5) – (7)) as the difference between the Upper and Lower South Fork monitoring sites since these sites are located just above and below the confluence of Davenport Creek and the South Fork. We then separated stream discharge from the Upper South Fork and Davenport Creek catchments into baseflow and quickflow. Since no direct measurements of baseflow or quickflow conductivities have been made, we adopted the conductivity mass balance method of Stewart et al. [2007] and Jarvie et al. [2001], which infers the end members from measurements made in the stream. For each catchment, we assigned the baseflow conductivity end member to be equal to the maximum streamflow conductivity, which occurs during the lowest flows (i.e., during the period when stream discharge is made up entirely of baseflow), and the quickflow conductivity end member to be equal to the minimum streamflow conductivity, which occurs during the highest flows (during the period when stream discharge is made up almost entirely of quickflow). End member concentrations were assumed to be constant. The continuous specific conductance and discharge records for each catchment, along with the derived end members,
were then used to calculate the contributions of baseflow and quickflow to stream discharge for
the period of record using equations (5) – (7).

### 3.8. Investigating Ecological Responses

Dissolved oxygen (DO) can be used as an indicator of the general health of a water body
and can be used to estimate community metabolism of a stream in terms of gross photosynthesis
and respiration rates [Wang et al., 2003]. Generally speaking, DO fluctuations that are near
saturation with diurnal variation that is due to temperature and metabolism are characteristic of
healthy waters, whereas marked depression of DO below saturation indicates that a stream has
been impacted by excess nutrients. Although DO concentrations are controlled by complex
physical, chemical, and biological processes, there are three primary processes that contribute to
DO dynamics. The first is air-water exchange, or reaeration, which regulates DO to its saturation
concentration through exchange with the atmosphere, the second is photosynthesis, which is the
process by which plants produce oxygen during the day, and the third is respiration, which is the
process by which plants consume oxygen during the night. These three mechanisms can be
applied in a mass balance model of the following form:

\[
\frac{dC}{dt} = k_a (C_s - C) + P(t) - R
\]

where \( C \) is the DO concentration (mg L\(^{-1}\)), \( t \) is the time (day), \( C_s \) is the saturation DO
concentration (mg L\(^{-1}\)), \( k_a \) is the reaeration rate constant (day\(^{-1}\)), \( P(t) \) is the photosynthesis rate
(mg L\(^{-1}\) day\(^{-1}\)), and \( R \) is the respiration rate (mg L\(^{-1}\) day\(^{-1}\)). This model assumes that the
dissolved oxygen deficit (\( C_s - C \)) does not vary spatially (\( \partial C / \partial x \approx 0 \), where \( x \) is longitudinal
distance). Reaeration is controlled by the physical characteristics of the stream (i.e., surface
area, depth, velocity, turbulence, and temperature). Photosynthesis and respiration, however, are
biological processes that can be influenced by land use and related pollutant loading and can be important indicators of ecological disturbance [Mulholland et al., 2005].

Using equation (8) and the Extreme Value Method (EVM) of Wang et al. [2003], we calculated average photosynthesis and respiration rates at four sites (Lower South Fork, Paradise, Wellsville, and Mendon) for a one week period at the beginning of July 2008. The EVM assumes that the change in DO concentration \(\frac{dC}{dt}\) is equal to zero at the minimum and maximum values of the DO diurnal curve and uses these extreme points to estimate the respiration and photosynthesis rates respectively. At the minimum DO concentration, which typically occurs at night or early morning when there is no photosynthesis \(P(t) = 0\), equation (8) simplifies to:

\[
R = k_a (C_{s,min} - C_{min})
\]  

(9)

where \(C_{min}\) is the minimum DO concentration (mg L\(^{-1}\)) and \(C_{s,min}\) is the saturation DO concentration corresponding to the temperature at \(C_{min}\) in the diurnal curve (mg L\(^{-1}\)). At the maximum DO concentration, which generally occurs during the early afternoon, equation (8) simplifies to:

\[
P(t_{max C}) = R - k_a (C_{s,max} - C_{max})
\]  

(10)

where \(P(t_{max C})\) is the photosynthesis rate (mg L\(^{-1}\) day\(^{-1}\)) at the time of the maximum DO concentration and \(C_{s,max}\) is the saturation DO concentration corresponding to the temperature at \(C_{max}\) in the diurnal curve (mg L\(^{-1}\)).

Photosynthesis as a function of time was approximated as a half sine wave during daylight hours and zero at night [Chapra, 1997]:

\[
P(t) = P_{max} \sin \left(\frac{\pi t}{f}\right), \quad 0 \leq tf \leq \pi
\]

(11)

\[
P(t) = 0, \quad f \leq t \leq \tau
\]
where $P_{\text{max}}$ is the maximum photosynthesis rate (mg L$^{-1}$ day$^{-1}$), $f$ is the photo-period (hr), $\tau$ is the diurnal period (24 hr), and $t$ is measured starting at sunrise. The maximum photosynthesis rate was calculated using equation (11) where $P(t) = P(t_{\text{max}C})$ and $t = t_{\text{max}C}$:

$$P_{\text{max}} = \frac{P(t_{\text{max}C})}{\sin(\pi t_{\text{max}C}/f)}$$  \hspace{1cm} (12)

Since solar noon occurs at 0.5$f$, $t_{\text{max}C}$ was calculated as:

$$t_{\text{max}C} = \Delta t + 0.5f$$  \hspace{1cm} (13)

where $\Delta t$ is the time shift of the maximum DO concentration from the solar noon (hr). Finally, the average photosynthesis rate was estimated from the maximum value as:

$$P_{\text{ave}} = P_{\text{max}} \left(\frac{2f}{\pi \tau}\right)$$  \hspace{1cm} (14)

where $P_{\text{ave}}$ is the average photosynthesis rate (mg L$^{-1}$ day$^{-1}$).

Using the EVM, average photosynthesis and respiration rates were calculated at each site for each of the days and then all of the days were averaged to estimate the overall average rates at each site for the entire period. Reaeration rate constants ($k_a$) were estimated for each site using empirical methods presented by Chapra [1997] that are based on stream depth and velocity. Saturation DO concentrations were also calculated using equations provided by Chapra [1997] based on water temperature and elevation.

4. Results

4.1. Synthetic Time Series Generated from Surrogate Measures

Figure 2 shows discharge and synthetic high-frequency time series of derived TSS and TP at the Paradise site for water years 2006 and 2007. During both years, predicted concentrations of TP and TSS associated with early spring snowmelt events were very high, exceeding 1,500 mg L$^{-1}$ for TSS and 1 mg L$^{-1}$ for TP, and daily fluctuations that were highly
dependent on discharge were as high as 1 mg L⁻¹ for TP and 2,000 mg L⁻¹ for TSS. Predicted concentrations tapered off through the remainder of the snowmelt period and were very low during the summer and winter baseflow periods except for a few spikes related to storm events. Similar timing was observed during both years; however, 2007 was a low water year in the Little Bear and the magnitude and duration of elevated spring snowmelt concentrations was lower during 2007.

The annual TP and TSS load estimates based on the high-frequency synthetic time series were vastly different for the two water years at Paradise. In 2006, the estimated annual TSS load was approximately 1.1 X 10⁷ kg and the TP load was approximately 1.2 X 10⁴ kg, whereas in 2007 the annual TSS load was approximately 1.8 X 10⁶ kg and the TP load was approximately 3 X 10³ kg. Figure 3 shows the estimated cumulative percent of annual discharge and the total annual TSS and TP loads as a function of time for the two water years. For both water years, and for both TSS and TP, the first 3 months of the water year and the last 4 contribute less than 10% of the total annual load each, which means that approximately 80% of the annual loading at this site occurs during only 5 months of the year. A single event that spanned several days during January of 2006 contributed approximately 5% of the total annual TP and TSS loads, demonstrating the importance of individual events, but the vast majority of the annual loading in all cases was associated with the period of spring snowmelt and, in particular, the beginning of the spring snowmelt period. Figure 4 shows discharge and 30-minute TSS loads for the 2006 water year and highlights the early spring loading. In 2006, approximately 60 – 65% of the annual TP and TSS load occurred over a period of approximately 2 – 3 weeks. Figure 3 also shows that in general, a greater percentage of the annual loads occurred earlier in 2007 than in 2006, although the last 5 – 6 months of the water years were similar on a percentage loading.
basis. The divergence between the cumulative TSS and TP loading during the snowmelt period (Figure 3) is due to the categorical variable in the TP model, which switches the relationship between turbidity and TP during the snowmelt period and is not present in the TSS model.

4.2. Effects of Sampling Frequency on Estimates of Constituent Fluxes

Figure 5, which shows synthetic TSS concentrations for the period between February and June of 2006 at the Paradise site, illustrates how much information is lost as sample frequency drops from half hourly (based on the high-frequency data) to weekly and monthly (based on random subsets of the continuous data), which are common sampling frequencies used in traditional monitoring programs. These results illustrate how weekly and monthly samples miss nearly all of the system dynamics and even daily samples fail to characterize the variability in TSS concentrations which, in this example, is primarily driven by the daily snowmelt cycle during spring conditions. Similar results have been generated for TP.

In Figure 6, annual loads at the Paradise site calculated using the entire synthetic time series (half-hourly resolution) are compared to annual load estimates created by sub sampling from the half-hourly data at hourly, daily, weekly, and monthly time scales. Across the sites and variables at which this analysis was completed there was relatively little difference between the half-hourly and hourly results, indicating that little resolution would be lost by sampling hourly. However, resolution was lost at the daily, weekly, and monthly time scales, and annual load estimates generated by random sub sampling at these time scales were often several times greater or less than the half-hourly estimates. Spackman Jones et al. [2008a] provide a more in depth analysis of the effects of sampling frequency on TP and TSS load estimates for the Little Bear that considers additional factors such as the hour of the day on which sampling occurs and the day of the week.
4.3. Source Water Contributions

The hydrochemical data collected at the two monitoring sites in the South Fork of the Little Bear (and those calculated for Davenport Creek) show a distinct difference in the specific conductance of baseflow conditions versus spring snowmelt conditions (Figure 7). In general, specific conductance is inversely related to discharge, and the patterns in specific conductance are similar at both monitoring sites and for Davenport Creek. Conductivity is high during baseflow conditions and is on the order of approximately 400 µS cm\(^{-1}\). As discharge increases with spring snowmelt, conductivity decreases to less than half of baseflow conductivity as the stream water becomes diluted with snowmelt. This pattern is most pronounced at the Upper South Fork site, where conductivity decreases from greater than 400 µS cm\(^{-1}\) under baseflow conditions to a minimum of 114 µS cm\(^{-1}\) during one of the spring discharge peaks. Figure 8 shows conductivity plotted versus discharge for the Upper South Fork and Davenport Creek.

The relatively consistent 1:1 relationship between discharge and conductivity in these figures indicates that this relationship has little hysteresis or seasonal dependence. Low flow conductivities are similar in both catchments, while high flow conductivities approach a minimum value that is a little different in each catchment (~100 µS cm\(^{-1}\) in the Upper South Fork and ~150 µS cm\(^{-1}\) in Davenport Creek).

Figure 9 shows the contributions of baseflow and quickflow in the Upper South Fork and Davenport Creek catchments resulting from the separation analysis. In this figure, precipitation and snow water equivalent data are from the Little Bear SNOTEL site. Over the period between November 1, 2007 and July 31, 2008, baseflow accounted for approximately 43% of the total discharge in the Upper South Fork catchment, and quickflow contributed approximately 57%.

Within the Davenport Creek catchment, the total discharge for the same period was made up of
approximately 37% baseflow and 63% quickflow. The greater contribution of quickflow in the Davenport Creek catchment is due to two later peaks in the quickflow hydrograph that occurred in mid May to early June in Davenport Creek but not in the Upper South Fork. Based on the precipitation data from the Little Bear River SNOTEL site, it appears that these two peaks are related to precipitation events. The snow water equivalent data indicate that the snow was gone in the Upper South Fork catchment at the time of these precipitation events, which explains the lack of observed response in the quickflow hydrograph for the Upper South Fork. However, the Davenport Creek catchment incorporates some higher elevation areas, and it appears that there may have been a rapid melt of remaining high elevation snow caused by these two precipitation events. Observations from nearby SNOTEL sites support this. The Ben Lomond Peak SNOTEL site at 2,438 m elevation and located southwest of the Little Bear SNOTEL site maintained snow well into June, and the Dry Bread Pond SNOTEL site at 2,545 m elevation did not melt out until the beginning of June indicating that there was likely still snow in the upper portions of the Davenport Creek catchment when these precipitation events occurred.

4.4. Diurnal Patterns in Hydrochemical Response

Diurnal variability in discharge and specific conductance at the Upper South Fork monitoring site is shown in Figure 10. Panel (a) shows the month of April 2008 and demonstrates diurnal patterns in specific conductance that occur during snowmelt. Discharge peaks occur during the late afternoon and early evening near the end of the snowmelt period each day, and the troughs in the daily discharge cycle occur in the early morning around sunrise when air temperatures are coldest. Observed daily fluctuations in discharge during the snowmelt period were as large as 7 m³ s⁻¹, but were generally on the order of less than 4.2 m³ s⁻¹ depending on the weather conditions. During the snowmelt period, conductivity behaved exactly opposite
to discharge. Conductivity peaks occur during the early morning when snowmelt is minimum, and daily troughs in conductivity occur simultaneously with the discharge peaks, with daily fluctuations in conductivity of 30 – 60 µS cm⁻¹.

Panel (b) of Figure 10 shows conductivity and discharge at the Upper South Fork site during the month of July 2008, which is within the period of baseflow recession. Air temperatures were hot during this period, there was no snowmelt, and very little precipitation occurred, indicating that all of the flow in the stream is from subsurface sources. Much smaller and more uniform diurnal fluctuations in discharge (on the order of approximately 0.03 m³ s⁻¹ per day) and conductivity (approximately 15 – 20 µS cm⁻¹) were observed during this period. Maximum conductivity values occur near or after midnight (approximately 11:00 PM – 3:00 AM), and minimum values occur during the afternoon (approximately 1:00 PM – 5:00 PM). Daily discharge peaks in the morning (8:30 AM – 12:30 PM), and daily minimum discharge values occur at night, just before maximum conductivity values (9:00 PM – 12:30 AM). The timing of these diurnal fluctuations indicates a time lag between discharge and conductivity.

4.5. Ecological Responses

Figure 11 shows DO concentrations and dissolved oxygen deficits at four of the seven stream monitoring sites during the first week of July 2008. The Lower South Fork and Paradise sites, which are located in the upper portion of the watershed, exhibit DO concentrations that are almost always near or above saturation concentrations, whereas the Wellsville and Mendon sites, which are located in the lower watershed and are influenced by higher density agricultural areas, exhibit DO concentrations that are primarily below saturation.

Table 3 shows that there are large differences between the respiration and photosynthesis rates among the four sites. Photosynthesis and respiration rates are low at the Lower South Fork
site, where we have observed relatively little periphyton growth and where there is little influence from agricultural lands. At the Paradise and Wellsville sites, our observations from the field are consistent with the much higher photosynthesis and respiration rates shown in Table 3. During July, the water is clear and periphyton are dense, especially at Wellsville where they sometimes fill the channel. At Mendon, the rates are much lower and may be limited by water clarity (average turbidity during these days at Mendon was 46 NTU, which is high compared to 6.4 NTU at Paradise and 1.2 NTU at Wellsville).

A closer inspection of the diurnal curves revealed that three out of the four sites have similar timing and follow the assumptions of the conceptual model described above. At Mendon, Wellsville, and Paradise, DO concentrations are lowest during the night or early morning when there is no photosynthesis and are highest during the early afternoon when solar radiation and photosynthesis are greatest. However, the Lower South Fork site does not follow this pattern. Figure 12 shows a close-up view of the diurnal curves for all four sites on July 5, 2008. DO at the Upper South Fork site peaks at 9:30 AM MST and is lowest at 7:30 PM MST. It appears that since the photosynthesis and respiration rates are relatively low at this site, DO concentrations are driven much more by diurnal temperature fluctuations than instream metabolism. The EVM estimate of the respiration rate (and the photosynthesis rate, which is calculated from the respiration rate) may be subject to error because the minimum DO occurs during the photo-period, when photosynthesis is likely not equal to zero.

5. Discussion

The need for high-frequency data is already well established [Kirchner et al., 2004; Tetzlaff et al., 2007; Jarvie et al., 2001]. Kirchner et al. [2004] liken trying to infer hydrochemical functioning of a catchment using weekly or monthly grab samples to trying to
understand a Beethoven symphony by hearing one note every minute or two. In the following sections, we discuss the value of high-frequency data and provide specific examples of how it has assisted us in evaluating dynamic catchment behavior.

5.1. Estimating Constituent Fluxes

Our loading analyses show that TP and TSS loads estimated using weekly or monthly sampling, which are frequencies widely used for assessing mass balances of water quality constituents, for calibrating dynamic water quality models, for assessing compliance with water quality standards, and for measuring trends are, at best, order of magnitude estimates of the true annual loading and tend to, in the majority of simulations, underpredict the true annual load when compared to loads calculated from the half-hourly synthetic data. There was even significant spread in annual load estimates from daily sampling. Because the distributions of discharge, TSS, and TP concentrations are skewed low (i.e., high discharge and concentrations only happen a small portion of the time), any one random set of weekly or monthly samples has a high probability of sampling only lower flows and concentrations, and thus the probability is high that the annual load estimated from the sample set will underestimate the true load. The means of the collections of 10,000 annual load estimates from daily, weekly, and monthly sub sampling were actually very similar to the annual load calculated using the half-hourly data; however, for both TP and TSS at Paradise approximately 53% of the annual load estimates calculated from random daily subsets were less than the mean of all of the annual load estimates from random daily subsets. This number was approximately 68% for random weekly subsets, and approximately 77% for random monthly subsets.

TSS loads estimated from the high-frequency synthetic time series were an order of magnitude greater in 2006 than they were in 2007, and TP loads in 2006 were nearly 4 times
greater than those in 2007. These differences demonstrate that year to year load variability is significant, that it is highly influenced by differences in discharge, and that characterizing multiple water years is important in understanding how watersheds behave. We also found that more than half of the annual loading of TP and TSS for both years occurred during a two week to one month long time window. Cumulative plots of loading and discharge over the two water years illustrate the timing of the TSS and TP loads and show that they do not simply follow the same timing as the discharge. The period of early spring snowmelt is critically important to TP and TSS loading in the Little Bear River, which is likely representative of many snowmelt driven watersheds in the western United States. Traditional grab sampling programs using a weekly or bi-weekly sample frequency would get one to two samples during this period, and monthly sampling might miss it entirely.

The observations made above demonstrate the type of information that can be extracted from high-frequency data. The implications of this type of information are far reaching in the water quality community where low frequency data are routinely used to estimate mass balances for water quality constituents under USEPA’s Total Maximum Daily Load (TMDL) program. Significant overestimation of loads would result in required load reductions that are too strict, an error that could have multi-million dollar consequences for point sources of pollution whose discharge permits are tied to TMDL load reductions. Conversely, underestimation of loads may result in required load reductions that do not fully restore water quality and are not protective of the environment.

In the absence of in-situ sensors for phosphorus and suspended solids, the methods that we have employed in the LBRTB hold much promise for application in environmental observatories for providing relatively inexpensive, high-frequency estimates of TP and TSS
concentrations, especially since large-scale environmental observatories will require estimates such as these at many locations and over long time periods to characterize the spatial and temporal variability in water quality constituent fluxes. To recreate the two year long time series shown in Figure 2 for the Paradise site using grab samples, the cost of sample analytical costs alone would exceed $500,000 (estimated using our current analytical costs for TP and TSS analysis), and the logistics of collecting, processing, and analyzing samples of this frequency over an extended time period would be impossible. We estimate that the total cost of developing the time series shown in Figure 2 using surrogate sampling was on the order of approximately $50,000, which includes the monitoring equipment, field work, sample analytical costs, and analysis time to develop the surrogate relationships.

5.2. Investigating Hydrologic Pathways and Hydrochemical Response

The conceptual model of discharge in the South Fork of the Little Bear River that we tested using the two-component separation is that stream discharge is made up predominantly of subsurface baseflow and quickflow from snowmelt that includes some surface runoff. The observed difference in conductivity between the portion of the hydrograph dominated by baseflow and the portion dominated by spring snowmelt (i.e., quickflow) is consistent with this model. Diurnal discharge and conductivity data during the spring snowmelt period also seem to be consistent with this two-component model. As low conductivity quickflow associated with snowmelt increases during the day, conductivity in the stream decreases.

An additional line of evidence is that TSS and TP concentrations and loads at Paradise are highest during the beginning of the spring hydrograph. In general, these constituents do not move via subsurface pathways, so the fact that spikes in TSS and TP concentrations occur suggests that some surface runoff occurs early in the spring when snow close to active streams is
melting, carrying high surface runoff loads of TSS and TP to the stream. This is likely augmented by mobilization of sediment from the stream banks and bed, which happens more during the rising limb of the hydrograph. As snowmelt progresses, it is likely that three things happen: 1) sediment stored within the channel is washed through the system by higher flows; 2) the flow pathway delivering water to the stream increasingly switches from surface to subsurface as snowmelt moves further from active streams, effectively eliminating the pathway carrying TSS and TP to the stream; and 3) snowmelt moves from the predominantly agricultural lowland areas that are close to active streams to upland areas where available sources of TSS and TP are reduced.

The hydrograph separation results show that the baseflow component is relatively constant throughout the year and that the baseflow does not extend into the peaks of the spring snowmelt hydrograph. This is somewhat at odds with some previous isotopic studies elsewhere that have shown a preponderance of “old” water in hydrograph peaks [McDonnell, 1990; Shanley et al., 2002; Kirchner, 2003], although these studies are generally done on an individual event basis and not over long periods of time. The observed decrease in specific conductance with increased discharge during the spring snowmelt hydrograph means that newer water from lower conductivity snowmelt is predominating in the stream, essentially diluting the baseflow, and that quickflow exhibits a chemical signature that is different from baseflow and likely results from a relatively short contact time with the soil when compared to baseflow, which is likely from a deeper flow pathway.

The period of baseflow recession presents a challenge for the two component model. During a period where there is no snowmelt and very little precipitation, conductivity is slowly increasing as discharge is slowly decreasing, with superimposed diurnal fluctuations in both.
The overall trend suggests that the watershed is drying as the remainder of the quickflow component leaves the system. However, the diurnal fluctuations in discharge and specific conductance that are superimposed on the overall trend are not explained by the model. Although these diurnal fluctuations appear to be inversely related (i.e., peaks in discharge generally line up with troughs in specific conductance), there is a time lag that offsets the curves, with conductance peaks lagging discharge troughs by a few hours, perhaps reflecting the difference in velocity of flow fluctuations that travel with a wave celerity compared to conductance that travels with water velocity.

Several other studies have attributed diurnal patterns in discharge and specific conductance during summer low flow periods to the effects of water use by vegetation and instream photosynthesis and respiration [Bond et al., 2002; Wondzell et al., 2007; Tetzlaff et al., 2007]. Tetzlaff et al. [2007] suggest that diurnal fluctuations involve increased capillary tensions in riparian groundwater arising from high rates of potential evapotranspiration restricting seepage during the day when transpiration rates are highest. Wondzell et al. [2007] examined the time lag between maximum estimated evapotranspiration and minimum discharge and attributed changes in the amplitude and time lag of the peaks over time to changes in flow velocity in the stream that affect the rate at which the effects of evapotranspiration are propagated through a catchment. Bond et al. [2002] conceptualize that changes in the timing and amplitude of the peaks that occur as summer progresses are related to a transition of streamflow to deeper flow paths with less vegetative water use from shallow flow paths. If we assume that the fluctuations we have observed are driven by evapotranspiration that peaks around midday, then the wave travel time from the effective location where evapotranspiration is impacting discharge to the monitoring site would need to be about 10 hours, as we observe troughs in discharge around
Evapotranspiration that removes water from the soil layers may increase specific conductance either by reducing dilution of the higher conductance baseflow or by not appreciably taking up constituents that contribute to conductivity. This effect should cause a peak in the specific conductance from evapotranspiration. The observed lag of about 14 hours from midday to the conductance peak (which usually occurs around 12:00 AM to 2:00 AM) would be consistent with a water velocity that is smaller than flow wave celerity.

The differences in diurnal behavior of discharge and specific conductance during the snowmelt period versus the baseflow recession period are somewhat of a serendipitous discovery. However, they also demonstrate an important limitation of hydrograph separation studies based on relatively infrequent isotope or chemical tracer samples that do not consider diurnal variability. Specific conductance is arguably not the best conservative tracer, but it can be measured in-situ with high-frequency and can provide an important line of evidence in investigating hydrologic pathways and hydrochemical response. Additionally, even though the diurnal variations in discharge and specific conductance observed during the baseflow recession period are relatively small when compared to the snowmelt period, they are still interesting and illustrative of how high frequency measurements provide opportunities for studying hydrologic processes and for connecting with other disciplines in studying potential linkages between hydrology and riparian and instream biological processes.

5.3. **Investigating Ecological Response**

The processes controlling dissolved oxygen concentrations are inherently diurnal in nature. The analysis that we performed to estimate photosynthesis and respiration rates would not have been possible without observations of DO concentrations that characterize the entire diurnal DO curve. The DO deficits and rates derived from the high-frequency data are useful
indicators of stream metabolism. Our results show that there are large differences in these rates at each site, and we are now investigating the degree to which they are useful in evaluating the effects of human disturbances at the catchment scale (i.e., why are metabolism rates higher at Paradise and Wellsville than at Mendon and the Lower South Fork site?). Although our analysis was limited to a brief period during critical summer low flow and high water temperatures, high-frequency data collected over long time periods also enable estimation of how photosynthesis and respiration rates change seasonally and in response to human disturbances such as agricultural diversions, reservoir releases, and agricultural return flows. Additionally, we have identified one out of four monitoring sites where the most basic assumptions of the EVM conceptual model are not met. It is anticipated that this will happen often within environmental observatories and that insights from high-frequency data will drive development of the next generation of hydrologic and water quality models.

5.4. The Supporting Role of Cyberinfrastructure

The cyberinfrastructure that we have implemented within the LBRTB provides an end-to-end system for collecting, managing, analyzing, and publishing observational data. The analyses presented in this paper made extensive use of this system. First, without the sensor network and the high-frequency data that it has produced, none of these analyses would have been possible. The communication system enables us to retrieve data in a timely manner, and it also enables us to monitor the status of the system in real time, which is important in identifying and responding to malfunctions within the sensor network to avoid data gaps.

Organization of the data within a central ODM database was perhaps the most critical step, with several important implications. First, the seamless, automated linkage between sensors and database reduces errors in transcription of the datalogger files, ensures the integrity
of the raw data streams, and ensures that data are organized and tagged with appropriate
metadata. Second, ODM and the ODM Tools application enable us to manage data versioning,
which is important in preserving raw sensor data streams and creating quality controlled versions
of the data for use in our analyses. Third, implementation of ODM within a Relational Database
Management System (RDBMS) enabled us to use Structured Query Language (SQL) to
manipulate and subset data through coded queries. This was important in correctly matching and
retrieving subsets of data. For some of our analyses, we were able to write code that directly
interfaced with the database to retrieve data in a structured way that eliminated the need for
intermediate data processing steps, saving time and eliminating potential data manipulation
errors. Finally, publication of the data using the CUAHSI HIS data publication system ensures
that the LBRTB data are publicly available and can be used by other investigators to support
additional analyses.

5.5. Where to Go From Here?

Our study of high-frequency water quality data collected in the Little Bear has informed
our conceptual model of the behavior of the Little Bear River watershed, but it has also raised
questions that we did not anticipate at the outset and that warrant further investigation. What is
the role of vegetation in the timing and magnitude of diurnal fluctuations in specific conductance
and discharge during the period of baseflow recession? Why do high flow specific conductance
values differ between the Upper South Fork and Davenport Creek catchments? Why don’t the
dissolved oxygen data at the Lower South Fork Site follow the conceptual model when the other
sites we examined do? These questions may be important, especially in linking understanding of
hydrologic processes with ecological responses.
Other, more practical questions related to the use of surrogate relationships for environmental observatory design and implementation have also emerged. How many grab samples are really needed to establish surrogate relationships between turbidity and TSS and TP, do the relationships change over time, how often do we need to sample to maintain the relationships, and when should the samples be collected to gain the most information? These questions aim at how to best quantify fluxes given the technology that we currently have while minimizing costs and achieving acceptable accuracy. While we estimated above the large (and unrealistic) cost of quantifying high-frequency TP and TSS using grab samples, the design of efficient sampling protocols that take advantage of the availability of high-frequency surrogate data generated by in-situ sensors needs to be informed by answers to these more nuanced questions.

6. Conclusions

This research has demonstrated how high-frequency sensor data collected at multiple sites can provide multiple lines of evidence to improve hydrologic and hydrochemical process understanding. Coupled with generation of surrogate relationships, the high-frequency data collected in the LBRTB suggest first that the spring snowmelt period is the dominant TSS and TP load generation period, and the period of early snowmelt generates the vast majority of the annual TSS and TP load via surface pathways from snowmelt close to the streams that carry TP and TSS loads. Second, water quality constituent loads estimated using weekly or monthly data are not representative of the high variability in discharge and constituent concentrations, and tend to, in the majority of cases, under predict the true loading because of the high probability that peaks in discharge and concentration are missed, and should be considered as order of magnitude estimates of the true loading.
The two component hydrograph separation supported our conceptual model of discharge in the unregulated portions of the Little Bear River, which may be applicable to many snowmelt driven watersheds that are similar to the Little Bear River. Discharge from slow subsurface pathways (i.e., baseflow) is relatively constant throughout the year and does not extend to a great degree into the peaks of the spring snowmelt hydrograph. According to the simple mixing model, more than half of the annual discharge is from fast pathways (i.e., quickflow) that dominate the spring snowmelt hydrograph and dilute the relatively constant baseflow. The chemical signatures of baseflow and quickflow appear to be distinct, suggesting that the two flow paths have very different residence times within the system.

Metrics based on high-frequency profiles of DO concentrations and saturation deficits, such as estimates of photosynthesis and respiration rates, are useful indicators of instream metabolism and can easily be calculated from high-frequency data. In the Little Bear River, we found that these rates were very different from site to site, and because they are related to physical, chemical, and biological processes, they represent an opportunity for better understanding the interactions among hydrologic, hydrochemical, and biological processes. They may also provide useful indicators for quantifying the degree to which sites and their contributing catchments have been affected by human disturbance.

The results of our analyses demonstrate the need for and value of high-frequency, continuous time series of discharge and hydrochemical variables. Indeed, the observing system, surrogate methods, and cyberinfrastructure that we have demonstrated are advances to the infrastructure available for the design and implementation of environmental observatories and together have enabled us to gain insights into the importance and relative magnitude of hydrologic pathways and responses that are only possible through high-frequency data. Data and
analyses such as these, as well as the cyberinfrastructure that enabled them, make it possible for us to better understand the processes that control the fluxes, flow paths, and stores of both water and water-borne constituents. They also present challenges for current hydrologic and water quality models, which typically lack appropriate mechanisms for representing these types of responses on the time scales at which they were observed. Without this type of information, we have no way of testing many of the concepts and assumptions that are the basis of our current understanding of hydrological processes, and our ability to predict hydrologic and water quality response will remain constrained.

7. Data Availability

The data referenced in this paper are available via the LBRTB website [http://littlebearriver.usu.edu](http://littlebearriver.usu.edu), which is maintained by the Utah Water Research Laboratory at Utah State University. Raw data streaming from the sensors in the LBRTB are available on the website within hours of being collected. Quality controlled data are also available, and are periodically added to the database as quality control procedures are completed.

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Figure Captions

**Figure 1.** Little Bear River watershed. Descriptions of sampling sites are contained in Table 1.

**Figure 2.** Continuous (half hourly) estimates of discharge (a), total suspended solids concentration (b), and total phosphorus concentration (c) at the Paradise site.

**Figure 3.** Cumulative percent of annual discharge, TSS, and TP loads contributed by date for water years 2006 and 2007 at the Paradise site.

**Figure 4.** Discharge and 30-minute total suspended solids loads estimated using the synthetic concentration time series for the Paradise site during water year 2006.

**Figure 5.** Total suspended solids concentrations at the Paradise site during spring of 2006 at varying sampling frequencies as sub sampled from the synthetic concentration estimates. The daily, weekly, and monthly time series are randomly selected points.

**Figure 6.** Box and whisker plots showing the results of varying sampling frequencies on estimated TP (a) and TSS (b) loads at the Paradise site for water year 2006. The half hourly result uses all of the continuous data, hourly represents the load estimate from sub sampling on the hour, and daily, hourly, and monthly box plots represent 10,000 estimates of the annual load given randomly selected sample times within each day, week, or month. The boxes represent the first and third quartiles and the whiskers represent the lower and upper adjacent values. The medians of each of the sets of realizations are also indicated. The percentages above the upper whisker represent the portion of load estimates that fell above the upper adjacent level.

**Figure 7.** Discharge and specific conductance for the period between November 1, 2007 and July 31, 2008 in the South Fork and Davenport Creek. Precipitation and snow water equivalent are from the Little Bear SNOTEL site.

**Figure 8.** Specific conductance plotted versus discharge for the Upper South Fork and Davenport Creek catchments for the period between November 1, 2007 and July 31, 2008.

**Figure 9.** Hydrograph separation results for the Upper South Fork and Davenport Creek catchments based on 30-minute discharge and specific conductance data for the period between November 1, 2007 and July 31, 2008. Precipitation and snow water equivalent are from the Little Bear SNOTEL site.

**Figure 10.** Diurnal patterns in specific conductance at the Upper South Fork monitoring site during April of 2008 (a) and July of 2008 (b).

**Figure 11.** Dissolved oxygen concentrations and dissolved oxygen deficits at the Mendon, Wellsville, Paradise, and Lower South Fork sites during the first week of July 2008.
Figure 12. Dissolved oxygen concentrations on July 5, 2008 at the Mendon, Wellsville, Paradise, and Lower South Fork sites.
Table 1. Little Bear River Monitoring Sites

<table>
<thead>
<tr>
<th>Site Number</th>
<th>Site Name</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Site Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Upper South Fork</td>
<td>41.4954</td>
<td>-111.818</td>
<td>Unregulated watershed relatively unimpacted by agricultural or urban pollutant sources.</td>
</tr>
<tr>
<td>2</td>
<td>Lower South Fork</td>
<td>41.5065</td>
<td>-111.8151</td>
<td>Unregulated. Located on the South Fork below the confluence with its major tributary, Davenport Creek.</td>
</tr>
<tr>
<td>3</td>
<td>East Fork</td>
<td>41.5292</td>
<td>-111.7993</td>
<td>Located below Porcupine Reservoir on the East Fork. During the summer irrigation season, the entire East Fork is diverted at this location, leaving the downstream river channel dry during most years.</td>
</tr>
<tr>
<td>4</td>
<td>Confluence</td>
<td>41.5361</td>
<td>-111.8305</td>
<td>Located below the confluence of the East and South Forks. During summer, this site is primarily South Fork water as the East Fork is entirely diverted for irrigation.</td>
</tr>
<tr>
<td>5</td>
<td>Paradise</td>
<td>41.5756</td>
<td>-111.8552</td>
<td>Located a short distance upstream of Hyrum Reservoir and representative of the cumulative effects of the watershed above Hyrum Reservoir.</td>
</tr>
<tr>
<td>6</td>
<td>Wellsville</td>
<td>41.6435</td>
<td>-111.9176</td>
<td>Located a short distance downstream of Hyrum Reservoir. Winter flow is primarily groundwater because there are no releases from Hyrum Dam. When Hyrum Reservoir fills in the spring, high flows associated with spills from the reservoir pass this site. Summer flow is essentially groundwater as releases from Hyrum Dam are diverted for irrigation immediately below the dam and do not contribute to river flow.</td>
</tr>
<tr>
<td>7</td>
<td>Mendon</td>
<td>41.7185</td>
<td>-111.9464</td>
<td>Near the terminus of the river, just upstream of the confluence with Cutler Reservoir. Influenced primarily by releases from Hyrum Reservoir and agriculture return flows.</td>
</tr>
<tr>
<td>8</td>
<td>Lower Watershed Weather Station</td>
<td>41.667</td>
<td>-111.8906</td>
<td>Located near the border of the watershed and characteristic of the lower watershed below Hyrum Reservoir.</td>
</tr>
<tr>
<td>9</td>
<td>Upper Watershed Weather Station</td>
<td>41.5355</td>
<td>-111.8059</td>
<td>Located near the confluence of the South and East Forks and characteristic of the mid to upper watershed.</td>
</tr>
<tr>
<td>10</td>
<td>Little Bear SNOTEL</td>
<td>41.40</td>
<td>-111.53</td>
<td>Located in the headwaters of the South Fork.</td>
</tr>
<tr>
<td>11</td>
<td>Dry Bread Pond SNOTEL</td>
<td>41.40</td>
<td>-111.82</td>
<td>Located in the headwaters of the East Fork.</td>
</tr>
<tr>
<td>Variable</td>
<td>Sensor Details</td>
<td>Specifications</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------------------------------------------------------------------------------</td>
<td>-------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stream Monitoring Sites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage</td>
<td>SPXD-600 Pressure Transducer KWK Technologies, Inc.</td>
<td>Accuracy: ±1% of the full measurement span</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbidity</td>
<td>DTS-12 turbidity sensor Forest Technology Systems, Inc.</td>
<td>Accuracy: ±2% 0 to 500 NTU and ±4% 501 to 1600 NTU</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Temperature</td>
<td>Hydrolab MiniSonde5 thermistor Hach Environmental, Inc.</td>
<td>Accuracy: ±0.1 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resolution: 0.01 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>Hydrolab MiniSonde5 optical LDO sensor Hach Environmental, Inc.</td>
<td>Accuracy: ±0.1 mg L(^{-1}) at &lt; 8 mg L(^{-1}) and ±0.2 mg L(^{-1}) at &gt; 8 mg L(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration</td>
<td></td>
<td>Resolution: 0.01 mg L(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>Hydrolab MiniSonde5 reference electrode Hach Environmental, Inc.</td>
<td>Accuracy: ±0.2 pH units</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resolution: 0.01 pH units</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Conductance</td>
<td>Hydrolab MiniSonde5 4-electrode, temperature compensated conductivity sensor Hach Environmental, Inc.</td>
<td>Accuracy: ±0.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resolution: 0.001 mS cm(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Weather Monitoring Sites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation</td>
<td>TE25 tipping bucket rain gage with a 20.32 cm orifice Texas Electronics</td>
<td>Accuracy: ±1% up to 2.54 cm hr(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Resolution: 0.254 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air Temperature</td>
<td>CS215 temperature and relative humidity sensor Campbell Scientific, Inc.</td>
<td>Accuracy: ±0.4 °C from +5 °C to +40 °C, and ±0.9 °C from -40 °C to +70 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>CS215 temperature and relative humidity sensor Campbell Scientific, Inc.</td>
<td>Accuracy: ±2% at 25 °C in the 10-90% range and ±4% in the 0-100% range</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind Speed</td>
<td>R. M. Young Wind Sentry Set</td>
<td>Accuracy: ±0.5 m s(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind Direction</td>
<td>R. M. Young Wind Sentry Set</td>
<td>Accuracy: ±0.5 degrees</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solar Radiation</td>
<td>PYR-P Silicon Pyranometer Apogee Instruments, Inc.</td>
<td>Accuracy: 5% for daily total radiation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barometric Pressure</td>
<td>Setra 278 Barometric Pressure Sensor</td>
<td>Accuracy: ±0.5 mb at +20 °C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Average DO Deficit (D), Rate Constant (k_a), Respiration Rates (R), and Photosynthesis Rates (P) Calculated Using the Extreme Value Method for the Period Between July 1, 2008 and July 7, 2008

<table>
<thead>
<tr>
<th>Site</th>
<th>D_{avg} (mg L^{-1})</th>
<th>k_a (day^{-1})</th>
<th>R (mg L^{-1} day^{-1})</th>
<th>P_{avg} (mg L^{-1} day^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mendon</td>
<td>-1.62</td>
<td>2.1</td>
<td>6.2</td>
<td>3.7</td>
</tr>
<tr>
<td>Wellsville</td>
<td>-0.97</td>
<td>44.1</td>
<td>100.8</td>
<td>58.1</td>
</tr>
<tr>
<td>Paradise</td>
<td>0.61</td>
<td>42.0</td>
<td>29.6</td>
<td>56.3</td>
</tr>
<tr>
<td>Lower South Fork</td>
<td>-0.06</td>
<td>12.3</td>
<td>4.7</td>
<td>6.2</td>
</tr>
</tbody>
</table>
Figure 1. Little Bear River watershed. Descriptions of sampling sites are contained in Table 1.
Figure 2. Continuous (half hourly) estimates of discharge (a), total suspended solids concentration (b), and total phosphorus concentration (c) at the Paradise site.
Figure 3. Cumulative percent of annual discharge, TSS, and TP loads contributed by date for water years 2006 and 2007 at the Paradise site.
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