# Monitoring and Modeling Valley Creek Watershed:2. Methods of Hydrologic Data Collection

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St. Croix Watershed Research Station SCIENCE MUSEUM OF MINNESOTA

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## Monitoring and Modeling Valley Creek Watershed:

## 2. Methods of Hydrologic Data Collection

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## **Extended Abstract**

Beginning in July 1997, the St. Croix Watershed Research Station (SCWRS) received funding from the Legislative Commission on Minnesota Resources to initiate a program of long-term hydrological monitoring on Valley Creek in Afton, Minnesota. This report describes the site installation procedures, field techniques, and analytical methods used in the study.

Four automated monitoring stations were installed along branches of Valley Creek by the SCWRS, and a fifth station was installed near the mouth of Valley Creek by the Metropolitan Council Environmental Services division (MCES). Station 1 was located on the South Branch of Valley Creek, station 2 on the North Branch, and stations 3 and 4 on intermittent tributaries to the South Branch. Each of the stations recorded continuous measurements of stage, temperature, and specific conductance. Stations 3 and 4, being on intermittent tributaries, only recorded data during flow events. Stations 1–4 measured stage using a stilling well, float and shaft encoder; station 5 measured stage with a gas purge system ( bubbler ). A combination temperature/specific-conductance probe was secured in a PVC housing mounted in the stream and measured hourly averages of temperature and specific conductance. All stations were equipped with automatic water samplers and were programmed to collect discrete samples once per week to characterize baseflow and during flow events to characterize storm water. A datalogger was interfaced to each station to record measurements and control the automatic samplers. Equipment at sites 1—4 was housed in a 3 ft x 4 ft x 3 ft steel shelter box. Site 5 was designed to be a year-round station and included a heated walk-in shelter, 110VAC, and a modem hook-up.

In order to convert continuous stage measurements into flow, a stage-discharge rating curve was constructed for each site. Periodic measurements of discharge were made with either a current velocity meter or a dye-dilution measurement. At most sites the dye-dilution technique yielded more reliable results and was eventually adopted as the standard procedure for measuring discharge at all sites. The principle behind this method is that the downstream diluted concentration of dye added to the stream at a known rate is a direct function of stream discharge. A known concentration of rhodamine dye was added to the stream at a precise rate with a metering pump. Well-mixed, downstream concentrations of dye were measured with a benchtop fluorometer and used to compute discharge. The dye-dilution method was repeated at a variety of stream stages to

construct a rating curve for each site. These rating curves will continue to be updated and verified for the duration of the monitoring study.

During weekly visits to the sites (bi-weekly during winter), a multiparameter water-quality sonde was used to measure dissolved oxygen, pH, temperature, and specific conductance. Since the sonde was calibrated in the lab before each use, the specific conductance values from the sonde were used to verify or modify the continuous in-situ probe measurements of specific conductance. Water samples were retrieved from the automatic water samplers, taken to the lab and stored a 4;C. A 60-mL portion of each sample was sub-sampled and stored for total nutrient analysis. The remaining sample was filtered under vacuum through a 1- m glass-fiber filter, and 0.45- m polycarbonate filter. The mass of sediment trapped on the glass-fiber filter was used to calculate total suspended solids and baked a 550;C to determine volatile suspended solids. The filtrate passing through the 0.45- m polycarbonate filter was split into a three 60-mL portions for dissolved nutrient, dissolved organic carbon, and dissolved inorganic carbon analyses. On selected samples two 20-mL sub-samples were taken and stored for cation and anion analysis, and a gravity filtered sub-sample was also collected for stable isotope ( $\delta^{18}$ O and  $\delta D$ ) analysis. A dual digestion method coupled with a dual channel nutrient autoanalyzer was used to measure concentrations of total and dissolved phosphorus and nitrogen. Dissolved organic and inorganic carbon were determined with a UV persulfate carbon analyzer. Cation and anion subsamples were sent to the University of Minnesota and analyzed with inductively coupled plasma-mass spectrometry. Isotope samples were also sent to the University of Minnesota and measured by mass spectrometry. Analysis for samples collected in 1997 and 1998 have been completed, and a database of the results is available (Almendinger and others, 1999).

## INTRODUCTION

Monitoring stream hydrology, *i.e.*, stream-water quantity and quality, is an efficient method of assessing cumulative, integrated effects of activities in a watershed. Surface-water runoff (also called overland flow) carries suspended and dissolved materials to the stream. Groundwater seeps into the stream channel and also carries dissolved materials into the stream. The stream is the low collection point for both the surface-water and groundwater flow systems in the watershed. Consequently, virtually all flow lines in a watershed converge on the stream, making it a useful focal point for hydrological monitoring. By the same token, these converging flow lines assure that the water in the stream is a mix from many different sources, and interpreting the composition of this mix can be difficult. Valley Creek is a relatively pristine trout stream that can provide a sensitive integrated measure of environmental quality in a region where, because of urbanization pressures such measures are most needed. Valley Creek was chosen as our study site because of the opportunity to obtain baseline data prior to such urbanization. The stream may also serve as a standard by which to compare other metro-area streams where substantial development has already occurred.

Beginning in July 1997, the St. Croix Watershed Research Station received statelegislature funding recommended by the Legislative Commission on Minnesota Resources (LCMR) to install four monitoring stations on Valley Creek and to initiate a program of long-term hydrological monitoring (sites 1—4, Figure 1). Sites 1 and 2 are on



**Figure 1.** Valley Creek Watershed and locations of long-term monitoring sites operated by the SCWRS and MCES.

the two main perennial branches of Valley Creek near their confluence, and sites 3 and 4 are on intermittent branches of the creek that may contribute runoff during snow melt or extreme rainfall events. A fifth station, site 5, was installed cooperatively with the Metropolitan Council Environmental Service division near the mouth of Valley Creek. Sampling began in August 1997 on a weekly basis (bi-weekly during winter). Flow measurements were taken about half as frequently. Each station measures stream stage (height), temperature, and specific conductance at hourly intervals. Automatic samplers were installed in August 1998 to allow precise storm-flow sampling.

The goal of this report is to summarize the methods used during the Valley Creek monitoring project. Hopefully, this summary will provide a framework for other projects wishing to study water quantity and quality issues on similar streams. The methods presented here are simply a summary of the techniques used in this project; other methods may be equally or more appropriate. Since Valley Creek is a low flow, groundwater-driven system, the techniques summarized are most applicable to systems with similar hydrology.

## SITE INSTALLATION

## Site Selection

Individual stream-water sampling sites are chosen for a variety of reasons including accessibility, position in watershed, stability, and hydrologic control. All of these considerations played a role in choosing the five sites in the Valley Creek study. Two monitoring stations (sites 1 and 2) were installed above the confluence of the two perennial branches of Valley Creek. Site 1, located on the South Branch of Valley Creek is a predominately groundwater-driven system, while Site 2 on the North Branch is heavily influenced by outflow from Lake Edith (Figure 1). Data from sites 1 and 2 provide a comparison of the variation of water quality, quantity, sources, and transport mechanisms between the two sub-watersheds. Site 5 was installed below the confluence of the two branches near the creek mouth and was monitored with an emphasis to calculate the sediment and nutrient loads that enter the St. Croix River from the entire Valley Creek watershed. Sites 3 and 4 were installed on intermittent tributaries to the South Branch. These sites were chosen based on their potential to reflect changes in surface-water hydrology and chemistry as land uses change in their respective sub-basins.

Each of the sites was located at an existing stream crossing. Sites 1, 2, and 5 were located near bridges that provided easy access to the stream. Sites 3 and 4 were located on the upstream side of culverts crossing under main roads. Sampling equipment was located at each site to take advantage of hydrologic controls necessary for developing discharge rating curves as well as in regions of well-mixed flowing water. Stagnant areas, backwaters, and debris dams were avoided when choosing locations for equipment. Site selection considerations for obtaining a good stage-discharge relation will be discussed further in a later section.

## **Permission/Permits**

In addition to private landowner permission, many townships, municipalities, local watershed districts, and state agencies have ordinances that regulate land use and disturbance along streams and riparian zones. Depending on the regulations, construction and maintenance of monitoring stations may require one or more permits. In Minnesota, any project that alters the course, current, or cross-section of a designated trout stream and other protected water will likely require a permit from the Department of Natural Resources (DNR). Permitting by the DNR does not necessarily supersede permit requirements from other local units of government; these local units may request additional permits.

Monitoring stations installed on Valley Creek, a designated trout stream, required a *protected waters permit* from the DNR, and a *special use* and *shoreline variance* request from the City of Afton. These permits were subsequently received by the Army Corps of Engineers and the local Soil and Water Conservation District. In combination, these permits required stream cross-sections, installation diagrams, construction dimensions, installation cost estimates, and site plans showing distances to ordinary high water mark, property lines, and set-back from public right-of-way. These permits also required a list of adjacent property owners and letters of permission from private landowners whose property was being used. While not all projects may require this amount of detail for permitting, it is advisable to check with all relevant parties before commencing work.

## Equipment

#### Shelters and Conduit

Steel shelter boxes were installed at sites 1—4 to house the automatic samplers, batteries, and dataloggers. Shelters were located as close to the stream as possible, but at sufficient elevation to avoid inundation during flood events. The shelters had dimensions of 40 x 24 x 30 (length, width, and depth, respectively). The front panel of the enclosure incorporated a fold-down section to facilitate access to equipment. Shelters were placed on concrete blocks to keep the box elevated and to discourage rodents. The box had two steel channels welded across the bottom extending beyond the box by about 6 inches. Short sections of receiver pipe were welded to the extensions and tapped with 3/8 course thread. Short sections (3 feet) of 3/4 pipe were slid through the receiver pipe and driven into the ground to act as anchors and to help level the shelter. The sections of pipe could be locked to any height by threading a bolt into the tapped hole on the receiver pipe. A 3 x 4 hole near the center of the bottom of the box served as an entrance port for cables, conduit, and sample lines. A 12 x 16 removable shelf was attached on the inside of the box and could be used to support the data logger, battery, and miscellaneous supplies. The other half of the box housed the automatic sampler. Shelter boxes were secured with a padlock.

At Station 5 the Metropolitan Council Environmental Services division installed a fiberglass walk-in shelter (Bevco Engineering, Milwaukee, WI) on an  $8 \times 8$  platform supported on treated posts. This shelter was designed to operate year-round. Standard electric power was wired to the site, and the shelter was equipped with lights and a small

electric heater to maintain a shelter temperature of a least 40°F. A telephone line connected to the station allowed for remote access to equipment through a modem hook-up.

Shallow trenches were dug from the shelter boxes to the stream edge. Two flexible black PVC tubes of 1 and 2 diameter were buried in the trench to serve as conduits for sampling lines, probes, and cables. Both tubes extended from approximately 1 ft in the stream to just inside the shelter box, entering through the 3 x 4 hole in the bottom (Figure 2). The water-sampling line from the automatic sampler and the combination temperature/specific-conductance probe were fed through the 2 tube into the stream. A perforated housing was slipped over the probe and sampling line and attached to the stream end of the tube with a rubber sleeve and band clamps. The housing was made from Schedule 40 2 PVC and constructed to form a T. Two ends of the T were fitted with threaded PVC caps and the remaining end was clamped to the black PVC conduit. The threaded end caps allowed access to the probes when the unit was in place. Using a 3 U-clamp, the housing was fastened to a stake driven into the stream bottom. The housing was oriented such that the end caps faced up and downstream, and the housing unit was mounted about 6 above stream bottom.



**Figure 2.** Setup of stream monitoring station including float and stilling well, automatic water sampler, temperature/specific conductance probe, and datalogger.

Numerous 1/4 holes were drilled throughout the PVC housing to allow free flow of water. A 5/8 hole was drilled through one side of the housing to allow the water sampling line to extend slightly outside the housing and perpendicular to flow. A barbed pipe fitting and band clamp kept the sampling line fixed to the outside of the housing. This PVC housing worked very well for protecting the sample line and temperature/specific-conductance probe; however, it also provided structure for macroinvertebrate communities. During the summer months at site 2, the end caps needed to be removed frequently, and the inside of the housing flushed with stream water to remove debris and sediment. A cable to connect the shaft encoder to the datalogger was slid through the 1 PVC conduit from the shelter box to the stream, and from there through a 6-ft length of 3/4 flexible galvanized Greenfield conduit. The Greenfield conduit was attached to the stream end of the PVC tube with band clamps, and to the housing on the stilling well with a threaded fitting and electrical nut. The flexible Greenfield conduit provided more versatility when connecting to the stilling well housing than the stiffer black PVC tube and was also more resistant to damage by rodents.

#### Samplers, Probes, and Dataloggers

Portable automatic water samplers (Model 6700, ISCO Environmental, Lincoln, Nebraska), outfitted with a carousel of 24 one-liter bottles, were installed at each of the stations. The automatic water samplers (AWSs) can either be programmed to sample at selected times or flow intervals, or be triggered by a signal from the datalogger. In this project, samplers were triggered by the datalogger, based on a flow (or stage) algorithm. At stations 1 through 4, discrete (non-composited), samples were taken when stage changes exceeded a preset threshold. This sampling routine provided detailed information on the relationship between water-quality parameters and an event hydrograph. Flow-weighted composite samples were collected at Station 5, thus reducing the number of analyses and facilitating the calculation of loading. Because sampling lines were not heated, the AWSs were deployed in the early spring and removed in late fall. Bi-weekly grab samples were collected during winter months. AWSs were programmed to back flush prior to sampling, thereby clearing any debris from the end of sampling tube and reducing the risk of contamination. AWSs could be programmed to take multiple samples per bottle or multiple bottles per sample depending on composite and sample volume requirements. At sites 1 through 4, a 12-V deep-cycle marine battery provided the necessary power to the automatic samplers. Since they are designed to perform on frequent pulse demand without continuous recharging, deep cycle lead-acid marine batteries are preferable to standard 12-V automobile batteries. The marine 12-V batteries would typically provide power for 4 months before requiring recharging. The sampler at site 5 was powered by conventional 110VAC electric current, coupled to a lead—acid battery backup in the event of a power failure.

A combination temperature and specific conductance (SC) probe was also installed at each of the stations (Model 247, Campbell Scientific Inc., Logan, Utah). The combination probe was mounted in the PVC housing discussed previously and connected directly to the datalogger by a 50 cable. Every minute the datalogger queried the probes and calculated a five-minute running average of the last five measurements. The most recent five-minute running average was recorded on the hour during baseflow conditions and on the quarter-hour during runoff events. Comparisons of temperature measurements taken with YSI multiparameter water-quality sonde (Model 6820, YSI, Yellow Springs, Ohio) consistently agreed to within 0.5; C of *in situ* Campbell probe measurements. Initial calibration of the SC probe was accomplished by placing the probe in known calibration solution and manipulating the cell constant in the datalogger program until measured values equaled the standard. Initially when the Campbell probe was deployed, measured SC values agreed well with values taken with the YSI sonde. Over time, however, because of bio-films and sediment deposits, measurements from the Campbell SC probe would decline relative to the YSI sonde measurements. Since the YSI is calibrated with each use, it was assumed that the YSI measurement provided the best estimate of the true value. Cleaning the probe and removing sediment and bio-films from the housing would usually restore agreement of the two measurements, and thus probes were cleaned routinely. To compensate for the drift in measurement between cleanings, SC values from the Campbell probe were adjusted in the database to match the YSI sonde values from the corresponding data and time, and intervening hourly measurements were weighted and interpolated accordingly.

A datalogger (Model CR10X, Campbell Scientific Inc., Logan, Utah) was used to control the samplers and record data from the temperature/SC probe. The datalogger was powered by a 6-V, 12 amp-hour sealed lead-acid (gel cell) battery. Batteries were replaced and recharged when the voltage dropped to 10.5 V. A 12 amp-hour battery powering probe measurements every minute would usually last for about 2 to 3 months before requiring recharging. Data were manually downloaded from the datalogger to an SM 192 storage module on a regular basis and subsequently transferred to a personal computer. All datalogger functions were controlled with a CR10KD keypad.

#### Weather Station

An existing weather station was upgraded to provide meteorological data for the study. The weather station was located within the watershed about 1 mile from Sites 1, 2, and 5 (Figure 1). While it was possible to get meteorological data from the Minneapolis-St. Paul International Airport station 25 miles to the west, having a station within the watershed was far superior, especially for spatially variable parameters such as precipitation. The weather station included the following Campbell Scientific Inc. (Logan, UT) equipment:

- Wind Speed sensor, Model 014A
- Wind Direction sensor, Model 024A
- Temperature and Relative probe, Model HMP35C
- Solar Radiation sensor, Model LI200S
- Tipping Bucket Rain Gauge, Model TE25

The weather station was powered by a 6-V, 8 amp-hour gel cell battery and was continually recharged by an attached solar panel. Each of the sensors was interfaced to a CR10 datalogger and was remotely accessible through a telecommunication-port modem connection.

## DISCHARGE

## **Rating Curves**

Measurement of flow, or discharge, is fundamental to the interpretation of streamwater data. Nearly all chemical, physical, and biological aspects of a stream are linked to discharge. Since discharge is difficult to monitor directly, a discharge rating curve is used to calculate flow.



Figure 3. Site VC5 rating curve.

A rating curve is the relation of flow  $(m^3/s)$  to water elevation or stage (m), and is simply an empirical curve fit to a series of discharge versus stage measurements. A continuous record of stage can be obtained from a variety of instruments that measure water-surface elevation. At selected different stages, initial discharge measurements are made to define the stage-discharge relationship. Subsequently, periodic discharge measurements are taken in order to test whether the stage-discharge relationship has shifted because of changes to channel geometry. A rating curve example is shown in Figure 3 and demonstrates a linear relationship between stage and discharge; however, the relationship is often non-linear since rating curves are a function of channel geometry. A simple rating curve of stage versus discharge is often composed of multiple segments constructed at low, medium, and high flow periods. Because flows at the station shown in Figure 3 are dominated by baseflow and flashy events, the medium flow regime has not been measured. Once these flows are added to the plot, the stage-discharge relationship may emerge as having several segments, each linear or curvilinear. Rating curves encompassing flows ranging over an order of magnitude may be best represented as loglog or log-linear plots. Seasonal changes, typically due to aquatic and streambank vegetation, can cause a shift in the rating curve. Accounting for these seasonal shifts is crucial in developing a rating curve that is accurate throughout the year. A complete and very useful discussion of rating curves, seasonal shifts, and complex ratings involving discharge versus multiple variables is covered in the U.S. Geological Survey publications, General Procedure for Gaging Streams (Carter and Davidian, 1968), and Discharge Ratings at Gaging Stations (Kennedy, 1984). Another useful reference for stream gauging is Chapter 8 of The Handbook of Hydrology (Mosley and McKerchar, 1993).

## Measurement of Stage

#### Site Selection

To maximize the stability of a stage-discharge rating curve, selected sites should be accessible in high and low flow periods, be free of groundwater or flood channel bypasses, be unaffected by backwater effects from downstream tributaries or rivers, and have a stable hydrologic control. A hydrologic control is any natural or artificial structure that produces a stable and reproducible stage-discharge relationship. Channel characteristics such as rock riffles, waterfalls, or steep, stable streambanks are all good natural hydrologic controls. Culverts, bridges, and low dams also often act as stable control structures. Artificial control structures such as weirs and flumes can be installed in unstable or low-flow stream reaches. Stage measurements should be made just upstream of a control structure, preferably in a pool created by the control. The flow of water over (or through) a control structure is related to the depth of flow. The stage in the pool upstream of the control is a direct measure of this flow depth, and is thus directly related to flow out of the pool rather than flow into the pool. For small pools, inflow and outflow may be equal under most conditions. However, for larger pools with significant storage time, outflow may substantially lag inflow. In this situation, only outflow discharge measurements should be used to construct a rating curve. Controls and restrictions to flow that are not stable or predictable should be avoided or removed. Thus, care should be taken to keep control structures free of debris, and impediments such as deadfalls should be removed to prevent debris from collecting. Sites prone to collecting debris should be checked often.

The five sampling sites on Valley Creek utilized both natural and man-made control structures. Sites 2 and 5 were located in small pools created by downstream riffles and in a stable constriction of the channel. Sites 3 and 4 were located upstream of man-made road culverts that controlled flow. Site 1 was located in the large pool created

behind a low dam constructed to divert part of water through a side channel. Because this pool was large enough to create a lag between upstream and downstream discharges, it was imperative that discharge measurements be take downstream of the stage measurements, *i.e.* outflow from the pool rather than inflow to the pool. This posed somewhat of a problem since the diversion required that discharge measurements be made on both portions.

#### Surveying and Bench Marks

Since staff gauges, stilling wells, and other stage-measurement equipment are susceptible to changes in elevation due to frost, ice action, erosion, or vandalism, a benchmark or reference elevation should be established at each site. Shortly after installation, the elevations of staff gauges and stilling wells should be established relative to local fixed reference points. A fixed reference point can be a spike driven in a tree, a large stable structure such as a bridge abutment, or a nearby U.S. Geological Survey benchmark. For Valley Creek sites, the elevation of a point on each stage measuring device and the reference point were taken with a surveyor s optical level and rod. In addition, at sites where tape-down measurements were being made from a bridge, dam, or culvert, the elevations of these measuring points were also established relative the reference point. All elevations should be re-surveyed periodically to check for any shifts in elevation relative to the reference point. Accurately surveying all stage measuring locations also allows for easy conversion of tape-down measurements to equivalent staff or other stage measures.

#### Staff Gauge

Staff gauges are an inexpensive and easy way of estimating stage. In addition to providing a quick visual means of determining stage, they are often used to reference other stage measuring devices and to provide a substitute measurement when continuous recording equipment is disabled. A staff gauge can be as simple as a graduated rod mounted to a stable location in the stream. Standardized, accurately graduated staff gauges are readily available from most natural resource equipment suppliers. Staff gauges are often mounted on bridges, dams, or posts driven into the stream. The disadvantage of a staff gauge is that levels can be difficult to measure within 5 mm because of turbulent flow and they require direct observation, *i.e.*, they are non-recording and thus do not provide a continuous record of stage. However, given their ease of installation, low cost, and on-site accessibility, staff gauges are an important compliment and to cross-reference continuously recording stage equipment.

An enameled steel staff gauge, graduated in 0.02-ft increments, was mounted parallel to flow on a concrete bridge abutment at Site 5 in Valley Creek. A flexible pocket leveling rod, graduated in 1-cm increments was used as the staff gauges at Sites 1 and 2. The leveling rod was mounted to the stilling well with band clamps, which allowed the staff gauge to be easily adjusted. While these flexible leveling rods are an economic and fast method of installing a staff gauge, they are not as durable as the standard enameled steel staff gauges.

#### Floats

A common way of sensing stage is through the use of a float in a stilling well. As water elevations rise and fall, the float in stilling will move accordingly. A nonstretching line from the float is run over a pulley and connected to a counterweight which balances the system and allows the float to move readily and rapidly with changing water levels. The stilling well protects the float and dampens fluctuations in the stream caused by wind and turbulence. The stilling well can be a pipe with a screened side opening driven directly into the streambed, or can be mounted on shore and connected to the stream via intake pipes. Traditionally, the float pulley would control the pen on a clock-driven strip-chart recorder and provide a continuous on-site record of water-level fluctuation. More modern gauges use the movement of the float to turn a wheel on a shaft encoder, which converts rotation into an electrical pulse. This signal is measured and stored on a datalogger.

A variety of float instrumentation is available through several hydrologic vendors. Float instrumentation was used at Stations 1—4 in Valley Creek. Stilling wells were constructed of 2 -diameter galvanized steel pipe 9 long, with a series of 3/8 holes drilled into the pipe 4 to 4.5 from one end and covered with a fine steel screen mesh. The stilling well was driven into the streambed to the depth of the perforated section. A steel box, housing the shaft encoder and counter-weight tube, was mounted to the top of the pipe. The stilling well must be long enough to be driven solidly into the streambed and yet extend up beyond the maximum expected water elevation. In shallow streams with flood peaks of less than 1 meter, it is possible to install the stilling well directly in the streambed without fear of flood events reaching the box housing the shaft encoder. In streams with larger stage fluctuations, it is advisable to mount the stilling well on shore near the stream and connect the well to the stream via intake pipes, or simply mount the well to a bridge abutment.

A 1 -diameter, 3 -long weighted float and a 4-oz lead counterweight were connected to the pulley on the shaft encoder with spider wire non-stretch fishing line, such that the counterweight was at the top of its travel when the float was at the bottom of its travel. The shaft encoder was connected by a three-wire cable to a Campbell CR10X datalogger, which was programmed such that the initial float reading was identical to the staff gauge reading.

The stilling well and float provided an efficient and accurate means of continuously measuring stage to within +/- 0.015 ft at Sites 1—4. The float performed better, however, on the rising portions of the hydrograph than the falling portions. During several events, the float would stick and not lower at the same rate the water level dropped. This resulted in small, but pronounced discrete drops in recorded stage. Adjusting the mass of the counter weight ameliorated this problem somewhat. In streams such as Valley Creek, small changes in stage may be accurately measured with more sophisticated instrumentation such as gas purge system, *viz.* a bubbler.

#### **Bubblers**

Gas purge systems, commonly known as bubblers, are a more sensitive and sophisticated way to record stage. In this system, a gas, usually nitrogen or air, is fed through a tube and bubbled freely through an orifice mounted at a fixed height in the stream. The gas back pressure in the tube is equal to the piezometric head exerted on the bubble orifice. At installation this head is calibrated to be equal to the current stage reading. Back pressure in the tube is measured using either a manometer or pressure transducer.

A Water Log H350/355 gas purge system (Design Analysis Assoc., Logan, UT) was installed at Station 5 on Valley Creek. Unlike many bubblers, which use replaceable nitrogen tanks to supply gas, the H355 uses a pump to continuously recharge a pressure tank with air which is then fed through a tube to a submerged orifice. While this is an expensive option, it is very accurate and requires less maintenance than earlier bubbler systems. A pressure transducer measures the back pressure of air, which is converted to stage and stored by the datalogger. Gas purge systems are accurate to  $\leq \pm 0.01$  ft, and can operate when air temperatures are below 0;C, whereas stilling wells are prone to freeze. For streams that require very precise, year-round gauging, gas purge systems such as the H350/355 provide excellent results.

#### Measurement of Flow

#### Vertical Axis Current Meter (AA Meter)

The current meter, in conjunction with a tag line and top-setting rod, is the conventional method for measuring discharge in small streams. The current meter is used to measure velocity of the stream, and the wading rod measures water depth and sets the position of the current meter. The tag line measures lateral position across the stream cross-section. Total discharge for stream cross section is calculated by measuring the area and velocity in a series of segments of a stream cross-section. Discharge through the cross-section is

$$\mathbf{Q} = \bullet(\mathbf{A}_{i} \mathbf{x} \mathbf{V}_{i}) \tag{1}$$

where Q is total discharge  $(m^3/s)$ , A<sub>i</sub> is the cross-sectional area of an individual segment  $(m^2)$ , and V<sub>i</sub> is the mean velocity of flow in that segment (m/s). A cross section is usually divided into at least 20 segments of approximately equal flow. This is done to ensure that any one cross-section segment comprises no more than 5% of the total flow. It may not be possible to divide the cross section into 20 segments in very narrow stream reaches; in these cases, care should still be taken to try and divide the stream into sections based on anticipated equal flow rather than equal lateral distance. Each segment or partial section is defined to be a rectangle of depth equal to the depth measured by the rod, and width equal to the sum of half the distances to each adjacent measured location. Depending on stream depth, discharge is calculated based on either a one or two point velocity measurement. For stream depths less than 2.5, velocity is measured at one point, 0.6 of the depth below the surface. In depths greater than 2.5, velocity for the segment.

The most common of vertical axis current meters are the Price type AA and Price type pygmy meter. The AA meter will accurately measure current velocities of 0.03 to 7.6 m/s, but is not recommended for velocities below 0.03 m/s. The pygmy meter or modified low-velocity AA meter is recommended for slower velocities. The pygmy

meter is also recommended for shallow water depths, <0.25 m. Velocity is determined by counting the number of revolutions of the rotating bucket wheels in a given period of time. Traditionally this was done with a stopwatch and headphones which converted rotations into clicks . Modern current meters can be equipped with a magnetic head that relays rotations into an electronic pulse measured and converted into velocity by a small datalogger mounted on the wading rod.

The current meter can be mounted to a top-setting wading rod for flow measurements in small streams. In larger streams, the meter can be suspended with a cable and sounding weight. The top-setting wading rod is a hexagonal rod available in lengths up to 10, and is graduated in either centimeters or tenths of feet. The rod has a base plate which rests on the stream bottom, and stream depth is read off the graduated main rod. A second round rod slides along the main rod and is used to set the depth of the current meter. The top-setting rod is the preferred choice in wading rods because it is equipped with a scaled adjustable handle which allows the current meter to be positioned easily at 0.2, 0.6, or 0.8 of the full stream depth. Lateral position along the cross-section is usually determined by a tag line. A tag line is basically a long measuring tape that is strung across the stream, normal to the direction of flow. Permanent marks measured along a bridge or culvert can be substituted for a tag line.

#### **Dye Dilution Method**

In small streams, and during low flow periods, dye dilution is a very efficient method to measure flow. Because stream depths were shallow and flows were generally quite low in Valley Creek, the dye dilution method proved more reliable for determining discharge than the current meter method. The basic principle of dye dilution is that the degree of dilution of tracer solution added to the stream is directly proportional to the discharge. A known concentration of a stable tracer, most often rhodamine dye, is added at a precise and constant rate to a stream. Measuring the well-mixed, diluted concentration of dye at downstream locations yields the stream discharge through the relationship:

$$Q_{\text{stream}} = Q_d \times C_d / C_s \tag{2}$$

Discharge of the stream ( $Q_{stream}$ ) is equal to the product of the rate at which the dye is added ( $Q_d$ ) and the known concentration of the dye ( $C_d$ ) divided by the concentration of dye measured in the stream ( $C_s$ ). Note that the discharge determined by equation (2) represents the discharge at the downstream location where the dye concentration is sampled, not the discharge at the location where the dye is added. The accuracy of this method is dependent on the following:

a) having a precisely known concentration of dye solution

b) an ability to add the dye solution at a constant and known rate

c) measuring the downstream concentration of dye at a steady state, well-mixed location

Rhodamine is a fluorescing dye that can be detected in the field with a flow-through fluorometer, or in the laboratory with a benchtop fluorometer measuring stream samples.

Low concentrations of rhodamine are usually more accurately measured with a benchtop fluorometer.

A detailed description of the dye-dilution method is summarized in the U.S. Geological Survey publications, Fluorometric Procedures for Dye Tracing (Wilson and others, 1986) and Measurement of Discharge Using Tracers (Kilpatrick and Cobb, 1985). Based on the procedures outlined in these reports, a dye-dilution method was developed for Valley Creek. A bulk solution of 0.5% rhodamine dye was prepared from a 21% commercial stock concentrate. The 0.5% solution was added to the stream using an FMI metering pump (Model QGB370, Fluid Metering Inc., Syosset, NY). Dye was typically dripped into the stream at a rate of 10 to 30 mL/min. Base flows and small events in Valley Creek have discharges varying from 0.1 to 1 m<sup>3</sup>/s. Based on these flows and drip rates, a 0.5% dye solution will produce a stream concentration of 1 to 10 g/L. These concentrations are well within the analytical range of the TD700 benchtop fluorometer (Turner Designs, Sunnyvale, CA) used to analyze the samples. During higher flow periods (and thus greater dilution), a faster drip rate of dye was used. Because the maximum rate of the metering pump is about 50 mL/min, a more concentrated stock solution is recommend for high flows (>1  $m^3/s$ ) or for turbid conditions that increase blank readings and decrease the sensitivity of the method.

Five calibration standards ranging between 0.25 to 25 g/L were prepared from the 0.5% stock solution. Standards and stock solution were prepared with tap water; thus tap water was used as the zero standard in the calibration curve. In addition, to account for any possible changes in stock solution over time, an aliquot of the stock solution used during each flow measurement was sub-sampled, diluted in the lab, and analyzed as a sample. While this concentration was targeted to be 0.5%, the actual measured value was used as  $C_D$  in eq. 2. Measured and expected concentrations varied by less than 10%.

For each measurement at a site, streamwater blanks were collected upstream of the drip location. During low-flow periods, blank concentrations were negligible. However, during high, turbid flows or when dye studies had been recently conducted at a upstream site, it was necessary to blank-correct the measured concentrations.

Suitable site selection is an important factor in dilution studies. Ideally, the dilution study/discharge measurement should be made as close to the gauging station as possible. As long as there are no other sources or sinks of water or lags caused by a large pool at the gauging station, the dilution study can be conducted just upstream or downstream of the gauging station and the measured discharge will still be representative of the site. Dye must be added over a long enough period to achieve a steady-state, well-mixed concentration at the sampling site. At most sites on Valley Creek, steady state was achieved in less than 15 minutes and sampling locations ranged from about 75 to 300 meters downstream from the drip location . During long dilution measurements, drip rate and stage should be measured at the beginning and end of the measurement.

If possible, dye should be added upstream of features that promote mixing. These include riffles, meanders, culverts, and waterfalls. Features such as large pools, dams, and debris dams should be avoided along the measured stream reach since these structures will increase the time necessary to reach a steady-state mixed concentration. Locations and time requirements to reach steady-state well-mixed conditions can be determined by collecting a number of temporally and spatially varying samples from a stream cross section at a given location. Once the samples have reached a maximum,

uniform concentration, the site can be assumed to be well mixed and at steady-state. Experimenting with drip location, duration, and collection points will ultimately shorten the time required to conduct a dye dilution measurement.

## WATER QUALITY

The Valley Creek study focused on water-quality variables that are critical to healthy trout populations and were likely to be affected by urbanization. Fundamental parameters such as water quantity, temperature, and specific conductance were monitored hourly during baseflow conditions, and at 15-minute intervals during events. Other variables such as total suspended solids (TSS), volatile suspended solids (VSS), dissolved organic and inorganic carbon (DOC, DIC), total and dissolved phosphorus (TP, DP) and nitrogen (TN, DN) were measured weekly during baseflow conditions, and more frequently during hydrologic events. Selected cations and anions, which can be related to the geology of an area and influenced by land-use practices, were measured periodically to give an overall indication of geochemistry within the watershed. Stable isotopes of oxygen and hydrogen ( $\delta^{18}$ O,  $\delta$ D) were measured less frequently during the study to serve as an indicator of different sources of water to the creek, *e.g.*, groundwater versus surface water influenced by evaporation.

## Sample Handling

Water samples (1 liter) were collected in the field via an AWS (described in the Site Installation section) or manually collected as a grab sample (such as in winter). Samples were brought back to the laboratory, stored at 4;C, and processed within 2 days of collection. A subsample was poured into a 60-mL high-density polyethylene (HDPE) or polypropylene (PP) acid-washed bottle and frozen for total phosphorus/total nitrogen (TP/TN) analysis. The remaining sample was filtered through a 1- m nominal pore size glass fiber filter (GF/B, Whatman International Ltd., Springfield Mill, Maldstone, Kent, England) under vacuum using a Millipore 47-mm stainless steel glass filter holder (XX10-047-30, Millipore Corporation, Bedford, MA). Three samples were processed at a time in this manner by using a manifold on the vacuum pump. The filtration apparatuses were fully rinsed with reagent-grade (ASTM type I) deionized (DI) water between samples. The filtrate collected in the vacuum flask was filtered a second time through a 0.45- m low extractable polycarbonate membrane (Poretics 13035, Osmonics Inc., Boston, MA) and poured into collection bottles for later analysis of dissolved phosphorus/dissolved nitrogen (DP/DN), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). The 60-mL HDPE or PP collection bottles for TP/TN and DP/DN and 40-mL glass vials for DOC and DIC were soaked for 24 hours in an acid bath (10% HCl) and rinsed with DI water. TP/TN and DP/DN samples were stored frozen. DOC and DIC samples were stored at 4;C.

At various sampling times, selected samples were analyzed for isotopes ( $\delta^{18}$ O,  $\delta$ D), cations, and anions. Isotope samples were filtered through an oven-baked glass fiber filter (GF/B, Whatman International Ltd., Springfield Mill, Maldstone, Kent, England), under no vacuum. Isotope samples were collected in a 20-mL glass scintillation vial, with a conical top, to ensure that no headspace remained in the vial.

Vials were cleaned by rinsing with DI water and were capped and stored containing DI water until use. Samples for isotopes were stored at 4<sub>i</sub>C prior to being sent to the University of Minnesota for analysis. Anion samples were subsampled from the filtrate passed through the 0.45- m low extractable polycarbonate membrane. Samples were poured into 20-mL plastic scintillation vials that were cleaned by rinsing with DI water, capped and stored containing DI water until use. Cation samples were also subsampled from the final filtrate. Cation samples were poured into 20-mL plastic scintillation vials that were soaked for 24 hours in a 10% HCl acid bath and rinsed with DI water. Vials were capped and stored containing DI water until use. Cation samples were preserved with 1—2 drops concentrated nitric acid. Both cation and anion samples were stored at 4<sub>i</sub>C until being sent to the University of Minnesota for analysis.

A select group of samples were also analyzed for nitrate-N and ammonia-N. Samples were collected, prior to filtration, in a 60-mL acid-washed HDPE or PP bottle. Unfiltered samples were stored frozen until analyzed. To verify the relationship between DIC and alkalinity, a select group of samples were analyzed for alkalinity. Samples were filtered through a 0.45- m low extractable polycarbonate membrane into 60-mL acid washed PP bottles and stored at  $4_i$ C.

## **Field Measurements**

As discussed in Section I, continuous (hourly) measurements of temperature and specific conductance were recorded by dataloggers at each of the monitoring stations. In addition, during weekly or bi-weekly sampling trips to the sites, temperature, specific conductance, conductivity, dissolved oxygen, % dissolved oxygen, and pH were measured with a YSI multiparameter water-quality sonde (Model 6820, YSI Incorporated, Yellow Springs, OH). Temperature was measured with a thermistor made of sintered metallic oxide contained in the YSI 6820 monitoring probe. The thermistor changes predictably in resistance with temperature variation. The algorithm for conversion of resistance to temperature is built into the YSI 6820 software, and temperature in degrees Celsius is given automatically. No temperature calibration is needed. The temperature range for the thermistor is -5 to 45<sub>1</sub>C with an accuracy of +/- 0.15<sub>1</sub>C and a resolution of 0.01<sub>1</sub>C.

The sensor used to determine specific conductance and conductivity in the YSI probe utilizes four pure nickel electrodes. Two of the electrodes are driven by current, while the other two are used to measure voltage drop. The measured drop in voltage is converted to a conductance value in milli-Siemens (mS, equivalent to millimhos) and is then multiplied by the cell constant (5.0/cm) to give a value in mS/cm. The multiplication of the cell constant and conductance is automatically performed by the software contained in the YSI probe. The conductivity range is 0 to 100 mS/cm while the accuracy is  $\pm 0.5\%$  of the reading plus 0.001 mS/cm. The resolution is range dependent and includes 0.001 mS/cm to 0.1 mS/cm.

Because the conductivity of solutions is highly dependent on temperature (varying as much as 3% for each 1;C change), specific conductance uses temperature and raw conductivity values to generate a value compensated to 25;C as shown in Equation 3:

Specific Conductance 
$$(25^{\circ}C) = \frac{\text{Conductivity}}{1 + TC (T - 25)}$$
 (3)

where

TC = temperature coefficient of 0.0191 (*i.e.* 1.91% per ;C) T = temperature

When calibrating the YSI sonde for conductivity, specific conductance is also calibrated. A 500 S/cm (0.00348 *M* KCl) conductivity standard was used to calibrate the YSI probe and was made by dissolving 1.0377 g KCl, dried overnight in a 105<sub>1</sub>C oven, in 4 L DI water.

The YSI model 6820 utilizes a patented YSI Rapid Pulse system for the measurement of Dissolved Oxygen (DO). One of the advantages associated with this system is that the liquid surrounding the DO probe does not need constant stirring to yield accurate readings. The Rapid Pulse system uses a Clark-type sensor which is similar to other membrane-covered, steady-state dissolved oxygen probes. The system measures the current associated with the reduction of oxygen which diffuses through a Teflon membrane. This current is proportional to the partial pressure (not the concentration) of oxygen in the solution. The Clark-type sensor consists of three electrodes (a cathode, anode, and reference electrode). It is continuously polarized at a voltage sufficiently negative to cause oxygen (which diffuses through the Teflon membrane) to be reduced to hydroxide ions at the cathode and silver metal to be oxidized to silver chloride at the anode. The current associated with this process is proportional to the oxygen present in solution outside the membrane. As the reaction proceeds, oxygen is consumed in the solution, resulting in a decrease in measured current (and measured oxygen content) if the solution is not stirred rapidly. To minimize this oxygen depletion, the probe electrodes in the YSI Rapid Pulse system are rapidly and reproducibly polarized on and depolarized off during a measurement sequence. The Rapid Pulse system measures the current summed over a specific time period associated with the reduction in oxygen. The net charge is proportional to the oxygen partial pressure in the solution. Oxygen consumption outside the membrane is kept to a minimum, and the stirring dependence of the system is greatly reduced.

Two oxygen calibration parameters are possible with the YSI 6820, DO mg/L and DO %. Calibrating for one automatically will calibrate for the other. We calibrated the YSI probe for DO %. Percent saturation is calibrated by placing the probe in the calibration cup which contains a small amount of water. The barometric pressure is entered into the YSI 6820 software, and after the readings have stabilized, the calibration is confirmed.

The YSI 6820 contains a replaceable pH electrode for the determination of hydrogen ion concentration. The probe is glass combination electrode and is calibrated using a one-point calibration with a pH buffer of 7.00. The accuracy of the probe is  $\pm$ -0.2 units and has a reported resolution of 0.01 units.

## Laboratory Measurements

#### Total Suspended Solids/Volatile Suspended Solids

Total suspended solids (TSS) and volatile suspended solids (VSS) were measured by filtering a sample through a pre-weighed oven-baked glass fiber filter (GF/B, Whatman International Ltd., Springfield Mill, Maldstone, Kent, England). Prior to filtering, glass fiber filters were baked at 550<sub>i</sub>C for one hour to remove any organic contaminants that might be contained on the filter. For suspended solid calculations, a known amount of sample passing through the filter must be measured. Prior to this, analyses that required unfiltered samples (*i.e.* TP/TN, and/or nitrate-N and ammonia-N) were poured off. After splitting the subsamples for unfiltered analysis, the mass of the sample bottle containing the remaining sample was measured. After filtering through the glass fiber filter, the sample bottle was measured again. By subtracting the two weights, a known amount of sample passing through the filter was determined. At least one liter of sample is desirable for suspended solid analyses. The filter containing the sediment was dried at 105<sub>i</sub>C overnight, cooled in a desiccator, and weighed to determine TSS by the following equation:

TSS (mg/L) = 
$$\frac{F_{105} - F}{V} x \, 10^6$$
 (4)

where

 $F_{105}$  = filter + dried sediment baked @ 105;C (g), F = weight of filter (g), and V = amount of sample passed through filter (mL)

Filters were then placed in a muffle furnace and baked at 550<sub>i</sub>C for one hour to remove volatile organics. Samples were cooled in a desiccator and re-weighed. VSS were calculated using the following equation:

VSS (mg/L) = 
$$\frac{F_{105} - F_{550}}{V} x \, 10^6$$
 (5)

where  $F_{550}$  = filter + dried sediment baked @ 550;C (g)

#### Nutrient Analysis

#### Sample Preparation and Quality Control

A sample dual digestion (modified from Ameel and others, 1993) for both total phosphorus and total nitrogen (TP/TN), and dissolved phosphorus and dissolved nitrogen (DP/DN) was performed in 60-mL HDPE bottles (*e.g.*, 02-923B, Fisher Scientific, Pittsburgh, PA). Digestions of samples in polypropylene bottles were found to contain small amounts of orthophosphorus, possibly coming from the bottle wall during the

digestion. High density polyethylene bottles were soaked in 10% HCl for 24 hours and rinsed with reagent-grade (ASTM type I) DI water.

Digestion reagents were made as follows: potassium persulfate (0.148 M) was made by dissolving 20 g low-nitrogen potassium persulfate (*e.g.* P282-100, Fisher Scientific, Pittsburgh, PA) in 500 mL DI water. Sodium hydroxide (3 N) was made by dissolving 12 g NaOH in 100 mL DI water.

About 15 g of sample or 30 g of standard was pipetted into a pre-weighed HDPE digestion bottle on an analytical balance; actual total weights were recorded. Then 5.0 mL or 10.0 mL of potassium persulfate along with 0.250 mL or 0.500 mL sodium hydroxide was added to the sample or standard respectively. Bottles were loosely capped and autoclaved at 121;C and 16 psi for 55 min. After the digestion, when the bottles had cooled, sample weights were recorded. Dilutions of samples and standards were calculated based on sample weight, reagent added, and weight loss during digestion.

Phosphorus calibration standards were diluted from a 250 g P/L working stock standard. The working stock standard was diluted from a 25 mg P/L stock standard made by dissolving 0.1099 g primary standard grade anhydrous potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>), dried for one hour at  $105_1$ C, in 1000 mL DI water. Nitrate calibration standards were diluted from a 200.0 mg N/L stock standard made by dissolving 1.444 g potassium nitrate (KNO<sub>3</sub>) in 1000 mL DI water.

Mixed quality control check standards (QCSPEX-Nut, SPEX CertiPrep, Inc., Metuchen, NJ) were purchased for both total phosphorus and total nitrogen and diluted to manufacture s specifications. A midrange and low check standard for total nitrogen were made at concentrations of 7.5 and 1.0 mg N/L. Separate dilutions were made for total phosphorus check standards at 100, 25, and 1.0 g P/L. Occasionally, a higher calibration curve for phosphorus was used. In these cases, higher check standards were prepared. Allowable recoveries for check standards were +/- 10% of the expected value. Instrument blanks as well as procedural blanks were included during analysis. Five percent of the samples were run in duplicate. All calibration and check standards as well as blanks, samples, and duplicates were digested in the same manner before analysis. Identical digestion procedures for samples, blanks, standards etc. is critical in determining phosphorus values because of the intricate chemical reaction sequence required by the phosphorus manifold of the auto analyzer (Lachat Instruments, method 10-115-01-1-B).

#### Total and Dissolved Nitrogen Analysis

Total and dissolved nitrogen analyses were determined on a QuickChem 8000 dual-channel nutrient autoanalyzer (Lachat Instruments, Milwaukee, WI). During the digestion, reduced nitrogen species (organic-N, ammonium-N, and nitrite-N) are converted to nitrate-N. This nitrogen plus the original nitrate was determined using the cadmium reduction method (Lachat Instruments, method 10-107-04-1-A). Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite reacts with added reagents and forms a magenta color that absorbs light at 520 nm. The absorbance is proportional to the concentration of nitrate in the sample. Seven nitrate calibration standards (0.0, 0.20, 0.40, 1.00, 4.0, 8.0, and 20.0 mg

N/L) were used to generate a first-order polynomial (linear) standard curve, which was then used for calculating concentration:

$$Concentration = C(1) Y + C(0)$$
(6)

where

C(1) = calibration curve first-order coefficient (slope),

C(0) = calibration curve constant term (concentration axis intercept), and

*Y* = analyte response (peak area of light absorbed)

Direct chemistry was the peak analysis and integration scheme that was used to detect and measure peaks formed from this method. Direct chemistry calculates only positive peaks (*i.e.* peaks above the baseline or peak area > 0). Peak base width and threshold values are assigned values and then calculated to activate this chemistry. Because a zero-concentration calibration standard is used, the calibration curve is not forced through zero. This is recommended because a zero calibration standard may not have a zero response or absorbance. A weighting method (1/x) was applied to the calibration data causing the data to be weighted proportionally to the inverse of the concentration standards. Calibration failure criteria were set for each calibration curve generated. The minimum correlation coefficient allowed (r value) was 0.9900, however, an r value >0.9999 was often observed. Every calibration standard must have a maximum residual from the curve fit of <10%.

#### Total and Dissolved Phosphorus Analysis

Total phosphorus and dissolved phosphorus were determined using a QuickChem 8000 dual-channel nutrient autoanalyzer (Lachat Instruments, Milwaukee WI). During the digestion, organic-P is converted to orthophosphate. The orthophosphate ion  $(PO_4^{3^-})$  reacts with an added molybdate reagent to form a complex, that absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample. Lachat method 10-115-01-1-B for orthophosphate (based on EPA method 365.1) was used to measure total phosphorus simultaneously with total nitrogen. The majority of the samples that were analyzed fell into the calibration range of 100, 75, 50, 25, 10, 3, and 0 g P/L. Occasionally samples had concentrations greater than 100 g P/L of total phosphorus and a calibration curve containing either 500, 450, 400, 350, 300, 250, and 0 or 1500, 1300, 1100, 900, 700, 500, and 0 g P/L was generated. A second-order polynomial produced a more suitable calibration fit for the total phosphorus calibration curve. The resulting equation for a second-order polynomial is as follows:

Concentration = 
$$C(2) Y2 + C(1) Y + C(0)$$
 (7)

where:

C(2) = calibration curve second-order coefficient,

C(1) = calibration curve first-order coefficient,

C(0) = calibration curve constant term (concentration axis intercept), and

Y = analyte response (area under light-absorption peak)

A 0.13 M H<sub>2</sub>SO<sub>4</sub> carrier was used on the phosphorus manifold to avoid sample/carrier mismatch. However, even by matching the sample matrix with this carrier, there is a refractive index that occurs at the sample/carrier interface, meaning the leading portion of the peak is negative (below baseline). A refractive index can also occur as the sample peak comes back to baseline commencing the start of the carrier. This occurrence is more pronounced at the lower-end samples (>10 g P/L). In the instance of blanks, not only does a portion of the blank dip below baseline, it also rises equally above the baseline. Because of these reasons, direct chemistry integration was not used to calculate the peaks. Instead, brackish chemistry integration, with manual peak parameters, was employed to integrate only a small portion of the peak dropping below and a significant portion rising above the baseline. To determine these parameters, the zero calibration standard was used to set the integration start and end times such that the peak integration was equally above and below baseline to give a value close to 0.0 g P/L for the zero calibration standard. By default, all other peak areas were calculated in this manner. A weighting method of 1/x was used, and the calibration curve was not forced through zero. An r value of 0.9900 was the minimum correlation coefficient, but typically r values were greater than 0.99.

#### Nitrate and Ammonia Nitrogen Analysis

Selected samples were also analyzed for NO<sub>3</sub>+NO<sub>2</sub>-N and NH<sub>3</sub>-N. These samples were not filtered, were kept frozen, and analyzed within three weeks of collection. The pH of our waters causes most of the ammonia (NH<sub>3</sub>-N) to be in the form of ammonium (NH<sub>4</sub>-N). Samples were run undigested on a dual channel Lachat Instrument using manifolds 10-107-04-1-A and 10-107-06-1-B for nitrate+nitrite-N and ammonia-N respectively. Nitrate reduction to nitrite and subsequent analysis was discussed previously (EPA method 353.2). The ammonia method is based on the Berthelot reaction and the absorbance of the reaction product is measured at 630 nm (EPA method 350.1). No changes were made between the manifold for nitrate and the manifold for total nitrogen (discussed earlier). Calibration peak integration parameters for both nitrate and ammonia included first-order polynomials, direct chemistry integration, a weighting method of 1/x, and a linear calibration curve that was not forced through zero. Nitrate standards generally included 20.0, 8.0, 4.0, 1.0, 0.4, 0.2, and 0.0 while ammonia typically used 2.00, 0.80, 0.20, 0.10, 0.04, 0.02, and 0.00 mg N/L. Mixed quality control check standards (OCSPEX-Nut, SPEX CertiPrep, Inc., Metuchen, NJ) were purchased for both nitrate + nitrite-N and ammonia-N and diluted to manufacture s specifications. Recovery of standards within 90-110% of the expected value was acceptable.

#### Dissolved Carbon and Alkalinity

#### Dissolved Carbon

Samples were analyzed for both dissolved organic and inorganic carbon (operationally defined as dissolved by filtering through a 0.45 m filter). On a select group of samples, alkalinity was measured to validate the relationship between dissolved inorganic carbon (DIC) and alkalinity. Samples were collected, filtered, and stored at 4<sub>i</sub>C until analysis.

Dissolved organic carbon (DOC) was measured directly using a Dohrman Phoenix 8000 UV persulfate carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH). Inorganic carbon is first removed by acidification and sparging. The remaining dissolved organic carbon is measured by oxidation to  $CO_2$ . The Phoenix 8000 simultaneously uses persulfate oxidation with UV irradiation to oxidize the sample. The  $CO_2$  produced is carried to a nondispersive infrared detector (NDIR) by a high purity nitrogen gas stream (99.998%). The detector is sensitive to the absorption frequency of carbon dioxide and provides a signal proportional to the concentration of  $CO_2$  in the carrier gas flowing through it. The instrument plots an output signal in real time and then computes total DOC concentration.

Dissolved organic carbon calibration standards are made from a dilution of 1,000 mg C/L working standard. The 1,000 mg C/L working standard is diluted from a 10,000 mg C/L stock solution which has been prepared by drying 2.126 g KHP ( $C_8H_5KO_4$ ) overnight at 105;C and diluting to 100 mL with DI water. Calibration standards of 1.00, 5.00, and 10.00 mg C/L were used.

Dissolved inorganic carbon (DIC) was also measured directly using a Dohrmann Phoenix 8000 carbon analyzer. Inorganic carbon includes carbonate, bicarbonate, and dissolved carbon dioxide. The liquid samples are acidified with phosphoric acid and then sparged with a stream of nitrogen gas. The acidification converts carbonate and bicarbonate to carbon dioxide, which is then removed along with dissolved  $CO_2$  by the high purity nitrogen carrier gas and measured by the NDIR detector to give a DIC value. Dissolved inorganic carbon calibration stock standards are made by drying anhydrous Na<sub>2</sub>CO<sub>3</sub> in an oven at 105<sub>1</sub>C overnight and subsequently diluting 0.883 g with DI water in 100 mL yielding 1,000 mg C/L. Working calibration standards of 20.0, 50.0, and 100.0 mg C/L were diluted from the stock standard. For both DOC and DIC analysis, an instrument calibration verification was performed prior to each run with an allowable 95—105% recovery.

The Phoenix 8000 carbon analyzer calibrates the mass of carbon (g C) versus NDIR detector raw counts of response (volt x sec x  $10^6$ ). The NDIR detector, does not detect concentration but rather mass of carbon (g C). The NDIR detector is rated for 0-100 g carbon and uses a linearized NDIR signal. The formula that describes this relation between the mass of carbon versus the raw counts of response is:

$$y = mx + b \tag{8}$$

where:

y = raw counts (volt x sec x  $10^6$ ) x = mass of carbon (g C) m = response factor (volt x sec x  $10^6/$  g C) b = y — intercept (volt x sec x  $10^6$ )

It is not valid to assume that a 0 mg C/L standard would yield 0 raw counts (in such a case y = mx), because carbon can be picked up from the standard preparation water, the reagents used, and the carbon introduced as the sample travels through the system. This can be significant compared to the carbon in the standard. Since these sources of carbon are constant for each standard, they are represented by the y-intercept only and do not affect the slope or response factor for the NDIR. This calibration equation is very accurate for standards, but fails to describe the correct response for most samples because samples do not contain the same water used to prepare the standards. The slope, or response factor m, from the calibration curve remains the same but the yintercept is lower by the raw counts of the preparation water used in the standards. To measure for the reagent and system carbon contribution, injection volume is taken into consideration and a blank is analyzed. The first blank replicate takes the reagent used in the method, plus rinsing water to mimic the sample. Since the rinsing water itself contains carbon, the first result will be inaccurate. When this reaction is done, however, the liquid in the UV reactor becomes carbon-free. The following replicates use the carbon-free water to mimic the sample adding only new reagents to each analysis. In this way, the Phoenix 8000 can give an accurate response for blanks.

#### Alkalinity

On select group of samples, alkalinity was determined and compared to dissolved inorganic carbon analysis obtained from the Phoenix 8000 carbon analyzer. A digital hand held titrator (model 16900, Hach, Inc., Loveland, Co.) was used to determine total alkalinity as CaCO<sub>3</sub>. Prior to analysis, samples were warmed to room temperature and volume was measured into a 250-mL beaker. A clean delivery tube was inserted into the  $1.600 \pm 0.005 N H_2SO_4$  titration cartridge, the titrant displaced, and the digital counter set to zero. A magnetic stirring bar was placed into the beaker containing the sample and set on a stirring plate. A pH probe (Accument model 25, Fisher Scientific) was lowered into the solution and pH recorded. Titrant was delivered slowly into the sample until a pH of close to five was achieved (titrant delivered was recorded in conjunction with pH). From pH 5 to pH 4, one digital increment of titrant was delivered at a time while recording pH at each increment. The largest pH change per digital increment indicates the endpoint of the titration. Total alkalinity was determined by the following equation:

Alkalinity as CaCO<sub>3</sub> = 
$$\frac{B \times F_3}{mL \text{ sample}} xCF$$
 (9)

where

- B = digital increments of titrant added to reach the endpoint,
- $F_3 = 100$ , a constant to account for sample volume differences from the typical 100 mL
- CF = correction factor to account for normality of titrant (CF = 1 for 1.600 N titrant, CF = 0.1 for 0.1600 N titrant)

#### Isotopes

A small number of samples were sent to the University of Minnesota (Department of Geology and Geophysics) for isotopic analysis ( $\delta^{18}O$ ,  $\delta D$ ) and analyzed on a Finnigan MAT delta E mass spectrometer.

#### Cations/Anions

A select group of samples were sent to the University of Minnesota Geochemistry Lab (Department of Geology and Geophysics) to be analyzed for cations on a Perkin Elmer Sciex Elan 5000 inductively coupled plasma mass spectrometer (ICP-MS). Cations measured included Al, Si, P, Sc, Fe, Mn, Sr, Rh, Ba, Ca, Mg, Na, and K. Anions were measured on an ion chromatograph and included F, Cl, NO<sub>2</sub>-N, Br, NO<sub>3</sub>-N, PO<sub>4</sub>-P, and SO<sub>4</sub>.

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