Watershed hydrology of Valley Creek and Browns Creek:
Trout streams influenced by agriculture and urbanization in eastern Washington County, Minnesota, 1998-99

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to the

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OTHER REPORTS

This TCQI project funded three separate reports, only the first of which is contained in this document:

1. **Watershed Hydrology of Valley Creek and Browns Creek** *(this document)*
2. **An Examination of the Relationship Between Watershed Structure and Water Quality in the Valley Creek and Browns Creek Watersheds**
3. **Atlas of Watershed Structure in the Browns Creek and Valley Creek Basins** *(available in both hard copy and as a searchable PDF document on CD-ROM)*

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Watershed hydrology of Valley Creek and Browns Creek:
Trout streams influenced by agriculture and urbanization in eastern Washington County, Minnesota, 1998-99

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ABSTRACT

Trout streams are sensitive to urbanization, which can alter the watershed hydrology by increasing runoff from impervious surfaces, thereby increasing summer water temperatures and inputs of sediment, nutrients, and other contaminants. Valley Creek is a healthy trout stream in southeastern Washington County that is facing potential urbanization in the coming decades. In contrast, Browns Creek has a less viable trout population and has already experienced significant urbanization in its lower watershed with imminent prospects of further development. The purpose of this report is to document the hydrologic characteristics of the two watersheds, thereby clarifying the critical impacts to explore in more detail for possible causal links between land use and hydrology. The scope of this report is limited to flow data from stations at the mouths of each watershed and to water-quality data collected from an array of 60 sampling points (stream, lake, and groundwater) within the two watersheds during 1998—99.

The principal findings of this report are that Browns Creek showed a demonstrable impact of urbanization on its hydrology, whereas Valley Creek was influenced by agriculture. Browns Creek stormflows had a double peak, the second of which was interpreted to be the result of runoff from local impervious surfaces; Valley Creek showed only one small peak per storm with virtually no contribution of overland runoff from either pervious or impervious surfaces. Per unit rainfall, Browns Creek produced twice the quickflow volume and 2.7 times the peak quickflow relative to Valley Creek. Browns Creek water had higher sodium and chloride concentrations than Valley Creek, a consequence of roadway and other urban runoff. In particular, South Branch Browns Creek received a nearly continuous input of urban-influenced water from Long Lake, which collected runoff from roadways, housing developments, and commercial parking lots and consequently warmed the South Branch in summer to temperatures not tolerated by trout.

Valley Creek was impacted from agriculture: the creek was dominated by discharge of groundwater contaminated with nitrate. Consequently, the annual output load of total nitrogen from Valley Creek (about 74,800 kg) was substantially greater than that from Browns Creek (about 11,500 kg). However, Browns Creek still had slightly larger annual output loads of suspended solids (185,000 kg) and total phosphorus (1,025 kg) than did Valley Creek (124,000 kg and 770 kg, respectively), despite Valley Creek having approximately twice the flow of Browns Creek. Compared to other metropolitan area streams, these loads from Browns Creek were not particularly high. Rather, Valley Creek had relatively low loads of suspended solids and phosphorus, especially for an

agricultural watershed, by virtue of having minimal overland runoff and a mostly forested riparian zone.

Because of the importance of groundwater discharge to these creeks, groundwater ages and flow paths were investigated with isotopic analyses of tritium (^{3}H), ^{18}O, and D (^{2}H). Tritium analyses indicated that young water (less than 50 years old) penetrated deeply into bedrock aquifers in the uppermost recharge areas of both watersheds. In the Valley Creek watershed, this young water extended all the way to the discharge area at the creek, whereas the deep groundwater near the mouth of Browns Creek was relatively older. Nonetheless, the creeks themselves and shallow groundwater under the creek beds were generally dominated by young water. Stable isotope analyses (^{18}O and D) indicated that most groundwater was meteoric, although recharge of evaporatively evolved water from lakes was mixed with meteoric water in nearly half of the groundwater samples. Still, most baseflows in both watersheds were dominated by essentially meteoric water, indicating that lakes were not an obvious, disproportionately large (relative to their areas) source of groundwater recharge. An exception was the baseflow of the South Branch Browns Creek, which was fed directly by outflow of evaporatively evolved water from Long Lake. Both creeks appeared to have a groundwater recharge area (groundwatershed) of about 60 km^2, perhaps larger for Valley Creek. Areal average recharge was about 24 cm yr^{-1} (or proportionately less over a larger area) in the Valley Creek groundwatershed, and about 13 cm yr^{-1} in the Browns Creek groundwatershed.

These results demonstrate that land use had significant and relatively fast impacts on stream hydrology, even for these groundwater-dominated streams where significant lags might have expected because of groundwater travel times. Most flow paths were apparently short and quick, especially those short-circuited by direct contributions from urban impervious surfaces. The longer groundwater flow paths in each watershed indicated that some impacts could linger for decades, but probably not centuries.

INTRODUCTION

Importance

Because water is an efficient vector of both dissolved and suspended constituents, and because both surface-water and groundwater flows in a watershed typically converge on streams as the ultimate point of discharge, the hydrology (quality and quantity) of stream water provides an integrated measure of nonpoint-source pollution and the overall environmental quality in a watershed. In addition to being highly valued resources in their own right, trout streams are particularly sensitive indicators of the cumulative impacts on the watershed because trout and their invertebrate food base depend on high water quality, dependable flows, equably cool temperatures, and clean stream-bed substrates. Monitoring such streams is therefore a critical component of understanding how different land uses such as urbanization and agriculture can impact not only the stream itself, but also by extension the downstream receiving waters.

Valley Creek, in southeastern Washington County near Afton, and Browns Creek, in east-central Washington County near Stillwater, are notable trout streams in the Minneapolis-St. Paul metropolitan area, and thus provide sensitive integrative measures of watershed quality in a region where, due to urbanization pressures, such measures are most needed. Valley Creek, variously called Valley Branch Creek (VBWD, 1995), Valley Branch (USGS, 1967), or previously Bolles Creek (Winchell, 1888), in southeastern Washington County near the historic village of Afton is generally regarded as the finest trout stream in the metropolitan area (Figure 1). All three species of stream trout (brown, rainbow, and native brook) reproduce successfully in the creek (Waters, 1983). The stream also harbors the American brook lamprey, a non-parasitic native species of special concern in Minnesota because of its rarity (VBWD, 1995). The watershed of Valley Creek has remained largely agricultural and rural-residential, with little urban component. There is virtually no fishing pressure on the creek, as nearly all adjoining lands are privately owned and public access is limited to a few bridge crossings.

In contrast, Browns Creek (Figure 2) has already experienced significant urbanization in its lower watershed and is facing further development pressure on land annexed by the city from the adjoining township. The trout population in Browns Creek is significantly smaller and less stable than that of Valley Creek and consists primarily of non-native brown trout sustained by stocking, although some in-stream reproduction has recently been demonstrated (J. Moeckel, Minnesota Department of Natural Resources [MDNR], personal communication, 2001). The stream receives significant fishing pressure on its lowest one-mile reach where the MDNR owns the adjoining land, but little above that point.

Only about 14 trout streams remain in the metropolitan area (MDNR, 1996), and so protecting the quality of Valley Creek and Browns Creek is a critical component of maintaining aquatic biodiversity in the metropolitan area. Moreover, both Valley Creek and Browns Creek are tributary to the St. Croix River, a designated National Scenic Riverway and one of the cleanest large river systems in the contiguous United States (Waters, 1977). Despite its perceived cleanliness, new evidence has shown that the St. Croix River is currently carrying two to three times the concentration of phosphorus it did prior to the time of settlement by European-Americans, and the base of the food chain has shifted from a dominance by benthic to planktonic algae (M. Edlund, St. Croix Watershed Research Station [SCWRS], personal communication, 2001). The cause of this eutrophication needs to be clarified, and maintaining or improving the quality of the St. Croix River requires protection of its tributary watersheds. In short, Valley Creek, Browns Creek, and the St. Croix River are highly-valued resources that add to the quality of life in the metropolitan area and deserve protection.

Background

Urbanization and agriculture can alter stream hydrology and aquatic habitats by increasing loads of nutrients and suspended sediment (Klein, 1979; Schueler, 1994; Booth and Jackson, 1997; Spahr and Wynn, 1997; Wahl and others, 1997; Wernick and others, 1998). Accompanying siltation degrades trout habitat by blanketing the gravelly streambed needed for spawning and for production of the macroinvertebrates that compose the trout food base (Richards and Host, 1994; Rabeni and Smale, 1995; Waters, 1995). In addition, urbanization tends to increase runoff from impervious surfaces to streams, thereby increasing summer water temperatures above cold-water range (about 10—20¡ C) required by trout (Hicks and others, 1991; Schueler, 1994; Kemp and Spotila, 1997). Several studies have indicated that degradation to aquatic habitats occurs when impervious cover due to urbanization reaches a threshold of about 10—15% of the watershed surface (Klein, 1979; Schueler, 1994; Booth and Jackson, 1997).

For Midwestern trout streams, strong groundwater discharge is essential for maintaining equable stream-water temperatures within the range required by trout. Groundwater discharge keeps streams cool enough in the summer to sustain juvenile and adult trout, and warm enough in the winter and spring to allow proper development of eggs deposited by fall-spawning trout. Nonetheless, groundwater flow is rarely studied comprehensively in trout stream studies, and little is known about how urbanization affects stream-groundwater interactions. Simmons and Reynolds (1982) demonstrated that stream baseflows decreased with urbanization, but there is question regarding the mechanism (Schueler, 1994). A reasonable hypothesis is that impervious urban surfaces reduce infiltration and therefore also lower groundwater recharge, water tables, and stream baseflows. However, further work needs to be done to corroborate the relationship and to determine if baseflows decrease because of reduced groundwater recharge and lower water tables, loss of diffuse inputs of water other than groundwater discharge to baseflow, reduction of the recharge area of the creek, or some combination of these causes. Other work has shown little resultant impact of urbanization on the rate of recharge (Yang and others, 1999), or possibly even an increase in recharge (Graniel and others, 1999).

However, urbanization can reduce baseflows of area streams by a more direct mechanism than reduced recharge: namely, groundwater withdrawals from public-supply and other well fields can capture water that would otherwise have sustained the baseflow of trout streams and other groundwater-dependent natural resources. Aquifers contain only a finite quantity of groundwater, and withdrawal of that groundwater without commensurate replenishment from increased recharge will necessarily reduce the amount water that eventually reaches area streams and wetlands. Quantification of the degree of baseflow reduction is difficult and requires sophisticated groundwater-flow models to estimate the cumulative effects of shifting groundwatersheds (capture zones) and aquifer interactions as the entire multi-aquifer system adjusts to the piezometric stress imposed by a new well field.

Purpose, Scope, and Principal Findings

The purpose of this project was to relate the hydrologic characteristics of the Valley Creek and Browns Creek watersheds to land use, primarily urbanization and agriculture. The purpose of this report, as part of the larger project, is to document the hydrologic characteristics of the two watersheds, thereby identifying the critical impacts to explore in more detail for possible causal links between land use and hydrology. Both physical (flow) and chemical aspects of watershed hydrology were investigated. The scope of this report is limited to flow data from stations at the mouths of each watershed and to water-quality data collected from an array of about 60 sampling points (stream, lake, and groundwater) within the two watersheds. At the time this report was compiled, the most reliable flow data came from just one year's data for each watershed: 1998 for Browns Creek, and 1999 for Valley Creek. The water-quality samples were collected primarily during 199899.

The principal findings of this report are that Browns Creek showed a demonstrable impact of urbanization on its hydrology, whereas Valley Creek was impacted by agriculture. Stormflow runoff from impervious surfaces created a higher, double peak and a greater volume in Browns Creek than in Valley Creek. The chemical content of Browns Creek water showed a stronger urban component with more chloride than Valley Creek. Output loads of suspended solids and phosphorus were also larger in Browns Creek, though similar to other metropolitan area streams. In contrast, Valley Creek was impacted by agriculture and dominated by discharge of groundwater contaminated with nitrate. Consequently, the annual output loading of total nitrogen (largely as nitrate) from Valley Creek was substantially greater (6.5 times) than that from Browns Creek. Analyses of tritium (^{3}H) indicated that most groundwater and stream water was relatively young (less than 50 years old) in both watersheds, except for a few wells in the Browns Creek watershed. Analyses of stable isotopes, ^{18}O and D (^{2}H), indicated that lakes were not a disproportionately large source of groundwater recharge, as both groundwater and baseflows were dominated by water of meteoric composition. These results demonstrate that land use has significant and relatively fast impacts on stream hydrology, even for these groundwater-dominated streams where significant lags might have been expected because of groundwater travel times.

SETTING

Valley Creek

Valley Creek has two main perennial branches, called here the North Branch (2.22 km long) and the South Branch (3.15 km), which combine to form a main stem (2.45 km) before entering the St. Croix River just north of the village of Afton in southern Washington County (Figure 1). From the headwaters of the South Branch the creek drops about 41 m to the St. Croix, for an average gradient of 0.74%; the gradient is about 1% in each of the two branches and about half that in the main stem. Median baseflow at the mouth was 0.43 cms (cubic meters per second), or 15.2 cfs (cubic feet per second) during 1973-93 (John Hansen, Barr Engineering, personal communication); it rose to 0.55 cms (19.4 cfs) during 1997-98, when precipitation was about 40% greater than the 1961-90 normal (Almendinger and others, 1999). The present surficial watershed is about 45 km^2 (square kilometers); about 20% of this area (the Fahlstrom Lakes drainage) is surficially closed and does not contribute directly to the channelized network. The groundwatershed of the creek, the area from which the creek captures groundwater, is on the order of 60—80 km^2 (Almendinger and Grubb, 1999), significantly larger than the surficial watershed. The creek lies in a bedrock valley cut deeply below the adjacent tablelands; the South Branch derives its baseflow exclusively from bedrock springs, whereas the North Branch originates as outflow from Lake Edith, a 30 ha (hectare) lake that is itself fed by spring-sourced wetlands. Overland runoff only occasionally flows in intermittent channels that spill over the lip of the tablelands into the bedrock valley of the creek, usually no more than one or two days per year during spring snowmelt or severe rainstorms.

The surficial geology of the watershed is dominated by highly permeable, flat to gently pitted Quaternary sandplain, although part of the southern watershed was unglaciated during Wisconsinan time. Aside from occasional interbedded sandy tills, over most of their area these outwash deposits directly overlie the Prairie du Chien and Jordan (PdC/J) formations, composed of highly permeable Ordovician dolostone (PdC) and Cambrian sandstone (J). Although the bottom of the PdC can be a leaky aquitard that can partially hydraulically separate the two aquifers, at the fractured edges of their subcrops near the head of Valley Creek they likely function as a single paired-aquifer unit. Both piezometric and chemical tracer data demonstrate that this paired-aquifer unit supplies most of the baseflow of Valley Creek (Almendinger and Grubb, 1999; Zapp and Almendinger, 2001). Groundwater originates as infiltration through the coarse outwash deposits mostly to the west and north of Valley Creek. Water from this surficial sand aquifer then passes relatively unhindered into the underlying PdC/J bedrock aquifers, whereupon it flows laterally to the east and discharges into the headwater springs and channel of Valley Creek.

Present land use in the watershed is largely agricultural and rural-residential, with several large tracts totaling almost 5 km^2 in the lower watershed set aside for preservation and educational purposes (Table 1). The riparian zone near the perennial reaches of Valley Creek is largely floodplain forest and shrubs that have revegetated the area during the past 30—40 years, although about 20 residential dwellings are within 100 m of the creek. The surficial watershed of Valley Creek is within boundaries of three local jurisdictions: 86% in the City of Afton (39 km^2), 13% in the City of Woodbury (5.7 km^2), and 1% in West Lakeland Township (0.3 km^2). A few scattered subdivisions exist with densities of one dwelling per one-half to five acres. The present total number of dwellings in the watershed is about 622. However, assuming existing agricultural and other lands become developed under present zoning regulations in Afton and Woodbury, this number would more than quadruple. Afton would absorb about 378 of these units, but most (about 1723) would be built in Woodbury, in the extreme western edge of the watershed (Pitt and Whited, 1999). The present impervious cover in the watershed has been estimated at about 4.6% (Table 1; D. Pitt and R. Bell, University of Minnesota, personal communication, 1999); if this increases commensurately with the increase in dwelling units, total watershed imperviousness could reach 20%.

Browns Creek

Browns Creek also has two main branches, here called the North Branch (5.69 km long) and the South Branch (2.09 km), which together join into a main stem (3.73 km) that enters the St. Croix River just north of the city of Stillwater in eastern Washington County (Figure 2). The North Branch arises from a headwater shrub-scrub wetland and is the dominant of the two branches; the South Branch originates as outflow from Long Lake, a 36-ha lake that receives urban runoff from large commercial parking lots and surrounding housing developments. Several storm sewers deliver urban runoff from the north end of Stillwater to the lower reach of the creek. From the headwater wetland that feeds the North Branch, the creek drops 76.2 m to its mouth, for an average gradient of 0.81%. However, most of the fall occurs in the lower 2 km with a gradient of 2.48% as the creek spills into its bedrock gorge leading to the St. Croix; the rest of the creek generally has a gradient below 0.5%. Baseflow at the mouth is about 0.28 cms (10 cfs), based on observations since 1997 (Mark Doneux, Washington County Soil and Water Conservation District [SWCD], personal communication, 1999). The surficial watershed is about 75 km^2; however, nearly half of this area (about 36 km^2, or 48%) includes surficially closed drainages that do not contribute directly to the creek. The groundwatershed has not been properly mapped in detail (see Groundwater Recharge section below), but may be inferred to be roughly 60 km^2 by assuming a baseflow of 0.28 cms and an annual recharge of 15 cm.

Most of the watershed is dominated by the Quaternary St. Croix moraine and the complex of ice-contact deposits and outwash that lie at the distal face of the moraine. The pocked surface has many closed drainages that encourage storage or infiltration, and limit direct runoff into the creek. However, residential development is creating pressure to engineer sewered outlets for these drainages, in order to stabilize lake levels and protect property values at the expense of increasing the area of watershed that contributes runoff directly to the creek. Part of the watershed is underlain by the Ordovician St. Peter sandstone, a highly permeable sandstone unit with an aquitard at its base. However, as at Valley Creek, most of the surficial Quaternary deposits overly the PdC/J aquifer. Because of the mix of till and outwash in the surficial deposits, the hydraulic connection between the Quaternary and bedrock units is likely to be locally variable. Conceptually, groundwater originates as infiltration in the moraine area to the west and north of Browns Creek, especially in patches of outwash and coarse ice-contact deposits. The upper reaches of the creek are likely fed by groundwater discharge from this surficial Quaternary aquifer. In contrast, lower reach of Browns Creek is presumably fed by water that originally infiltrated near the watershed boundary, migrated downward into the bedrock aquifer units, and moved laterally eastward toward the bedrock gorge of the creek. An ancient bedrock valley, now filled with glacial deposits, cuts across the lowermost reach of Browns Creek, just upstream of its mouth. Tripoli clay deposits have been described from the valley of Browns Creek (Winchell, 1888); if from this buried valley, they may limit groundwater discharge from this unit.

Land use in the subwatershed of the North Branch is presently largely rural-residential, with occasional hobby farms and little row-crop agriculture (Table 1). In contrast, the subwatershed of the South Branch has considerably more urban and medium- to high-density residential development, with an estimated 12% impervious area. Stillwater recently annexed 7.4 km^2 of the adjacent township in this subwatershed, 72% of which is designated for single family dwellings (City of Stillwater, 1997). The number of dwelling units is planned to increase from 203 to 1473, giving a gross density over the total annexation area of one unit per 1.25 acres. The City of Stillwater (1997) has estimated that imperviousness would rise to 13.7% (from its present level of 3.8%) in the annexation area as a result of development; i.e., about 0.73 km^2 of impervious surface would be added. If these values are consistent with land-use data presented in this report (Table 1), then the development of the annexation area would increase the total imperviousness from 12% to about 14.8% in the subwatershed of South Branch Browns Creek. Because of the potential adverse impact of urbanization on the trout habitat of Browns Creek proper, the City of Stillwater has plans to divert the South Branch through an alternative drainage (Lake McKusick), which would reduce urban influence on Browns Creek.

METHODS

Standard methods were used to collect data on the physical hydrology and water quality of the two study watersheds and are discussed in this section of the report. Specific methods of data analysis will be discussed in the appropriate sub-sections of the Results and Discussion.

Physical Hydrology

Streamflows were measured by either of two methods: the standard flow-meter method, or the dye-dilution method. The SCWRS used both methods, but especially the dye-dilution method, in determining the flows of Valley Creek, starting in 1997. Earlier measurements in Valley Creek were determined by Barr Engineering with the flow-meter method. Most of the flows in Browns Creek were determined with the flow-meter method by the MDNR, with auxiliary measurements by Emmons and Olivier Resources (EOR) and the SWCD. Ancillary measurements of flow in Browns Creek were determined by the SCWRS using either of the two methods.

Rating curves were established for flow at the mouths of both creeks. The SCWRS established a second-order log-log rating curve for the mouth of Valley Creek:

$$\log10(Q) = -4.021*[\log10(H)]^2 + 4.6192*\log10(H) + 0.9492$$

for log10 = base-10 logarithm, Q = discharge in cfs, and H = stage in feet relative to the established staff gauge affixed to the culvert wingwall. The MDNR established a fifth-order rating curve for the mouth of Browns Creek. Because this equation gave negative estimated flows for very low stages, the curve was re-plotted by the SCWRS and fit with a single-order log-log curve to better represent low-flow conditions:

$$\log10(Q) = 2.8957*\log10(H) + 0.862$$

(with the same symbols and units as above). Automatic data loggers were used to record hourly stages of the creeks with float or bubbler stage sensors. Stages were then converted to flows with the above rating curves. All flow data were converted to cms for data analysis presented in this report.

Local stream-groundwater interactions, defined here as advective flow through the stream bed, were investigated with piezometers pounded through the stream bed at five sites in Valley Creek (sites 1, 2, 3, 5, and 7; Figure 1) and six sites in Browns Creek (sites 1, 2, 3, 4, 5, and 6; Figure 2). Each piezometer consisted of 3.2-cm (1.25-in) diameter galvanized pipe with a 15-cm (6-in) stainless-steel 10-slot well-screen drive point. Each piezometer was driven so that the mid-point of the well screen was 1.5 m (5 ft) below the stream bed. Although groundwater equipotential and streamline configurations are likely complex and spatially variable near stream channels, in general, groundwater flow from more regional sources is more likely to enter the stream at mid-channel rather than near either stream bank, yet placing a piezometer in the middle of the stream channel might unacceptably obstruct debris. As a compromise, the piezometer at each site was placed about one-third of the way across the stream channel. Each piezometer was flushed and surged with a plunger to clear the well screen and establish hydraulic connection with the substrate, to the degree possible.

Precipitation was measured with automated tipping-bucket rain gauges and electronic data loggers at hourly intervals. In the Valley Creek watershed, the rain gauge was located 1 km to the northwest of the stream gauging station near the mouth. For the Browns Creek watershed, the nearest rain gauge was located outside the watershed on the property of the SCWRS, approximately 13 km to the north of the creek. The rain gauges were not heated and so likely underestimated winter precipitation amounts, although collected snow did melt periodically during the winter and was thus recorded at that time. From National Weather Service data, winter precipitation (Dec-Jan-Feb) typically accounts for only about 10% of the normal annual precipitation. Climatic normals (1961—90) for the area were based on data from the weather station at the Minneapolis-St. Paul international airport, about 35 km to the west of the St. Croix River.

Water Quality and Isotopes

The goals of the water-quality sampling were to characterize the water quality of each creek at selected points along its course corresponding to natural sub-basin divisions of the watershed, and to characterize the different possible source waters (groundwater, lake, intermittent runoff) that could contribute to the creek. The 60 sampling sites were categorized as either primary sites (sampled on about a bi-monthly or more frequent basis) or secondary sites (sampled once or twice, typically, during the course of the project) (Tables 2 and 3). The primary sites (three per watershed) were located at the mouths of the main segments of each creek, namely, the north branch, south branch, and main stem (Figures 1 and 2). All other stream sites, lake sites, groundwater sites, and intermittent runoff sites were considered secondary (or grab) sites. In the Valley Creek watershed, 40 sampling locations were chosen: 16 stream sites, 11 lake sites, and 13 groundwater sites (plus three groundwater sampling sites co-located at sites 1, 5, and 7). In the Browns Creek watershed, 20 sampling locations were chosen: six stream sites, eight lake sites, and six groundwater sites (plus six groundwater sampling sites co-located at sites 1—6). Stream sites included both perennial and intermittent-runoff sites; groundwater sites included in-stream piezometers, springs, and domestic wells (Figures 1 and 2; Tables 2 and 3). Outflows from Lake Edith and Long Lake were sampled more frequently than most secondary sites because these lakes are directly connected to the creek channels and deliver a significant portion of flow to North Branch Valley Creek and South Branch Browns Creek, respectively.

Most samples were collected manually, except for some storm samples from Valley Creek, which were collected with an automated sampler controlled by a stage-triggered data logger. When stream samples were collected by hand, an attempt was made to obtain a representative vertical profile; automated samplers had inlet hoses fixed at about mid-depth in the creek. Lakes outlets were sampled when possible; closed-basin lakes were sampled from the middle part of the lake, usually from about 30 cm below the lake surface. Most lakes were sampled twice, once in the summer and once in the winter, just below the ice surface. Groundwater from piezometers was sampled with a peristoltic pump after purging several well volumes. Groundwater from domestic wells was sampled from an outdoor tap after about 15 minutes of flow to purge the pressure tank. Typically, a 1-L sample was collected in the field, chilled, and processed (filtered and split into lab bottles for different analyses) within 24 hours of collection.

Selected subsets of samples were analyzed for different components. Nearly all samples (about 600) were analyzed for field variables (temperature, T; specific conductance, SC; dissolved oxygen, DO; and pH), nutrients (total phosphorus, TP; and total nitrogen, TN). All field variables were determined with a Yellow Springs Instruments (YSI) multi-parameter water-quality sonde calibrated daily. Most samples were also filtered through 0.45- low-extractable membrane filters to quantify the dissolved nutrient fractions (dissolved nitrogen, DN; dissolved phosphorus, DP; dissolved organic carbon, DOC; and dissolved inorganic carbon, DIC). A smaller subset was analyzed further to quantify the component nitrogen species (nitrate-nitrogen, NO_3-N; ammonium-nitrogen, NH_4-N; and organic nitrogen, N_{org}). Nutrient samples were frozen for preservation between sample processing and analysis. All nutrient analyses were performed with a Lachat autoanalyzer. Carbon was determined on a Dorhman Phoenix UV-persulfate carbon analyzer. Samples from the creeks and lakes were also analyzed gravimetrically for total suspended solids (TSS) and volatile suspended solids (VSS) by filtration through 1- pre-ashed glass-fiber filters and weighing the filter after 24 hours at 105¡C and after 1 hour at 550¡C, respectively.

Smaller subsets of filtered samples were analyzed for major ions (160 samples) and trace metals (24 samples). Samples for cation and trace-metal analysis were preserved by acidification to below pH 2 with high-purity concentrated nitric acid. Samples for anion analysis were stored in amber bottles and refrigerated for preservation. All major ion analyses were performed at the University of Minnesota geochemical laboratory in the Department of Geology. Cations and trace metals were determined by ICP-MS analysis, and anions by ion chromatography.

Isotope analyses helped determine sources and ages of source water contributing to the creeks. The content of the stable isotopes oxygen-18 (^{18}O) and deuterium (^{2}H, or D) was determined on 137 samples. Samples were gravity filtered through 1- glass-fiber filters into 20-ml glass vials with conical-seal caps to preclude head space and reduce the chance of post-collection evaporative fractionation. Analyses took place at the University of Minnesota stable isotope laboratory in the Department of Geology on a Finnigan mass spectrometer. The average difference between lab replicates was 0.08

for $\delta^{18}O$ (n = 26) and 1.12 for $\delta^{2}H$ (n = 36). If this difference can be treated as a range for a typical pair of analyses (n = 2), then the standard deviation for each analysis would be 0.07 for $\delta^{18}O$ and 0.99 for $\delta^{2}H$ (Snedecor and Cochran, 1967). Tritium was analyzed on 24 samples to categorize the age of groundwater and to compare the tritium content of groundwater to that of streamwater. Scintillation analyses took place at the University of Waterloo, as arranged through the Department of Geology, University of Minnesota.

A few samples (12) were screened for common pesticides by the Minnesota Department of Agriculture. Analyses were performed on a GC-MS.

Field duplicates and blanks were collected throughout the course of the sampling. Field duplicates differed by less than 3% for carbon and nitrogen species. On a percentage basis, duplicates differed more for suspended solids (TSS 13%, VSS 17%) and phosphorus (TP 12%, DP 11%) because of the typically low values of these variables during baseflow. Analyses for cations and anions were checked for charge balance errors, which averaged 3.8% for stream, lake, and shallow groundwater samples. In contrast, deep groundwater samples had an average charge balance error of 10.4%. This relatively large error was most likely caused by degassing of CO_2 after sampling, which reduces the apparent carbonate content when analyzed as DIC in the laboratory. Field and lab blanks did not indicate significant contamination of any constituent, except perhaps DOC. Deionized water stored more than a few days in plastic bottles could acquire 0.3-0.5 mg/L DOC, and samples collected by automatic samplers tended to have higher DOC than grab samples taken manually at the same time. DOC data from these samples were excluded from the data base. Increasing the number of pre-sampling intake rinses by the automatic samplers should help minimize this effect, but more investigation needs to be done.

RESULTS AND DISCUSSION

Runoff Analysis

Runoff analysis, as defined in this report, included three steps of increasing complexity: *basic hydrograph analysis*, in which the timing and shape of the storm peak in response to a precipitation event are analyzed; *hydrograph separation*, in which the streamflow is separated into components from presumably different sources and summed for the year; and *unit hydrograph analysis*, in which hydrographs from selected storms are first separated and then normalized by rainfall amount over an effective contributing area. Data from 1998 were used for Browns Creek, and from 1999 for Valley Creek, because these were the most complete data sets for discharge available at the time.

Basic Hydrograph Analysis

Basic hydrograph analysis entails determining the shape a typical hydrograph resulting from selected storms. Streams do not respond identically to every storm event because storms differ greatly in their duration and intensity, and because antecedent conditions differ. Each storm also varies greatly in spatial distribution of rainfall amounts; because only one rain gauge was available per watershed, this variability was unable to be addressed. In any event, storms and responding stormflows must be selected carefully to remove as many of the variables as possible. In this report, only storms with greater than 10 mm total rainfall, with gaps no longer than one hour between measurable rainfall amounts, were deemed significant. Of these storms, only those where more than 80% of the total rainfall occurred within a 1-hr period (i.e., those with a clear peak in precipitation) were chosen for analysis. Some storms that fit these criteria were likely excluded inadvertently from analysis simply because the peak rainfall occurred near an even hour: part of the total rainfall would be recorded in first hour, and the rest in the following hour.

For Valley Creek in 1999, 22 storms had greater than 10 mm total rainfall, but only three of these had an hourly rainfall peak exceeding 80% of the total rainfall. These three storms lasted from 1—4 hr each, averaged 21.3 mm in total amount, with 88% of this falling within a 1-hr period. The hydrograph from each of these events showed a well-defined single peak in discharge that lagged the precipitation peak by 1.5 hours (e.g., Figure 3a). (The precipitation peak was defined as the mid-point of the hour during which the most rainfall accumulated.)

In contrast, Browns Creek typically showed a double peak in discharge in response to selected storms in 1998 (e.g., Figure 3b). There were six storms in 1998 that exceeded 10 mm and had more that 80% of that total falling in one hour. These storms lasted 2—3 hours and averaged 20 mm in total amount, with 91% falling within a 1-hr period. On average, the first peak in discharge lagged the peak in precipitation by 1.5 hr, just as at Valley Creek. Thus despite the differences in the land cover between the two watersheds, the primary peak in flow may derive from similar mechanisms that translate precipitation into streamflow. However, the secondary peak in stormflows at Browns Creek had no counterpart at Valley Creek and thus appeared to derive from a separate mechanism of runoff generation. A reasonable hypothesis is that this second storm peak, which lagged the peak in precipitation by an average of 6.25 hr, resulted from the delivery of urban runoff into Browns Creek.

Hydrograph Separation

Hydrograph separation is an art wherein the area under a discharge hydrograph is graphically separated into different components based purely on the shape of the hydrograph. Even "automated" methods of hydrograph separation require parameterization to produce results that conform to good judgement based on experience. The analysis is based on the reasonable hypothesis that different sources of water to the stream   overland runoff, subsurface hillslope flow, groundwater, and so forth deliver their water at different characteristic rates to the stream. Hence, breaks in slope of the hydrograph during a runoff event may represent times when these different sources begin and end their contributions to the stream. Unfortunately, obtaining the field evidence to confirm the proportions of potential source waters contributing to stormflows inferred from hydrograph separation has proved difficult in detail (e.g., see Rice and Hornberger, 1998).

In this report, while hydrograph separations were done with accepted manual or automated methods, the components of flow so determined were defined strictly on the basis of their graphical origin. Hypotheses regarding the actual sources of these components will be put forth, but it is important for the reader to recognize foremost the empirical nature of the definitions. *Baseflow* is defined as the flow that occurs under that part of the hydrograph with very low slopes, and is presumed to continue at similar rates to those before, and after, a storm peak. *Intermediate flow* is defined to be that flow above baseflow that begins at the time of peak flow and rises to a maximum at the break in slope of the hydrograph marking the end of the steep decline from the peak. *Quickflow* is defined to be that flow above baseflow plus intermediate flow that begins at the start of a steep rise in the hydrograph and ends where the steep decline from the peak breaks to a lesser slope, i.e., at the peak of intermediate flow as defined here. In general, determining this point the end of quickflow was rather subjective. An obvious break in slope may not be present, or there may be more than one.

Figure 3 gives examples of manual hydrograph separations for two selected stormflows in Valley Creek and Browns Creek. The separation for Browns Creek was fairly straightforward. For Valley Creek, there were two breaks in slope that could mark the end of quickflow: an obvious break at about hour 9, and a less obvious break at hour 23. Examination of other storm peaks and comparison with automated hydrograph separation methods indicated that choosing the second point was justified, although either choice resulted in similar conclusions. In fact, these two breaks indicate that quickflow itself could be decomposed into two separate components, an "early" and "late" quickflow, but the quantities seem too small here for their differentiation to be justified. Comparison of the two hydrographs indicates that baseflow was a larger component of total flow in Valley Creek than in Browns Creek, and that intermediate flow appeared to be a larger component in Browns Creek than in Valley Creek. However, more than two storms need to be examined to reach any defensible conclusion.

Manual hydrograph separation is useful for inferring details from individual storms but is too time-consuming for analysis of annual flows. Automated methods of hydrograph separation can be adjusted to capture the essence of manually separated hydrographs and applied uniformly to large data sets. The method used by the program HYSEP (Sloto and Crouse, 1996) is based on defining baseflow on a given day as the minimum flow that occurred during the previous *n* days, *n* being selected either based on judgement or on watershed dimensions. That is, baseflow is calculated as a daily running minimum discharge of a sliding window of the previous *n* days. Provided the selected window is wider than the storm peaks, this method effectively "cuts off" storm peaks from lower flows and separates the annual flows into baseflow and stormflow (or quickflow, as termed in this report). Unfortunately, this program is not optimal for use with small streams such as Valley Creek and Browns Creek, for two reasons. First, the daily time step is much too coarse for these streams, with storm peaks that respond quickly and last a matter of hours. The hydrograph separations produced by this method simply cannot mesh with the natural breaks in slope evident on the hourly hydrograph. Second, the program only separates flow into baseflow and quickflow; other components of flow are lumped into one of these two categories. The intermediate flow component, evident on the manually separated hydrograph, would mostly be lumped with the quickflow component by this program.

Consequently, the running-minimum method of Sloto and Crouse (1996) was modified to use an hourly time step and to allow more than two components to be separated. Implementation of this modified method was trivial with spreadsheet calculations. Figures 4a and 5a show examples of this automated method of hydrograph separation in detail for the same two storm hydrographs separated manually in Figure 3. Baseflow was calculated as the hourly running minimum of the previous 7-day window of total discharge (dotted line). Intermediate flow plus baseflow was calculated at the hourly running minimum of the previous 12-hr window of total discharge (dashed line). Intermediate flow was then calculated as the difference between the dashed and dotted lines. Quickflow was finally determined as the difference between total discharge (solid line) and baseflow plus intermediate flow (dashed line). The 7-day and 12-hr time windows were chosen to reproduce the features of the manually separated hydrographs to a reasonable degree for both watersheds.

For Valley Creek in 1999, the total annual volume of flow was 15.8 x 10^6 m^3, amounting to about 35 cm of runoff over the 45 km^2 surficial watershed (Figure 4b). The long-term average runoff for this area is only about 15 cm (Gunard, 1985), implying that Valley Creek discharges more water than is accountable from its surficial watershed alone. As noted in the background section, this large runoff depth is likely due to a groundwatershed that extends beyond boundary of the surficial watershed. It was not due to excessive precipitation that year, which totaled 676 mm in the watershed, about 6% less than the 1961—90 normal amount (719 mm). Of this total annual volume of runoff, fully 92% was baseflow, as separated by the automated method described above. Intermediate flow accounted for 5% of the annual runoff volume, and quickflow for only 3%. Of this quickflow, 11% occurred on the single-day snowmelt event of 17 March.

For Browns Creek in 1998, streamflow data were available for only 87% of the year; annualized values were obtained by presuming this period was representative of the missing part of the year (Figure 5b). Total annual runoff volume was 9.3 x 10^6 m^3, suggesting a runoff depth of about 24 cm over the 39 km^2 of the surficially contributing watershed, substantially greater than the expected 15 cm of runoff. As at Valley Creek, Browns Creek also evidently receives water from an area beyond its directly contributing surficial watershed. If the annual runoff volume is distributed over the entire 75 km^2 of the watershed district (39 km^2 directly contributing, and 36 km^2 surficially closed), then the runoff depth would be 12 cm, much closer to the expected value. Precipitation in 1998 totaled 736 mm at the nearest hourly recording station, about 2% above normal. Of the total annualized runoff volume, 87% was baseflow, 9% was intermediate flow, and only 4% was quickflow. As indicated by the example hydrographs (Figure 3), baseflow was lower and intermediate flow higher for Browns Creek than for Valley Creek. Somewhat surprisingly, the percentage of quickflow was similar in the two watersheds, despite the influence of urban runoff on Browns Creek. Aside from causing the double-peaked storm hydrograph, urban runoff appeared most influential in increasing the percentage of intermediate flow, at least for the precipitation patterns that occurred in 1998-99.

Unit Hydrograph Analysis

Unit hydrograph analysis is a technique to normalize the storm response of watersheds by the amount of precipitation. For example, a unit hydrograph could predict the timing and volume of runoff (as centimeters over a selected area) per centimeter of rain received in one hour. Originally developed by Sherman (1932), the unit hydrograph is the unit pulse response function of a linear hydrological system (Chow and others, 1988, p. 213). Unit hydrographs are constructed empirically by carefully selecting typic storms, separating the amount of quickflow, and adjusting the height of the quickflow hydrograph ordinates so that the total area under the curve equals the volume due to a unit rainfall (1 cm per hour in this case) over a selected area of the watershed. In this report, the same procedure was followed to construct unit hydrographs for the intermediate flow component as well. An important utility of unit hydrograph analysis is that the storm response of different watersheds may be compared, having removed rainfall amount and intensity as variables.

In typical unit hydrograph construction, the runoff volume is calculated as a depth (cm) over the entire surficial watershed area, as though the entire watershed were contributing overland runoff to the storm peak. However, because of the rapid timing and relatively small volumes of quickflow in both Valley Creek and Browns Creek, and because the permeable soils of both watersheds usually preclude overland runoff, most of the runoff reaching the creeks must arise from near-channel sources over a much smaller area of the watershed. Also in "standard" unit hydrograph construction, the precipitation must be partitioned into "effective precipitation," which is that amount of precipitation available for overland runoff, after an initial amount is subtracted for interception by vegetation and after the measured rainfall rate is reduced by the infiltration capacity of the watershed soils. Again, this calculation assumes that the upland soils of the watershed actually contribute overland runoff to the stream. If this conceptual model is correct, then a representative infiltration capacity of the watershed may be obtained by trial and error, reducing each hourly rainfall measurement (to no less than zero) by the trial infiltration capacity to obtain an hourly effective precipitation, summing the total annual volume over the area of the watershed, and adjusting the trial infiltration capacity such that the total volume of effective precipitation equals the total quickflow volume calculated by separation of the annual hydrograph. When this exercise was carried out for Valley Creek, a watershed-wide infiltration capacity of only 19.6 mm hr^{-1} was obtained, and only three values of hourly rainfall exceeded this amount. Clearly, the infiltration capacity of the sandy soils in the Valley Creek watershed typically exceed 19.6 mm hr^{-1}; there were far more than three runoff events during 1999; and most of the watershed by far did not contribute overland runoff to the creek. Consequently, a different conceptual model had to be developed.

For Valley Creek and Browns Creek, the assumption was made that quickflow arose in or very near the channel from an "effective contributing" area that was considered impervious. This assumption allowed all rainfall to be considered effective, without the need to subtract portions for interception or infiltration. The water surfaces in the creek channels themselves fit this assumption exactly, as do in-channel lakes and fully saturated wetlands. The effective contributing area may be calculated for each storm by dividing the quickflow volume for that storm by the rainfall amount (depth) that generated it, and then this area should be checked to see whether or not this conceptual model is sensible. For the events of 18 August and 11 September, the two typic events chosen for unit hydrograph construction in the Valley Creek watershed, the effective contributing area to quickflow averaged 0.24 km^2; four other events examined had effective contributing areas ranging from 0.20 to 0.27 km^2. This area is roughly equivalent to the area of the creek itself plus a buffer of about 15 m on either side (7.82

km long by 30 m wide). This seemed reasonable, especially as the area of Lake Edith (about 0.3 km^2) was not included even though it must contribute. In other words, essentially all of the quickflow in Valley Creek from these storms came from rain that fell either on the creek itself, on Lake Edith, or very close to the channel.

Consequently, unit hydrographs were constructed for both Valley Creek and Browns Creek under the assumption that quickflow was generated from an effectively impervious near-channel contributing area (Figures 6a and 7a). Hydrographs from typic storms (two per watershed) were separated manually to obtain quickflow and intermediate flow volumes for each storm, rather than relying on the automated running-minimum method. The area under each quickflow hydrograph totals 1 cm of runoff; these unit hydrographs, then, show the timing of how each centimeter of rainfall becomes a centimeter of runoff in each watershed. In other words, the hydrographs are normalized for both the amount of rainfall and the effective contributing area and the resulting shape of the hydrograph should be a function of the rainfall-runoff response of the land cover specific to that watershed, which should be different for urban versus agricultural landscapes.

The quickflow unit hydrograph for Valley Creek (Figure 6a) had a duration of about 21 hours and a peak flow of about 0.18 cm hr^{-1} runoff generated per centimeter of hourly rainfall over an effective area of 0.24 km^2. This peak rate, when multiplied by the contributing area, translated into a flow rate of 0.12 cms (m^3 s^{-1}) quickflow for each centimeter of hourly rainfall. In comparison, the quickflow unit hydrograph for Browns Creek (Figure 7a) had shorter duration of about 13 hours and a higher peak of about 0.24 cm hr^{-1} runoff per centimeter of hourly rainfall over a larger effective area of 0.49 km^2. This peak rate, when multiplied by the effective area, produced 0.33 cms of quickflow per centimeter of rain. Thus, per unit rainfall and per unit land area, Browns Creek produced about a 35% larger peak flow (0.24 versus 0.18 cm hr^{-1}). When its larger effective contributing area was factored in, Browns Creek produced over twice the quickflow volume and a 2.75 times larger peak flow per centimeter of rainfall relative to those of Valley Creek. Urban impervious surfaces in the Browns Creek watershed may be the source of both the sharper peak as well as the larger effective contributing area. For both watersheds, the effective contributing area of quickflow was a tiny part, about 1%, of the directly contributing watershed area.

Unit hydrographs were also constructed for the intermediate flow component under the same assumption of an effective near-channel source (Figures 6b and 7b). However, because the intermediate flow component lingered for days after the rainfall event, not all of the rain that fell originally would be available for runoff because of losses to evapotranspiration. Consequently, the available rainfall depth was reduced hourly by an amount equal to the potential evapotranspiration (PET) rate, calculated simply from the monthly Thornthwaite PET. Certainly more sophisticated methods of calculating evapotranspiration could be employed if the meteorological data were available, but the main purpose here was to place bounds on the main variables to check the reasonableness of the assumption regarding the size and proximity of the effective contributing area. The unit hydrograph was constructed by starting at zero flow at the time of peak quickflow, and rising linearly to a peak at the time quickflow ended. Rather than have hourly ordinates for the duration of intermediate flow contributions, which could extend over 100 hours, a negative exponential curve was fit by eye to the hydrograph recession (Figures 6b and7b). For Valley Creek, the equation for this curve was $0.0123*e^{-0.025t}$, and for Browns Creek $0.0176*e^{-0.045t}$, for t in hours after the peak in intermediate flow (peak flow is the constant factor in each equation). As with the quickflow unit hydrographs, these intermediate flow unit hydrographs represent the flow (cm hr^{-1} over the effective contributing area) resulting from a 1 cm hr^{-1} rainfall pulse. However, in contrast to the quickflow unit hydrograph, the area under the curve is less than 1 cm of runoff because of evapotranspirative losses. The results were quite variable from storm to storm, not only because of the difficulty in objectively identifying the end of intermediate flow during hydrograph separation, but also because intermediate flow was influenced by antecedent conditions and evapotranspiration. In contrast, the quickflow unit hydrographs were more consistent because of the less variable antecedent conditions of impervious surfaces and the insignificant amount of evapotranspiration during the short period of flow.

For Valley Creek (Figure 6b), intermediate flow peaked at an average of about 0.0123 cm hr^{-1} of runoff per centimeter of hourly rainfall over an effective contributing area of ranging from 0.4 to 1.0 km^2, or about 1 to 3% of the directly contributing watershed (Figure 6b). When multiplied by the contributing area, the peak intermediate flow rate translated into a flow of about 0.02 cms, a sixth of that attributable to quickflow. The calculated contributing areas seemed reasonable, as they were the equivalent of the creek length buffered by roughly 25—65 m on both sides, which approximately corresponds to much of the valley floor of the Valley Creek gorge. The intermediate flow unit hydrograph for Browns Creek (Figure 7b) peaked somewhat higher at an average of 0.0176 cm of runoff per centimeter of hourly rainfall. The effective contributing areas ranged from about 2 to 4.6 km^2 (5—12% of the directly contributing watershed), several times larger than those of Valley Creek. From the effective contributing areas, the peak in intermediate flows resulted in 0.10 to 0.15 cms being delivered to the creek, about 30—45% of the quickflow peak. As with Valley Creek, the effective contributing area for Browns Creek intermediate flow approximated the valley floor areas, about 85—200 m on both sides of the creek over its length.

These hydrograph separations and analyses suggest a conceptual model of how storm water moved through the Valley Creek and Browns Creek watersheds. In Valley Creek, the relatively small quickflow component arose from rainfall on the channel itself and on in-channel wetlands and lakes, including Lake Edith. Some near-channel overland runoff was probably generated by the bedrock walls of the gorge and from roadway runoff. The intermediate flow component came from rain falling on, or delivered to, the valley floor as well as to Lake Edith. The alluvial aquifer and associated riparian wetlands stored the water, gradually releasing it to the creek (and losing some to evapotranspiration) over the days following the storm. Browns Creek was very similar to Valley Creek in that the quickflow component also appeared to derive from rain falling on or near the channel, with the addition of a second peak (or shoulder) of flow that may have come from the input of urban runoff, farther removed from the channel. Likewise similar to Valley Creek, the intermediate flow component may have come from rain delivered to the riparian zone, including Long Lake on the south branch and extensive wetlands along the north branch. However, the intermediate flow component of Browns Creek was much larger than that of Valley Creek, perhaps because of the delivery of urban runoff to Long Lake, which then gradually released water to the creek. Overland runoff from most of the watershed uplands did not appear to be a significant component of stormflow in either watershed, except for unusually intense storms not encountered during this study. Baseflow in both watersheds was due not only to groundwater discharge but also to outflow from the in-channel lakes and wetlands. Hence baseflow could have a significant non-groundwater component in some cases, for example in South Branch Browns Creek, which receives some urban runoff nearly continuously via the outlet of Long Lake.

Surface-Water/Groundwater Interactions

Because these two trout streams are so dominated by baseflow composed largely of groundwater discharge, understanding stream/groundwater interactions is fundamental for optimal management. Although in detail such interactions can be extremely complex, basic knowledge of where groundwater discharge occurs in the streams and some inference about the source and travel time of that groundwater can help guide policy decisions.

Groundwater Discharge

Pattern of Groundwater Discharge

Assuming the baseflow of a stream derives primarily from groundwater discharge, streamflow measurements made incrementally along a stream can quantify the cumulative groundwater discharge (or recharge) in the stream channel between measuring points. To provide more detail, small piezometers (small diameter wells with short screens) may be driven below the stream bed to check the direction of seepage at that point. If the water level in the piezometer is greater than the stream level, groundwater is seeping into the stream channel. If the piezometer water level is below that of the stream, then stream water is leaking out of the channel into the ground. Water-level differences were typically about 3 to 10 cm; differences smaller than about 1 cm indicated little or indeterminate interactions (assuming silty or finer-grained alluvial deposits).

For Valley Creek, where hourly flows were calculated from stage data recorded by automated monitoring stations, median flows were used to represent baseflows for the three primary sites during 1999 (Figures 1 and 8). The baseflow near the mouth at site 5 was 0.486 cms (17.2 cfs), which represents the typical (median) total rate of groundwater discharge into Valley Creek. Of this baseflow, about 50% came from groundwater discharge into the South Branch (0.245 cms, or 8.6 cfs), about 40% came from groundwater discharge into the sources of the North Branch (0.190 cms, or 6.7 cfs), and about 10% (0.051 cms, or 1.8 cfs) came from groundwater discharge along the main stem, below the confluence of the two branches. The dominance of the South Branch in providing groundwater discharge to Valley Creek is not surprising, given the evident springs and the positive piezometer readings in its headwaters area (Figure 8). In fact, if the single flow measurement from late spring 1999 is representative of baseflow just below the headwaters area (0.230 cms), then the headwaters area contributed 94% of the flow in the South Branch (and 47% of the total baseflow of Valley Creek at its mouth).

In contrast, piezometer readings in the channel of the North Branch were negative, implying a loss of stream water to the aquifer at these points. In fact, the piezometer at site 2 was dry, indicating that the channel is perched (overlying unsaturated sediments) at that point. Nonetheless, the baseflow of the North Branch demonstrates that groundwater discharge must be supplying water to the sources of the North Branch, namely Metcalf Marsh and (possibly) Lake Edith. The negative piezometer reading near the mouth, at site 5, was very small, indicating little seepage at that point

For Browns Creek, incremental streamflow measurements were taken over a few days under baseflow conditions in July 1998 (Figure 9). (Median values of hourly flows, as used for Valley Creek to determine baseflow, could not be used for Browns Creek because such data were available only for the mouth.) During those days, the baseflow at the mouth was about 0.320 cms (11.3 cfs), of which 39% (0.124 cms, or 4.4 cfs) came from the North Branch, 27% (0.085 cms, or 3.0 cfs) came from the South Branch, and 34% (0.111 cms, or 3.9 cfs) came from the main stem, below the confluence of the two branches. For the North Branch, only 28% of the flow originated from the headwaters wetland, and another 40% was added by the next wetland downstream. Flowing piezometers at the upgradient boundary of the headwaters wetland demonstrated the strong groundwater discharge at that point; the slightly negative piezometer level below the headwaters wetland was apparently insignificant or anomalous. Strongly positive piezometer levels (over 20 cm higher than stream level) near the confluence with the main stem indicated significant groundwater discharge there as well. Hence groundwater discharge appeared to occur along most of the channel of the North Branch, rather than being concentrated in the headwaters as at Valley Creek. For the South Branch Browns Creek, small negative piezometer readings below Long Lake indicated some groundwater recharge (leakage of lake and stream water into the streambed) at that point; in contrast, strongly positive piezometer readings near the confluence with the main stem indicated significant ground water discharge there. Despite the groundwater input near the confluence, much of the baseflow in the South Branch appeared to derive as outflow from Long Lake. While Long Lake itself may have received groundwater discharge along its upgradient margin, it also received significant urban runoff from nearby developed areas, and hence its outlet baseflow was composed of a mixture of waters, much of which was never derived from groundwater.

The lowermost 2-km reach of Browns Creek falls steeply through a bedrock gorge to its confluence with the St. Croix River. This reach is important to management agencies, because it is where some of the best trout habitat has been identified and where there is public access for fishing. Groundwater discharge over this reach has been critical for maintaining the stream temperature within the range favored by trout. Because of its critical role, we examined the pattern of groundwater discharge in detail throughout this reach by performing a day-long drip of rhodamine dye to obtain a series of incremental baseflow measurements by dye dilution at 27 points approximately 75 meters apart between sites 2 and 1 (Figures 9 and 10). The negative piezometer level at site 2, just above where the creek spills down into the gorge, was expected, as regional piezometric surfaces tend to dip at the head of escarpments in response to discharge points lower in the gorge. Below that short segment, however, the creek picked up about 0.080 cms of flow over this reach, or about 25% of the flow at the mouth. There were a number of small springs along this reach, and it was hypothesized that groundwater discharge may be influenced by the locations of geologic contacts in the gorge. However, the dye-dilution flow data indicated that groundwater discharge occurred rather uniformly along the entire reach, i.e., there was no obvious change in slope or discontinuity in the incremental flow measurements (Figure 10). The average rate of increase of flow over this reach was about 0.0048 cms per 100 m of stream length. Correlation between slight changes in slope and a detailed analysis of geologic contacts along the gorge might be possible but was beyond the scope of our expertise.

Influence of Groundwater Discharge Pattern on Stream Temperature

Midwestern trout streams require significant groundwater discharge to maintain equable water temperatures within the range preferred by trout, roughly 10¡ to 20¡ C (about 50¡ to 70¡ F). Both Valley Creek and Browns Creek have contrasts between their two main branches, one of which is fed almost exclusively by groundwater and the other fed by lake outflow. In both cases, the groundwater-fed branch had more equable stream temperatures because of the moderating effect of the discharge of groundwater that has relatively stable temperature. In contrast, the lake-fed branches have much wider temperature variations, in particular higher summer temperatures that may hinder or exclude trout. For example, the groundwater-fed South Branch Valley Creek remained below 15¡ C except for a few hours during the hottest days of each year, whereas the lake-fed North Branch Valley Creek exceeded 20¡ C for many days and even 25¡C at times (Figure 10a and b). Likewise, the groundwater-fed North Branch Browns Creek generally remained below 25¡ C (though already too warm to be favored by trout), but the lake-fed South Branch Browns Creek exceeded 30¡ C at times, much too warm to sustain trout (Figure 10c and d). The high variability of the South Branch Browns Creek temperature probably was related to varying proportions of groundwater discharge and Long Lake outflow entering to the creek. Note the smoothly varying groundwater temperatures (Figure 10c and d, gray lines for Browns Creek branches), which apparently lag the stream-water temperatures by a month or two and never exceed 15¡ C. Groundwater temperatures were measured in piezometers with 15-cm screens set 1.5 m below the stream bed.

Groundwater Discharge Summary

In summary, both creeks had one branch dominated by direct groundwater discharge: South Branch Valley Creek and North Branch Browns Creek. However, groundwater discharge in South Branch Valley Creek was concentrated strongly in the headwaters area and appeared to derive from bedrock aquifers, whereas groundwater discharge in North Branch Browns Creek occurred more uniformly along its channel and derived primarily from unconsolidated glacial deposits. This incremental groundwater discharge in North Branch Browns Creek suggests that it could become suitable habitat for trout. At present the North Branch Browns Creek has temperatures above 20¡ C for several weeks each summer, which makes it sub-optimal for trout. Proper restoration of its riparian zone to provide shading and a source of woody debris might help reduce summer temperatures enough to sustain a viable trout fishery. On the other hand, the water may be warmed primarily by slow transit through several wetland complexes along its course, in which case reducing temperatures could prove difficult.

Both creeks also had one branch dominated by outflow from a lake: North Branch Valley Creek from Lake Edith, and South Branch Browns Creek from Long Lake. These lakes made summer water temperatures in the stream branches too warm to be favored by trout. However, the influence of Long Lake was more severe than that of Lake Edith and perhaps demonstrated the negative impact of urban runoff.

Groundwater Recharge, Path, and Age

Groundwater recharge is difficult to characterize because it likely occurs in a non-uniform manner over both space and time. Spatially, the rates or amounts of recharge are probably patchy, presumably being greater over landscape units that have high infiltration capacity and a flat or pocked landform that retains runoff and melt water. Temporally, recharge is probably episodic, occurring during times of moisture excess beyond soil moisture deficits and evapotranspirative losses. In contrast, groundwater discharge from a watershed is comparatively easy to characterize because it is spatially focused toward stream channels and temporally steady, making baseflow measurements of streams a good proxy for groundwater discharge. The measurement of discharge adds an important constraint on characterizing recharge, because on an annual (or better, decadal or longer) time scale, the quantity of recharge can be assumed to be similar to that of discharge. But even if the quantity of recharge can be estimated, determining the size and location of the recharge area, and the groundwater travel times through the aquifers, is much more difficult. Yet, these are important factors to determine in protecting the quantity and quality of groundwater that sustains trout streams such as Valley and Browns creeks.

The tools to investigate groundwater recharge, flow paths, and age include piezometric maps and hydrologic tracers. A piezometric map is a contour map of the hydraulic heads in any selected aquifer; groundwater flows from higher heads to lower heads in a direction perpendicular these contours. Such maps can be used to estimate the groundwater capture zone, or "groundwatershed," for a creek for each aquifer by following two traces from each side of the creek mouth upgradient (perpendicular to the contour lines) to the point where they meet. The groundwatershed is generally synonymous with the recharge area of a creek, although, as noted above, recharge is likely to be non-uniform with certain areas having much more importance in promoting recharge because of their geomorphology. Piezometric maps are limited by the quality and spatial distribution of the hydraulic head data points, typically derived from well data and from surface-water bodies assumed to be in hydraulic connection with the selected aquifer. Groundwater flow models may also be used to construct groundwatersheds, although typically such models are (or should be, if possible) "tuned" to match the piezometric maps anyway.

Hydrologic tracers may be used to infer the source and path of groundwater under certain circumstances. A water molecule containing the heavier isotope of oxygen or hydrogen is a particularly good tracer because it behaves essentially identically to the bulk of the water in the aquifer. In this study, water containing the stable isotopic forms of hydrogen and oxygen was used to infer the seasonality of recharge and whether lakes were a significant source of recharge. Water containing tritium, the unstable isotope of hydrogen, was used to determine the age category of groundwater. Other chemical tracers dissolved in the water can be used to identify influence of human activities. In particular, nitrate was used here primarily to indicate the influence of agriculture, which can give clues about the source, path, and age of groundwater.

Groundwatersheds

A groundwatershed could be defined as the three-dimensional aquifer body that contributes groundwater to the creek. Unlike surficial watersheds, its shape is not static but varies with slight changes in hydraulic pressures within the aquifer due to recharge pulses, water-supply withdrawals, base-level alterations, and so forth. Because most groundwater flow is horizontal, and because three-dimensional bodies are difficult to depict, this report operationally defines a groundwatershed as the plan view, or projection onto the x-y plane, of this aquifer body. More simply, a groundwatershed, or groundwater capture zone, herein refers to the area of aquifer that contributes groundwater to the creek. For a layered aquifer system, the contributions of all layers should be included; however, for matters of practicality in this report only the most important layer (or two) was chosen to determine the groundwatershed. In general, all of the groundwater inside the groundwatershed will eventually discharge to the creek (except for losses to pumping and phreatophytic evapotranspiration). Piezometric maps were used to construct groundwatersheds for Valley and Browns creeks. However, the quality of the resulting groundwatershed maps differs significantly and must be used with caution.

For Valley Creek, piezometric maps were constructed for each possible aquifer layer that could contribute to the creek, including the surficial Quaternary aquifer, the Prairie du Chien (PdC) aquifer, the Jordan aquifer, the Franconia-Ironton-Galesville (FIG) aquifer, and the Mount Simon aquifer (Almendinger and Grubb, 1999). Data were too sparse in the lower aquifers (the FIG and Mt. Simon) to draw clear inference about their possible contributions to the creek; because of their depth their influence was hypothesized to be minimal. In contrast, piezometric contours in the PdC and Jordan aquifers showed a clear influence of discharge to the creek. As the creek is fed by springs that come directly from exposed PdC bedrock and the streamwater chemistry is consistent with that from both the PdC and Jordan aquifers, we concluded that the PdC and Jordan aquifers were the main contributors of groundwater to the creek and hence mapped the contributing area (the groundwatershed) for those layers. In particular, the mapped groundwatershed is based on data from the PdC aquifer because data points (wells) for that aquifer were much more numerous than for the Jordan. In addition, a groundwater model was calibrated for the region in south Washington County surrounding the creek; an envelope around the groundwater flow lines that were traced from the stream edge upgradient to the top of the PdC aquifer provided a second estimate of the groundwatershed (Almendinger and Grubb, 1999). The model assumed that the PdC and Jordan aquifers acted as a single unit, and thus may be in error to the degree that they are separated by a leaky aquitard.

Because these postulated groundwatersheds for Valley Creek refer to the PdC aquifer (and the Jordan, as well, in the model), rather than for the surficial aquifer, identifying landscape units within which to protect groundwater recharge is hindered by the imperfectly known interactions between the PdC aquifer and the aquifer layers above it extending to the surface. A useful extension of the groundwater model results for

Valley Creek would have been to trace the flow lines from the top of the PdC layer all the way to the land surface to give a better idea of where, on the surface, groundwater recharge actually contributes groundwater that eventually feeds the creek. Nonetheless, a reasonable assumption would be that the uppermost groundwatershed for Valley Creek would be similar to that delineated in the PdC aquifer, perhaps displaced slightly in the upgradient direction.

The resulting estimated groundwatersheds for Valley Creek (Figure 12a) include most of the surficial watershed but extend considerably beyond to the north and west, with a minor excursion to the south. Whereas the surficial watershed has an area of 45 km^2, the groundwatershed appears to encompass about 60 km^2 (both possible groundwatersheds shown in Figure 10a have about the same area, within a few square kilometers). How does this conform to our general understanding of possible groundwater recharge in the area and baseflow of the creek? The long-term average runoff depth from this part of the state is about 15 cm per year (Gunard, 1985), and consequently areal-averaged groundwater recharge would be expected to be no more than this amount, under typical conditions. According to the hydrograph separation analysis above, baseflow accounted for 92% of the total runoff volume of 15.8×10^6 m^3 in 1999, or 14.536×10^6 m^3. If this baseflow volume is distributed evenly over the 60 km^2 of the postulated groundwatershed, the average groundwater recharge rate would have been about 24 cm, considerably greater than the 15 cm maximum expected value. Alternatively, if 15 cm is assumed to be the recharge rate, then a groundwatershed of 97 km^2 would be required to generate the measured baseflow volume in 1999. While recharge rates greater than 15 cm are conceivable, these calculations suggest that the area of the possible groundwatersheds shown in Figure 12a are, if anything, conservative and could be much larger.

For Browns Creek, detailed piezometric maps generated from the latest data local to the creek were not available. Instead, county-wide piezometric maps (Kanivetsky and Cleland, 1990) were used to delineate an approximate groundwatershed for Browns Creek. Because most of the streamflow appeared to derive from discharge from the surficial Quaternary deposits, the piezometric map of the water-table system was chosen for analysis. The resulting groundwatershed covers about 60 km^2 (Figure 12b), nearly identical to the groundwatershed area delineated for Valley Creek. The hydrograph separation analysis for Browns Creek indicated that in 1998 baseflow accounted for 87% of the total runoff volume of 9.2×10^6 m^3 in 1998, or about 8.0×10^6 m^3. If this volume is distributed over the 60 km^2 of the postulated groundwatershed, then groundwater recharge would have been about 13.3 cm, slightly less than the approximate expected maximum of 15 cm. Hence the postulated area of the groundwatershed for Browns Creek seems about right, even though its size, shape, and position were determined from very sparse data. (Note that the groundwatershed area or recharge amount may be overestimated to the degree that part of the baseflow is not groundwater, but overland runoff from the Long Lake system.) Nonetheless, the reader is cautioned that the groundwatershed boundary shown in Figure 12b can only be considered a very rough approximation of the true groundwatershed. In particular, because the lowermost 2 km of the creek does receive significant groundwater discharge from the PdC bedrock aquifer, a groundwatershed delineated for that aquifer may be quite different in size and shape from that estimated for the surficial aquifer, probably being much narrower and possibly extending much further to the north.

These recharge estimates compare well with other published values for the region. Ruhl and others (2002) used a variety of methods to estimate recharge in the Minneapolis-St. Paul metropolitan area. Hydrograph recession analysis for seven streams and rivers gave a range of estimated recharge from about 1 to 34 cm yr^{-1}, and well-hydrograph analysis from 11 wells in glacial outwash gave a range of recharge from about 11 to 35 cm yr^{-1}. Recharge estimates for Valley Creek (about 15 to 24 cm yr^{-1}) and Browns Creek (about 13 to 15 cm yr^{-1}) fit comfortably within these ranges.

Source of Groundwater Recharge: Stable Isotope Tracers

Whereas the groundwatersheds delineated above represent the general areas from which groundwater is contributed to the creeks, they do not identify specific areas where most of the groundwater recharge occurs. As noted above, groundwater recharge does not occur in a spatially uniform manner, and a detailed analysis of the soils, surficial geology, and topography would be necessary to pinpoint areas on the ground to protect in order to preserve the bulk of the groundwater recharge. A relatively straightforward geographic information system (GIS) analysis of existing data would be very worthwhile in identifying such areas in theory, although field verification could prove labor and data intensive. As an alternative, stable isotope tracers of water can provide clues about some sources and timing of groundwater recharge.

Stable isotopic forms of water (mostly $H_2{}^{18}O$ and DHO, where D symbolizes deuterium, ^2H) can indicate the seasonality of the precipitation supplying recharge, as well as whether the recharge originated from a lake. The stable isotope content of water is expressed as a per mil (, or parts per thousand) difference in the atomic ratio of the heavy isotope to the more common light isotope in the sample compared to that ratio in standard mean ocean water (SMOW):

$$\delta^{18}O = 1000 \cdot \frac{\left({}^{18}O/{}^{16}O\right)_{sample} - \left({}^{18}O/{}^{16}O\right)_{SMOW}}{\left({}^{18}O/{}^{16}O\right)_{SMOW}}$$

and

$$\delta D = 1000 \cdot \frac{\left({}^{2}H/{}^{1}H\right)_{sample} - \left({}^{2}H/{}^{1}H\right)_{SMOW}}{\left({}^{2}H/{}^{1}H\right)_{SMOW}}$$

In general, the colder the ambient temperature at the time of precipitation, the lighter the isotopic content (i.e., the less ^{18}O and D in the water molecules), because the these heavier isotopes have been lost preferentially to previous precipitation events as the moisture in the air mass has migrated from its source (typically the Gulf of Mexico for Minnesota) to a mid-continental location. Thus, snowmelt in Minnesota tends to be depleted in both ^{18}O and D (i.e., they have more negative $\delta^{18}O$ and δD values). Summertime precipitation has greater proportions of ^{18}O and D (i.e., they have less negative values of $\delta^{18}O$ and δD). Whether the precipitation occurs as "light" winter snow or as "heavy" summer rain, the ratio of δD to $\delta^{18}O$ in precipitation is rather constant at about a value of eight, and hence a plot of δD versus $\delta^{18}O$ for precipitation tends to fall on a "meteoric water line" with a slope very close to eight (Figure 13). The "global meteoric water line" is described by the following equation (Yurtsever and Gat, 1981):

$$\delta D = 8.17 \cdot \delta^{18}O + 10.56 \qquad \textit{(global meteoric water line)}$$

The water tends to retain this characteristic "meteoric" isotopic ratio (with a slope of about eight), unless it is exposed to evaporation. Evaporation from a water body not only makes the remaining water "heavier" (as the lighter isotopic forms of water evaporate preferentially, leaving behind the heavier forms), but it also alters the isotopic ratio so that the slope of the relation between δD and $\delta^{18}O$ will be closer to five than to eight. Samples that are evaporatively evolved, then, fall on an "evaporative water line" with a slope close to five.

These differences in isotopic content can give clues about the timing and source of groundwater recharge. If the groundwater is "light," then it probably originated as snowmelt (from winter precipitation); otherwise, it originated as precipitation from other times in the year. If the groundwater is heavier (i.e., enriched in δD and $\delta^{18}O$) and with an isotopic ratio that deviates from the meteoric water line, then that water was exposed to significant evaporation and probably came from a lake at some time in the past.

Water samples from the watersheds of Valley and Browns creeks tended either to be "light" and fall on the meteoric water line, or to be "heavy" and fall on the evaporative water line (Figure 13a). A "local meteoric water line" was estimated by fitting a line to all the samples that were "lighter" (more negative) than the median groundwater sample:

$$\delta D = 8.05 \cdot \delta^{18}O + 12.04 \qquad \textit{(local meteoric water line)}$$

This line is very similar to the global meteoric water line (Figure 13a).

Nearly all lake water samples (Figure 13b; n = 42) showed some evaporative effect, with isotopic values deviating to the right of the meteoric water line. The only exceptions were several samples from open-basin lakes sampled through the ice during winter, when isotopic values tend to be lighter. Because closed-basin lakes tend to have longer hydraulic residence times than open-basin lakes, their water is generally exposed to evaporation for long periods of time and are thus more likely to develop an unambiguous evaporative signature. Consequently, a line was fit to all closed-basin lake samples to determine a "local evaporative water line" (Figure 13b):

$$\delta D = 4.59 \cdot \delta^{18}O - 20.34 \qquad \textit{(local evaporative water line)}$$

Clearly, closed-basin lakes from both watersheds tend to cluster at the "heavy" end of the evaporative water line, especially those samples collected during the summer. The few open-basin lakes that also fell in this "heavy" cluster were those that receive significant runoff from impervious surfaces, Long Lake and Lake McKusick in the Browns Creek watershed. Perhaps summer runoff from warm impervious surfaces develops an evaporative signature before reaching the lake, thereby intensifying the evaporative evolution of the water beyond that expected from residence time considerations alone. Interestingly, Long Lake had the widest range of isotopic values, from the lightest, most meteoric water in the wintertime (runoff from de-iced roads and parking lots?) to some of the heaviest, most evaporatively evolved water in the summertime (pre-evolved runoff from warm surfaces?). Lake samples that clustered most closely to the median groundwater value were those most closely associated with groundwater discharge in the Valley Creek area, namely, those ponds near the headwater springs of South Branch Valley Creek.

Groundwater samples (Figure 13c; n = 30) clustered closely around their median value, with a much narrower range of values than either lake or stream samples. The median groundwater sample value was a key variable in understanding isotopic relations in the Valley and Browns creek watersheds. This point (where $\delta^{18}O = -9.50$ and $\delta D = -64.14$; white crosses in Figure 13) happens to be essentially at the intersection of the local meteoric and evaporative water lines. In other words, the median groundwater value is apparently a typical, representative starting point for the water that may later evaporatively evolve (in a lake) to have a heavier isotopic content.

The groundwater samples that are lighter (less negative) than the median are tightly clustered near the meteoric water line and are probably best considered to be uninfluenced by evaporation. The water in these samples must have infiltrated quickly without a prolonged period of time of exposure, much as rainfall might infiltrate an upland soil. Groundwater recharge is commonly believed to occur mostly during the spring snowmelt period; however, none of the groundwater samples had an isotopic content nearly as light as the snowmelt runoff samples collected. This paradox is not easily explained. Evidently, by the time water percolates through the vadose zone to the water table, it has become so thoroughly mixed with previously infiltrated water from all seasons that the resulting groundwater has a rather uniform content with only a narrow range of isotopic values. Consequently, the seasonality of the major recharge period cannot be determined from these data.

Most of the groundwater samples heavier than the median appear to have been influenced by evaporation. That is, the samples deviate to the right of the meteoric water line and approach the evaporative water line (Figure 13c). This implies that nearly half of the groundwater samples collected were composed at least partially of water that had spent some time in a lake or was otherwise exposed to evaporation even though surface-water bodies occupy only about 2.5% of the total basin area in Valley Creek watershed, and about 11.5% in the Browns Creek watershed. Part of the influence of lake water on groundwater can be attributed to closed-basin lakes being collectors of runoff (even if only minor amounts) and sites of focused groundwater recharge, particularly in Browns Creek watershed where drainage development is poor and many surficially closed depressions exist.

However, a greater influence can more likely be attributed to mixing of lake and groundwater simply because the lake is situated within a regional groundwater flow field. As groundwater flows downgradient from water-table highs to the regional point of discharge, it can pass through lakes along the way, seeping into a lake along its upgradient boundary and back into the aquifer along the downgradient boundary of the lake. As a rough rule of thumb, a closed-basin lake "captures" groundwater from an upgradient strip of aquifer about twice the lake diameter, and recharges water back into the aquifer to a downgradient plume, also about twice the lake diameter in width and extending (in theory) all the way to the point of discharge. The area of these large plumes, rather than the actual area of the lakes, determines the overall area of aquifer influenced by lakes, and thus it is not terribly surprising that about half of the groundwater samples appeared to be influenced by lakes to some degree. Note that this mixing of lake and groundwater can occur whether the lake is a net contributor of water or not -- it does not necessarily imply that the lakes are sites of significant focused recharge, although they could be if large amounts of runoff are routed to them. The mixing does demonstrate the high degree of connectivity between surface-water bodies and groundwater.

A few groundwater samples stand out as being obviously impacted by recharge from lakes in the Browns Creek watershed. The heaviest groundwater sample came from the piezometer at the outlet of Long Lake, with an isotopic composition similar to that of Long Lake summertime water. Taking median isotopic composition of all groundwater samples to represent typical "meteoric" groundwater, and that of all lake samples to represent typical lake water, then the Long Lake piezometer water was a mix of 7% meteoric groundwater and 93% lake-influenced water. The next two heaviest groundwater samples came from the piezometer at site BC-3, under North Branch Browns Creek just above its confluence with the south branch (Figure 2), with an approximate mix of 41% meteoric groundwater with 59% lake-influenced water. This site is just south of South Twin Lake, which lies outside of the surficial watershed but is clearly supplying groundwater to Browns Creek at this point. The next heaviest sample was from a deep bedrock well (site BC-19, Figure 2) on the south side of the creek near its mouth, with an approximate mix of 78% meteoric groundwater and 22% lake-influenced water; the nearest lake source would be Lake McKusick (site BC-8, Figure 2), which had a very heavy isotopic content. This site demonstrates that the influence of surface-water/groundwater exchange is not limited to surficial aquifers. All of the other "heavy" groundwater samples would be a mixture of greater amounts of meteoric groundwater and lesser amounts of lake-influenced water.

Collectively, these data indicate that lakes are not a disproportionate contributor of net groundwater recharge, despite the popular perception that they are sites of focused recharge. Had this been the case, the median groundwater isotopic content would have lain somewhere between the median lake-water isotopic content and the meteoric water line, whereas in fact the median groundwater value was meteoric. Except for the few obvious cases where the groundwater was collected in the plume downgradient from an isotopically heavy lake, even the heavier-than-median groundwater samples contained a mix of meteoric and lake-influenced water that approximated the general proportion of uplands versus surface-water bodies in the watersheds. However, the fact that nearly half the groundwater samples were influenced by lake water does demonstrate the high degree of lake-groundwater interaction and its potential to impact even deep bedrock wells.

With the above conclusions in mind, the interpretation of the isotopic content of stream water (Figure 13d) was fairly straightforward. For this analysis, only the highest 20% of flows were categorized as "runoff events," to make sure that water collected during these times would have the greatest influence from runoff from the watershed. All other flows were categorized as "baseflow," even though some of these samples may have had some minor contribution from overland runoff. Most baseflow samples (open symbols) cluster near the median groundwater value, indicating a strong dominance of groundwater input to the creeks. Exceptions include the heavy baseflow samples in Browns Creek, which were summertime samples from those reaches downstream from Long Lake which can deliver isotopically heavy water to the creek even during baseflow conditions. Likewise in Valley Creek, samples downstream from Lake Edith, which has isotopically heavy water by the end of summer, can also have a slightly heavier-than-median isotopic signature during baseflow.

Runoff event stream-water samples had the widest range of isotopic values, from being slightly heavier during summer to being especially light (more negative) during the snowmelt period. The "heavy" runoff events were really very close to the median value and were caused by summer rainstorms that simply mixed with already-heavy water in the lakes that feed directly to the creeks, namely Lake Edith (for Valley Creek) and Long Lake (for Browns Creek). Most of the light runoff samples came from ephemeral channels in the Valley Creek watershed which flowed only during snowmelt and almost certainly had no groundwater component. The lightest sample in the dataset, however, came from the South Branch Browns Creek (site BC-4) during an unusual thunderstorm on 11 February 1999 which created significant runoff from both the rain and snowmelt.

Whereas the light snowmelt water in the channels of Valley and Browns creeks evidently got flushed out of the system within a day or two, this water represented only a fraction of the total snowmelt that occurred over the rest of the two basins. Surely some of this snowmelt pooled and infiltrated to some degree, especially given the high permeability in the Valley Creek watershed and the degree of closed-basin drainage in the Browns Creek watershed. Yet, the light signature of this water was not apparent in the groundwater dataset. Perhaps this was because the wells sampled in this study were typically either bedrock wells deep below the surface, or shallow piezometers near the stream at the terminus of groundwater flow lines. Both situations would give groundwater ample travel time to become well mixed and to obscure the isotopic signal from episodic input pulses of light snowmelt. This explanation is possible, but not particularly satisfying.

Groundwater Age and Depth of Flow Path: Tritium and Nitrate Tracers

The age of water is defined here as the length of time since that water fell as precipitation and entered the integrated surface-water/groundwater system. The age of groundwater typically refers to the time since precipitation infiltrated into the subsurface and began its journey along a flow path to the point of discharge. Within an aquifer groundwater flow paths (streamlines) do not cross each other, and a parcel of water moving along a flow line can remain relatively intact with regard to its age. Any mixing due to hydrodynamic dispersion would be among adjacent parcels of similar age, with little net effect. Under such conditions, groundwater age and travel time are synonymous and meaningful.

In contrast, lake and stream water (surface water) is commonly a mixture of recent precipitation and runoff, as well as "older" groundwater. Even under baseflow conditions for streams fed exclusively by groundwater, stream water is a mixture of different-aged groundwater. Because of this mixing, the concept of the "age" of a parcel of lake or stream water is nearly meaningless. By extension, the "age" of groundwater derived in part from infiltrated lake or stream water has little meaning. Such groundwater does have a travel time, but its age is indeterminate because of the mixed-age nature of its source.

The age of groundwater can be bracketed by tracers such as tritium and nitrate that have entered the hydrologic system at known periods of time. Tritium (^{3}H, symbolized by T) is an unstable isotope of hydrogen that has a half life of 12.43 years and is measured in TU (tritium units), where 1 TU equals one tritium atom per 10^{18} other hydrogen atoms. Prior to the mid-1950s, it occurred naturally in very low concentrations, about 5-10 TU in precipitation as THO (Ingraham, 1998). However, atmospheric testing of thermonuclear bombs injected large quantities of tritiated water into the atmosphere. Tritium content of precipitation peaked in the early 1960s to as high as 10,000 TU in the northern hemisphere (Ingraham, 1998); tritium content of modern precipitation in Minnesota ranges from about 8 to 15 TU (S. Alexander, Univ. of Minnesota, unpublished data). Water older than about 50 years, before then influence of bomb tritium, would have a residual tritium content of less than 1 TU today, assuming it began with a content of about 10-15 TU and has now passed through at least four half-lives (about 50 years), thereby reducing its tritium content to no more than one-sixteenth $(1/2)^4$ of its original value. Water with tritium content above 1 TU is therefore younger than about 50 years, or, if a mixture, contains some portion of young water. Unfortunately, because the tritium content of precipitation has fluctuated significantly since the influence of nuclear testing, tritium cannot be used to obtain absolute ages of water younger than 50 years (Ingraham, 1998). In summary, a tritium content <1 TU implies water older than 50 years; a tritium content >1 TU implies water with at least some component younger than 50 years.

Like tritium, nitrate occurs naturally in low concentrations, probably less than 1 mg/L nitrate-N (nitrate as nitrogen), and human activities have greatly increased its mobility and supply. The early spread of agriculture across the upper Midwest in the mid-19th century almost certainly increased nitrogen mobilization and subsequent delivery to aquatic systems. However, the major rise in nitrogen supply to the landscape has occurred since the 1940s, with the exponential increase in application of inorganic fertilizers. On a global basis, human activities have more than doubled the rate of supply of biologically available nitrogen to ecosystems (Vitousek and others, 1997). Consequently, levels of nitrate-N above 1 mg/L most likely imply an anthropogenic source and an age of less than about 150 years, and commonly less than 60 years. However, because nitrate can be removed from water by bacterial denitrification, low levels of nitrate do not necessarily imply an older age.

In the Valley and Browns creek watersheds, wells were sampled for tritium and nitrate to give clues to the path and age (travel time in some cases) of groundwater feeding the creeks. These variables are important in understanding lags between activities in the watershed and subsequent impacts to the creek from water-quality constituents of groundwater. The very small sample size necessarily limits the conclusions of this study; within this constraint, the sampling was designed to provide evidence regarding the general hydrogeologic flow pattern in each watershed. How deeply does young groundwater penetrate into the bedrock aquifers? To answer this question, wells screened in each of the major aquifers (from the Quaternary down to the Jordan) were sampled near the upgradient watershed divide in each groundwatershed, because this is where groundwater should move vertically downward and penetrate the deepest first, before moving laterally to other areas of the aquifers. What is the age of groundwater reaching the stream, and where is it the oldest? Groundwater entering the stream channel at its bank is likely shallow and young, so we placed piezometers nearer to the middle of the stream channel to increase the chance of intercepting older groundwater. We also hypothesized that in-channel piezometers nearer the stream mouth could tap older water than those upstream, because groundwater flow lines discharging near the mouth may be the oldest and deepest of the entire flow system. However, the pattern of different-aged groundwater flow lines converging on a creek channel can be extremely complex and would require a much greater spatial sampling density than that executed here to better characterize the system.

In the Valley Creek groundwatershed, all of the groundwater samples were young, less than 50 years old, with tritium contents all being greater than 1 TU and many above 10 TU (Table 4a). In the recharge zone, young water clearly penetrated down to at least the Jordan aquifer; its tritium content was lower than that of the overlying Prairie du Chien aquifer, either because it actually is older (as one might expect), or because it is mixed with much older water. In the discharge zone, stream water and groundwater from in-channel piezometers all had tritium contents greater than 10 TU. The Prairie du Chien was not sampled in the discharge zone; the Jordan well sampled there (VC-27) had a lower tritium content than its counterpart in the recharge area (VC-26), perhaps reflecting the travel time between recharge and discharge zones. There was no indication from the in-channel piezometers that the age of discharging groundwater increased downstream, although a sample was not collected from near the mouth. The similarity of the tritium contents of streamwater and Prairie du Chien wells indicates that this aquifer may be the main contributor of groundwater to the baseflow of Valley Creek. Somewhat surprisingly, the deepest well sampled in the discharge zone was screened in the Ironton-Galesville aquifer, and its tritium content indicated young water (less than 50 years), although not necessarily younger than water in overlying aquifers with smaller tritium contents.

In the Browns Creek groundwatershed, the tritium contents likewise indicated mostly young water, with some exceptions (Table 4b). In the recharge zone, young water penetrated to the Jordan aquifer (site BC-17). However, the sample taken about 1.5 km away from the overlying Prairie du Chien aquifer (site BC-16) was older than 50 years, demonstrating spatial variability in the recharge process. In the discharge zone, streamwater and groundwater from in-channel piezometers all indicated young water. The tritium contents of groundwater from in-channel piezometers at the headwater wetland (BC-14) and at the mouth (BC-01-GW) were both similarly low (3.1 and 3.2 TU respectively), neither supporting nor disproving the hypothesis that age of discharging groundwater increases in the downstream direction. As in Valley Creek, the Jordan wells in the discharge area (BC-18 and BC-19) had lower tritium contents than the Jordan well in the recharge area (BC-17), possibly indicating an older age because of travel time. Site BC-19 was certainly older, as its tritium content (<0.8 TU) unambiguously demonstrated water older than 50 years.

In both watersheds, the nitrate concentrations generally supported the conclusions based on the tritium data that most of the water sampled was young, with nitrate concentrations greater than 1 mg/L nitrate-N. Furthermore, the two samples older than 50 years (BC-16 and 19) also had nitrate concentrations less than 1 mg/L nitrate-N. However, the nitrate data by themselves were more ambiguous and potentially misleading in the absence of the stronger tritium data. Agriculture has resulted in a strong nitrate signal in the Valley Creek watershed, with most samples exceeding 4 mg/L nitrate-N. However, because of less intense agriculture in the Browns Creek watershed, the nitrate signal there is not as reliable an indicator, with most samples only slightly exceeding 1 mg/L nitrate-N. A number of young samples (based on tritium) had nitrate concentrations below 1 mg/L nitrate-N, probably because of denitrification (especially in the Valley Creek watershed) or because of a lack of significant agricultural input (possibly in Browns Creek watershed).

Suspended Solids and Nutrients

Suspended solids and major nutrients, specifically phosphorus and nitrogen, are probably the most common non-point source (NPS) pollutants and are known to increase under both urban and agricultural landscapes, relative to fully vegetated landscapes. Input of suspended solids (and their subsequent siltation) is probably the greater problem for trout streams, as it can degrade the quality of spawning beds and the macroinvertebrate food base required by trout. Phosphorus and nitrogen are more of a problem to lacustrine receiving waters where nutrients can be recycled many times through the biota, thereby causing persistently high algal growth. In small streams, nutrients are mostly on a one-way path downstream and planktonic algae have little chance to bloom and accumulate, although continued inputs of high nutrient concentrations may cause excessive growth of benthic algae and rooted aquatic macrophytes.

Land use can impact the *concentration* of NPS pollutants (mass per unit volume of water) as well as their annual *load* (total mass moved per year) and *yield* (load per unit watershed area). For pollutants that build up slowly and are washed off quickly from the landscape, concentrations could vary widely, being high in dry years and low in wet years. Annual yields would be a more stable and appropriate measure to characterize exports of these types of pollutants per unit area of different land uses. In contrast, for constituents that have a large accumulated reservoir on the landscape, such as exposed soil and nutrients in agricultural settings, concentrations are less affected by runoff volume, and consequently annual yields tend vary greatly and in concert with annual runoff volume. Concentrations would be the more stable and appropriate measure to characterize land-use effects on exports of these pollutants. In fact, concentration (on an annual volume-weighted basis) is simply the annual yield normalized per unit runoff depth, or annual load normalized by runoff volume. These two conceptual models of NPS pollutant transport   complete wash-off of a limited supply, versus limited wash-off of an infinite supply   are idealized end-members, and reality must lie somewhere in between. Consequently, both concentrations and yields should be determined where possible when trying to link land use to NPS pollution.

Concentrations in Groundwater and Lakes

The nutrient content of stream water is clearly affected by that of its source waters, including both groundwater and lake water. Even closed-basin lakes may influence streamwater chemistry by a groundwater flow connection. Hence a brief characterization of the nutrient contents of groundwater and lake water is relevant to a discussion of the nutrient contents of Valley and Browns creeks.

Groundwater was relatively low in dissolved phosphorus (DP) in the watersheds of both Valley Creek (median 17 g L^{-1}) and Browns Creek (median 28 g L^{-1}) (Figure 14a). The higher values were all from shallow piezometers that may have been influenced by surface water. All bedrock wells had DP concentrations below about 30 g L^{-1}, and most were below 10 g L^{-1}. Groundwater typically has low DP concentrations because the particle reactivity of phosphorus tends to limit its transport into aquifers. As noted earlier, the dissolved nitrogen (DN) concentration in groundwater in the Valley Creek watershed was relatively high (median 2.4 mg L^{-1}; Figure 14b), but variable depending on the redox condition of the groundwater. Oxygenated groundwater tended to have high DN, whereas deoxygenated groundwater had little DN, probably because of denitrification. The median value given here, derived from all samples taken at all study sites in the watershed, certainly underestimates the typical DN of the groundwater feeding the creek, because a number of small, deoxygenated seeps along the creek were sampled as part of our survey of the creek channel. In contrast, the high-discharge springs that supplied most of the groundwater to Valley Creek had much higher DN concentrations (5.8—9.4 mg L^{-1}). Groundwater in the Browns Creek watershed was uniformly low in DN (median 1.0 mg L^{-1}) with little variability, apparently because of the limited row-crop agriculture in this watershed.

Lake water was higher in phosphorus (as total phosphorus, or TP) compared to groundwater (Figure 14a), as expected because lakes can receive phosphorus from surficial runoff (often increased by shoreland residential development) and from litterfall from riparian vegetation. The median lake-water TP concentration was 54 g L^{-1} in the Valley Creek watershed, and 77 g L^{-1} in the Browns Creek watershed. The highest concentrations in the Valley Creek watershed were from the Fahlstrom closed-drainage basin: average TP values were 273 g L^{-1} for Fahlstrom wetland (site VC-22) and 217 g L^{-1} for the Fahlstrom Lakes (sites VC-17 and 18). However, the site that most directly affected Valley Creek was Lake Edith, whose outlet initiates the north branch of the creek. The TP concentration of Lake Edith was the lowest measured in the watershed with a median value of 25 g L^{-1}, implying a mesotrophic status that is quite good for the corn-belt ecoregion. In the Browns Creek watershed, nearly all of the ultraeutrophic values (those greater than 100 g L^{-1}) were from repeated samplings of Long Lake (BC-5), which receives mostly urban runoff and directly feeds South Branch Browns Creek. Goggins Lake (BC-7) ranged from 69—127 g L^{-1}, and Benz Lake ranged from 100—104 g L^{-1}. Lake McKusick (BC-8), another urban lake, ranged from about 50—70 g L^{-1}, as did South Twin Lake (BC-13). Several lakes in the Browns Creek watershed had TP concentrations in the mesotrophic range (between about 10 and 35 g L^{-1}): Pat Lake (23 g L^{-1}), Lake Masterman (28 g L^{-1}), and Plaisted Lake (34 g L^{-1}). These are the averages of typically two measurements per lake; winter values tended to be higher than summer values. Note that a full trophic-status characterization of a lake should include chlorophyll and secchi-disk readings, and not just phosphorus concentrations alone.

The median lake-water concentration of total nitrogen (TN) was 2.6 mg L^{-1} in the Valley Creek watershed and 2.0 mg L^{-1} in the Browns Creek watershed (Figure 14b), both values slightly higher than the corresponding groundwater DN concentrations. Interpretation is problematic because lake processes can either increase nitrogen concentrations via cyanobacterial nitrogen fixation, or reduce concentrations via denitrification in littoral wetland sediments. Lakes with high TN concentrations, however, probably received most of it from groundwater discharge or surficial runoff. Internal nitrogen fixation is not likely a significant source in comparison to agricultural or urban inputs.

Lakes may typically carry higher nutrient concentrations than groundwater, with the exception of nitrate in shallow aquifers under row-crop agriculture. Outlet streams from lakes may therefore likewise have higher nutrient concentrations than those fed by groundwater alone. However, it is not fair to characterize lakes as being the source of these nutrients. The source is the surrounding land use that inputs nutrients to the lake, and the lake modifies these inputs before passing them downstream. Lakes are nearly always a net sink for nutrients, especially phosphorus, and the downstream receiving waters would typically have even higher nutrient loads if runoff were routed downstream directly, rather than passing first through a lake.

Concentrations in Stream Water

The concentrations of suspended solids and nutrients in stream water were generally related to flow in Valley and Browns creeks, as is commonly assumed. By inspection of the Valley Creek data, the greatest difference in water quality appeared to be between "high-flow" samples collected above the 90th percentile of hourly discharges for the year, and "typical flow" samples collected at all other times. Flow data were not available for Browns Creek in 1999, when most of the samples were collected; flow categories were assigned based on those at Valley Creek (about 30 km to the south) and professional judgment. In practice, very high flows were obvious in Browns Creek during the snowmelt sampling in 1999, which constituted essentially all of the sampled high flows for the creek: no unambiguously high stormflows were sampled during the rest of the year. Mean values, rather than medians, were used as the measure of central tendency, because extreme values in runoff are important in influencing loads and should not be de-emphasized. However, because the distributions tended to be non-normal due to right-skewness, the non-parametric Mann-Whitney test was used to test the differences in concentration between typical and high flows, most of which were significant at the $p = 0.05$ level or smaller.

Suspended Solids

Total suspended solids (TSS) concentrations were uniformly low under typical flow conditions in both creeks, and especially so in Valley Creek (Table 5). TSS concentrations were not significantly different in the three main branches of Browns Creek (Kruskal Wallis test). In Valley Creek, the North Branch had significantly higher TSS concentrations than the other two main branches (Mann Whitney tests), despite the fact that the lake at its source should shield that branch from TSS inputs from most of the watershed. The solids were largely inorganic (more so than in the other branches), suggesting channel scour or bank erosion as the source, rather than lacustrine algal particles.

TSS concentrations were significantly higher under high-flow conditions in essentially all cases. In Valley Creek, the highest TSS values came from the South Branch, which can receive significant overland runoff from agricultural fields during snowmelt. Somewhat surprisingly, many of these solids apparently were trapped between the South Branch and the mouth, as mean TSS concentrations dropped from 170 mg L^{-1} to 19 mg L^{-1} over this distance. Browns Creek followed a different pattern: TSS more than doubled along the main stem to reach 344 mg L^{-1} at the mouth. The sources of this additional sediment load to the main stem of the creek could include new sediment delivered by urban storm-sewer "tributaries" as well as stored valley-floor sediment that was mobilized by increased flows from storm sewers and along the main channel.

TSS was composed of about 55% volatile suspended solids (VSS, the organic particulates), the balance being mineral particulates, averaged over all flows in both watersheds. The VSS percentage varied with flow, being about 70% of TSS in flows at or below the 10th percentile, and decreasing to about 40% in flows above the 90th percentile.

Phosphorus

Total phosphorus (TP) concentrations showed a very similar pattern to that of TSS, which was expected because of the common association of phosphorus with particulates (Table 5). Under typical-flow conditions, TP concentrations were low in Valley Creek and several times higher in Browns Creek. This difference between the creeks is substantial from the viewpoint of Lake St. Croix, the receiving water body. TP inputs from Valley Creek were in the range of mesotrophic lake-water concentrations, considered rather desirable in this ecoregion and near the natural levels of the St. Croix. In contrast, TP inputs from Browns Creek were at the level of the eutrophic/hyper-eutrophic boundary (around 100 g L^{-1}). TP concentrations in both creeks were greater than that of discharging groundwater, probably because of the particulates moved even under typical flow conditions that added to the phosphorus content.

Under high-flow conditions, TP concentrations increased significantly in most cases, and dramatically so for South Branch Valley Creek, which received snowmelt runoff from fields spread with manure. As with TSS, TP decreased over Valley Creek's main stem, implying storage of particulate-bound phosphorus in the near-channel bars and terraces. And, again as with TSS and in contrast to Valley Creek, TP concentrations increased over the main stem of Browns Creek, implying inputs over this reach from storm sewers or mobilized valley-floor sediments with associated adsorbed phosphorus.

Even though phosphorus is particle-reactive, the dissolved fraction (DP) played a substantial role in both watersheds. DP averaged 49% of TP in Valley Creek, and about 35% in Browns Creek; percentages were slightly higher under very low flow conditions, when TSS was correspondingly low. These fractions are substantially greater than reported for other river water, where DP constituted only 5% of TP (Meybeck, 1982; as cited by Hem, 1985).

Nitrogen

Total nitrogen (TN) concentrations showed a different pattern in the two watersheds (Table 5). In Valley Creek watershed, the South Branch had very high TN concentrations (mean 6.5 mg L^{-1}) under typical flow conditions because of being fed by high-nitrate groundwater. Increased flow volumes during high-flow conditions diluted the stream with respect to TN and concentrations were correspondingly lower; this reduction in TN concentration was small but highly statistically significant. TN concentrations were little affected by flow conditions in North Branch Valley Creek, as fluctuations in its flow and chemistry are buffered by being fed by Lake Edith. At the mouth of Valley Creek, TN concentrations were simply the mixture of the two branches, with no significant relation to flow, and with no evidence of sources or sinks along the main stem channel.

In contrast, Browns Creek had relatively low TN concentrations under typical flow conditions, and only slightly higher concentrations during high-flow conditions. The increase in concentration was significant in the North Branch ($p < 0.01$), but only weakly significant in the South Branch ($p = 0.09$) and the main stem ($p = 0.07$). As all branches had similar TN concentrations under both flow conditions, no obvious source or sink was evident along the length of the creek.

The nitrate fraction of TN differed between the two watersheds and with flow. In Valley Creek, nitrate composed about 95% of the TN measured during typical flows, but only 57% of TN during high flows, when the overland runoff delivered more particulate-N, organic-N, and ammonia-N from local fields. In Browns Creek, nitrate composed about 67% of TN during typical flows, and only 37% during high flows.

Loads and Yields

Because of a fairly complete data set for Valley Creek in 1999, loads could be calculated as directly as possible. By triggering an automatic sampler every 50,000 ft^3 of flow during an event, volume-weighted composite samples were collected for the one snowmelt event and 12 subsequent storm events; only two storm events were missed. Concentrations of constituents in these composite samples were multiplied by their respective volumes and summed to obtain loads due to snowmelt and stormflow; average stormflow concentrations were used for the two missed storms. Grab samples collected during non-stormflow periods (baseflow, or baseflow plus residual intermediate flow) were used to obtain average non-storm concentrations ($n = 23$ for TSS and TP; $n = 14$ for TN), which were multiplied by the remaining volume (total annual volume minus stormflow volume) to obtain loads due to non-stormflows. As a check, loads were also calculated by manually breaking the annual hydrograph into storm and non-storm periods and multiplying the volume for each period by the concentrations from individual samples collected within each period. This method gave slightly higher annual loads by 7% for TSS and TP and 1% for TN.

Because the data set for Browns Creek was much more incomplete, load calculations were much less certain. The general method was to estimate the periods of snowmelt, stormflow, and non-stormflows from the hydrograph, and to estimate representative concentrations of constituents for these periods of flow. The main problems were that the data logger missed the snowmelt period during 1998; the snowmelt samples analyzed were from 1999; and no other samples purely representative of stormflows (non-snowmelt) were collected. Hence the following methods and assumptions were used in calculating loads for Browns Creek in 1998:

¥ The 1998 hydrograph was annualized, with the assumption that gaps in the flow record were adequately represented by the characteristics of the flow record during the rest of the year.

¥ The 1998 hydrograph was separated into baseflow, intermediate flow, and quickflow components. Runoff-event periods were then defined to be those times during which quickflow constituted 20% or more of the total flow. These runoff events produced 5% of the total annual volume, which was partitioned into 1% being attributed to snowmelt, and 4% being attributed to stormflow. These assumptions were based approximately on comparable data from Valley Creek combined with results from the unit hydrograph analysis. In Valley Creek, runoff events corresponded to those times during which quickflow was about 15% or higher of total flow and accounted for 2.6% of the total annual volume, partitioned into 0.5% snowmelt and 2.1% stormflow. In comparison to Valley Creek, unit hydrograph analysis indicated that stormflow in Browns Creek should have a higher proportion of quickflow (i.e., greater than 15%) and about twice the proportional volume (i.e., about twice 0.5% and 2.1%, giving about 1% and 4% for snowmelt and stormflow, respectively), as asserted.

¥ Samples collected during 1999 were assumed to be representative of water quality during similar flow conditions in 1998.

¥ Concentrations corresponding to stormflows were not available for Browns Creek. In Valley Creek, stormflow concentrations were intermediate between snowmelt and non-stormflow concentrations. Consequently for Browns Creek, stormflow concentrations were assumed to be the average of snowmelt and non-stormflow concentrations. This assumption is probably the most serious shortcoming of the load analysis for Browns Creek and lends considerable uncertainty to the resulting conclusions.

Yields are simply loads divided by the watershed area, in theory allowing a direct comparison of land-use effects per unit area (assuming loads are not largely proportional to runoff volumes; see discussion above). However, "watershed area" can have several definitions. For constituents that are delivered to the creek via overland flow during runoff events, the most appropriate definition is the *directly contributing basin*, i.e., only that part of the landscape wherein runoff can follow a continuous downhill slope to the creek channel (at least, as determined at the scale of conventional topographic maps). However, in glacially pocked landscapes such as the watersheds of Valley and Browns creeks, topographically closed depressions are common. Though they do not contribute overland runoff, they are typically included by hydrographers in the watershed of the creek to which they would spill, should they ever flood. This type of watershed is herein referred to as the *inclusive watershed*. The inclusive watershed area for Valley Creek is 45 km^2, 36 km^2 of which is directly contributing. For Browns Creek, the inclusive watershed area is 75 km^2, 39 km^2 of which is directly contributing. A third definition of watershed, appropriate for those components transported by groundwater flow, would be the *groundwatershed*, the area of aquifer that discharges groundwater to the creek. The groundwatershed is commonly assumed to be similar to the inclusive watershed area, which seems reasonable for Browns Creek. However, as noted earlier, the groundwatershed for Valley Creek is roughly 30—80% larger than its inclusive watershed area. Most reports likely use the inclusive watershed area definition, which is a fair compromise that includes the directly contributing basin and at least some, if not all, of the groundwatershed. In this report, yields were calculated based on both directly contributing areas and inclusive watershed areas.

Suspended Solids

The annual load of TSS of Browns Creek was about 186 metric tons in 1998, about 50% higher than that of Valley Creek in 1999, despite Browns Creek having a total runoff volume about 40% lower than that of Valley Creek (Table 6). The suspended loads had a slightly higher organic content in Valley Creek (VSS about 44% of TSS) than in Browns Creek (VSS about 33% of TSS). The directly contributing area is probably the most appropriate basis for calculating yields, because suspended solids can be transported only by overland runoff. Annual yields so calculated were about 4.8 metric tons km^{-2} for Browns Creek and about 3.4 metric tons km^{-2} for Valley Creek. This difference is somewhat surprising: higher sediment yields would normally be expected for agricultural watersheds because of their greater area of disturbed and exposed soil. However, the high infiltration capacity of much of the Valley Creek watershed made overland runoff infrequent, and soil erosion was less than expected.

The distribution of TSS load among different flow regimes was very different between the two creeks. By far, most of the TSS load in Valley Creek was carried by non-stormflows (85.5%), with runoff events (storm and snowmelt) carrying only about 14.5%. In contrast, the majority (52.3%) of the TSS load in Browns Creek was carried by storm and snowmelt flows. Although part of the load during runoff events is likely from channel scour, the much greater TSS runoff-event load in Browns Creek implied a commensurately greater delivery of TSS to the creek from the watershed.

Note that the TSS load consisted primarily of particles finer than sand (particle diameters less than 62 μm). Both creeks appeared to move substantial amounts of sand as bedload, which was not measured in this study.

Phosphorus

Annual TP load was higher for Browns Creek (1,025 kg yr^{-1}) than for Valley Creek (770 kg yr^{-1}; Table 6). The fraction of the dissolved phosphorus (DP) was very similar for both watersheds, about 40% in Valley Creek and 37% in Browns Creek. Annual yields based on directly contributing watershed area were also higher in Browns Creek at 26 kg km^{-2}, versus 21 kg km^{-2} for Valley Creek.

The distribution of TP load among different flow regimes was very similar in the two creek, in contrast to TSS loads. Nearly all (88—89%) the TP load was carried during non-storm periods. Apparently the particles delivered to the creeks during storm and snowmelt events have a much lower adsorbed-P content than the particles moved during non-storm periods. Groundwater was a probably significant source of DP in both watersheds. Calculated as annual baseflow volumes multiplied by median DP concentrations in the groundwater of each watershed, the groundwater-contributed DP load was 247 kg in Valley Creek and 224 kg in Browns Creek. If the minimal bedrock-well-water concentration of 10 μg L^{-1} DP is used instead, then the groundwater delivered at least 145 kg DP to Valley Creek and 80 kg to Browns Creek. Still, most of the TP load must have originated from particulates either scoured from the channel and banks or delivered during runoff events.

Nitrogen

Annual TN load was much higher in Valley Creek (74.8 metric tons) than in Browns Creek (11.5 metric tons; Table 6), in contrast to TSS and TP loads. Because the groundwater component in the transport of nitrogen, yields were based on the inclusive watershed area, rather than the directly contributing basin. Annual yields so calculated were even more different between the watersheds, with the TN yield of Valley Creek watershed (1,661 kg km^{-2}) being more than ten times larger than that of Browns Creek watershed (153 kg km^{-2}). In both watersheds, nitrate constituted the largest component of TN (85—86%), and non-stormflows carried well over 90% of the load. Groundwater was clearly the major source of TN (as DN, including nitrate) to the creeks. In Valley Creek, the entire load could be explained by the baseflow volume multiplied by a groundwater DN concentration of 5.1 mg L^{-1}, well within the range of groundwater DN concentrations known to feed the headwater springs. In Browns Creek, baseflow volume multiplied by the rather low median groundwater DN concentration of 1.0 mg L^{-1} would result in a load of 8.0 metric tons, about 70% of the total load.

Comparisons with Other Studies: Suspended Solids and Nutrients

Concentrations and yields of TSS and TP in Valley Creek and Browns Creek (Tables 5 and 6) were generally similar to or lower than those found in other area streams. Talmage and others (1999) sampled 13 streams in the Twin Cities metropolitan area during baseflow conditions in September, 1997. TSS concentrations in their study ranged from 3 to 50 mg L^{-1}, in contrast to typical-flow means in the main branches of Valley and Browns creeks ranging from 4 to 17 mg L^{-1}. During the 1997 snowmelt season for tributaries feeding Lake St. Croix, Lenz and others (2001) found TSS concentrations ranging from 2 to 424 mg L^{-1}; in comparison, mean values for high-flow concentrations in Valley and Browns creeks fit well within this range, being from 19 to 344 mg L^{-1}. Low-flow yields for TSS calculated by Talmage and others (1999) ranged from 231 to 12,491 kg km^{-2} yr^{-1}; comparable non-storm yields were about 2,950 kg km^{-2} yr^{-1} in Valley Creek and about 2,270 kg km^{-2} yr^{-1} in Browns Creek (Table 6, from yields based on directly contributing areas, then multiplied by the percentage of load carried by non-stormflows). Total annual TSS yields in 1999 were also estimated for tributaries to Lake St. Croix by Lenz and others (2001) and ranged from 1,270 to 3,780 kg km^{-2} yr^{-1}. Yields comparably calculated based on inclusive watershed areas for Valley and Browns creeks fit about mid-way within this range.

Talmage and others (1999) found low-flow TP concentrations in the range of 20 to 190 g L^{-1}; non-storm TP concentrations in Valley Creek (19—31 g L^{-1}) fit into the lower part of this range, and those in Browns Creek (91—103 g L^{-1}) fit into the middle part. Lenz and others (2001) found TP concentrations in the range of <10 to 1,320 g L^{-1} for Lake St. Croix tributaries during snowmelt, whereas high-flow values for Valley and Browns creeks ranged from 84—427 g L^{-1}. Low-flow yields of TP calculated by

Talmage and others (1999) ranged from about 13—41 kg km^{-2} yr^{-1}; comparable non-storm yields from the watersheds of Valley Creek (about 19 kg km^{-2} yr^{-1}) and Browns Creek (about 23 kg km^{-2} yr^{-1}) were below the middle of this range. Total annual TP yields for other Lake St. Croix tributaries were estimated by Lenz and others (2001) at 6—33 kg km^{-2} yr^{-1}; comparable yields based on inclusive watershed area were 17 and 14 kg km^{-2} yr^{-1} for Valley and Browns creeks, respectively. For the St. Croix watershed as a whole, Kroening and Andrews (1997) estimated a TP yield of about 10 kg km^{-2} yr^{-1}, based on at least 10 years of data from the mouth of the St. Croix River. It is not surprising that Valley and Browns creek watersheds exceed this value, given the amount of agriculture and urbanization in their watersheds relative to the rest of the basin.

The TN concentrations followed a different pattern from that of TSS and TP, namely, Valley Creek stood out by having generally higher concentrations and yields than other area streams, whereas Browns Creek was similar to other streams. Valley Creek had TN concentrations of 2.6—6.5 mg L^{-1} during typical flow conditions, whereas Browns Creek had 1.2—1.4 mg L^{-1} and the streams Talmage and others (1999) sampled had 0.8—2.2 mg L^{-1}. Tributaries to Lake St. Croix sampled by Lenz and others (2001) during snowmelt had TN concentrations ranging from 0.3 to 5.5 mg L^{-1}, slightly exceeded by the high-flow means of the branches of Valley Creek with 2.7—5.7 mg L^{-1}. Non-storm yields of TN were even more nearly singular for Valley Creek: the non-storm TN yield for Browns Creek was about 142 kg km^{-2} yr^{-1} and those low-flow TN yields of the streams sampled by Talmage and others (1999) ranged from 64 to 730 kg km^{-2} yr^{-1}, whereas Valley Creek had a non-storm TN yield of 1,628 kg km^{-2} yr^{-1}. In terms of total annual yields, Lenz and others (2001) estimated a range of about 240 to 1,160 kg km^{-2} yr^{-1} for Lake St. Croix tributaries in 1999, and for the St. Croix basin as a whole Kroening and Andrews (1997) estimated a TN yield of 252 kg km^{-2} yr^{-1}. In contrast, Browns Creek was lower at 153 kg km^{-2} yr^{-1} and Valley Creek was again much higher at 1,661 kg km^{-2} yr^{-1} for yields based on inclusive watershed area. The exceptionally high TN yield of Valley Creek simply reflects the large amount of groundwater discharge feeding Valley Creek and its high TN concentrations (87% of which was nitrate).

Nearly direct comparisons of TSS and TP loads calculated by other were available for Valley Creek in 1999 (Lenz and others, 2001), for Valley Creek in 2001 (Champion and others, 2003) , for Browns Creek in 1998 (C. Champion, Metropolitan Council Environmental Services [MCES], written communication, August 2003), and for Browns Creek in 1999 (Lenz and others, 2001). Champion and others (2003) used daily average data and the computer program FLUX (Walker, 1986) to calculate loads, whereas Lenz and others (2001) used regression equations based on land use in the watershed to estimate loads. Yields were not comparable, because Champion and others (2003) used jurisdictional watershed-district areas as their basis for calculation, rather than either inclusive watershed areas or directly contributing areas. For Valley Creek, loads from Champion and others (2003) agreed to within about 15% of TP and TSS loads presented in this report. TP loads from Lenz and others (2001) were very similar to those in this report, but their TSS loads were about 50% higher.

Loads calculated for Browns Creek were somewhat more different among the sources. Whereas this report estimated the annual TSS load of Browns Creek to be 186 metric tons, Lenz and others (2001) estimated 280 metric tons, and Champion (MCES, written communication, 2003) estimated 597 metric tons. This report estimated the TP load of Browns Creek to be 1,025 kg yr^{-1}; Lenz and others (2001) estimated the load at 2,950 kg yr^{-1}; and Champion (MCES, written communication, 2003) estimated the load at 1,764 kg yr^{-1}. However, the values from Champion (MCES, written communication) may be overestimated (perhaps for TSS) and are considered provisional at the present time, pending further quality control analysis of the data.

Major Ions and Trace Constituents

Major ion content of environmental waters commonly results from rock-water interactions in the watershed, although human activities (such applications of road salt for de-icing) and biological activities in lakes and wetlands can alter ionic content. Major cations commonly include calcium (Ca), magnesium (Mg), sodium (Na), and sometimes potassium (K); major anions commonly include carbonate species (mostly as bicarbonate, HCO_3), chloride (Cl), and sulfate (SO_4). In this report, trace constituents refer to a suite of metals and other inorganic ions that may be associated with urbanization and roadways, and to man-made organic pesticides (herbicides or insecticides) that may be associated with either agriculture or urban turf care.

Major Ions

The chemistry of a stream is influenced by that of its source waters. Below, the major ion contents of groundwater and lakes are discussed first to lay the background for the subsequent discussion of stream water. The relative percentages of major ions, based on cation and anion charge sums, were plotted on Piper diagrams (Figures 15 and 16) to either demonstrate differences between categories determined *a priori* (groundwater and stream water), or to look for clusters to define categories *a posteriori* (lake water). Mean concentrations of categories were tabulated (Table 7) to more fully characterize differences among groups and between watersheds.

Major Ions in Groundwater

Under humid climates, groundwater commonly has higher ionic concentrations than surface waters, because the intimate contact of groundwater with a large surface area of mineral grains for long periods of time allows for dissolution of minerals to their saturation points. Other sources of water to streams and lakes (precipitation and overland runoff) tend to be more dilute than groundwater, and ionic concentrations greater than those found in groundwater often point to human activities. And so, among the source waters that are mixed together to form streamflow, groundwater is a critical end-member in determining the ionic content of stream water. Groundwater samples were categorized *a priori* according to whether they came from in-stream piezometers, Quaternary domestic wells, or bedrock wells.

In Valley Creek watershed, all groundwater sites clustered tightly with similar chemistries, with Ca and Mg making up 56% and 39%, respectively, of the cation sum (in meq L^{-1}), and HCO_3 making up about 80% of the anion sum (Figure 16a). In-stream piezometers had slightly higher Na and Cl concentrations than bedrock wells did (Mann

Whitney test, p † 0.01), possibly because of mixing of ground water and stream water in the hyporheic zone.

In Browns Creek watershed (Figure 17a), groundwater chemistries did not cluster quite as tightly as in Valley Creek watershed. Two in-stream piezometers (sites BC-5 and 6, near the headwaters of the south and north branches, respectively) stood out by having higher proportions of both Na and Cl, and the two Quaternary domestic wells (sites BC-14 and 15) stood out by having high Cl values. The two piezometers (both located at road crossings) may have been influenced by road-salt runoff, whereas the two Quaternary wells were not adjacent to roads and instead may instead have been influenced by water-softener exchange water passing through septic systems, with Na being retained in the aquifer by cation exchange.

Concentrations of Ca, Mg, HCO_3, and SO_4 in groundwater tended to be higher in Valley Creek watershed than in that of Browns Creek (Mann Whitney tests, p † 0.02 for all four variables; concentrations given in Table 7). Groundwater from bedrock wells in Valley Creek watershed had very similar concentrations of these four ions (within 2 mg L^{-1} for each ion) to median values reported in Fong and others (1998) for 25 wells in the unconfined part of the PdC/J aquifer across the Upper Mississippi basin. Groundwater from Browns Creek watershed thus appeared to be the less typical data set. The differences between Valley Creek and Browns Creek watersheds were not due to any obvious difference in geologic setting, because both watersheds have low-carbonate Superior-lobe drift overlying the same stratigraphic sequence of pre-Cambrian and Paleozoic sandstones, dolostones, and mudstones. The equilibrium concentrations of Ca, Mg, and HCO_3 (when dissolved from dolomite and calcite) are sensitive and proportional to the partial pressure of carbon dioxide in the soil atmosphere in the groundwater recharge zone (see, for example, Garrels and Christ, 1965). This partial pressure typically ranges from 10 to 100 times that of the free atmosphere (Drever, 1988); because of this variability it is not surprising to find different concentrations of carbonate-mineral components in groundwater despite similar geologic settings. Alternatively, because lakes selectively remove Ca and HCO_3 (and perhaps small amounts of Mg) by sedimentation, and as the stable isotope data demonstrated substantial influence of lake water on groundwater chemistry, the lower concentrations of Ca and HCO_3 in Browns Creek watershed may be explained by having a higher portion of its watershed covered by lakes and wetlands (about 11.5%, versus about 2.5% for Valley Creek).

Major Ions in Lake Water

As noted before, lakes are almost always net sinks for dissolved constituents (except, for example, dissolved organic carbon derived from algal photosynthesis). Lakes process inputs from groundwater, overland runoff, and atmospheric deposition; trap some components as sediment; and pass the remainder through its outflow. Sedimented components can include carbon, nitrogen, and phosphorus in dead algal cells, and calcium carbonate precipitated from the water column. Outflow may be either as a channelized surface outlet, or as diffuse seepage into a downgradient aquifer. In the following discussion, lakes were categorized *a posteriori* after plotting suggested different types of lakes: rural lakes little affected (chemically) by human activities, urban lakes substantially impacted, and lakes with an intermediate amount of impact perhaps due to proximity of highways and limited development.

Lake-water chemistry in the Valley Creek watershed did not cluster as tightly as did groundwater chemistry (Figure 15b), and the main cause of variability was in the Na and Cl contents, by inference in the impact of road-salt runoff. Rural lakes plotted in a cluster similar to that of groundwater samples, but intermediate lakes had higher percentages of Na and Cl than did either rural lakes or groundwater samples (no lakes were designated as "urban" in the Valley Creek watershed). Both rural and intermediate lakes had proportions of Ca, Mg, and HCO_3 similar to those of groundwater (Table 7). However, the concentrations were lower: compared to groundwater, concentrations in rural lakes were about 8-33% lower, and concentrations in intermediate lakes were fully 71-72% lower (the range depends on which constituent is compared). None of the intermediate lakes were in the directly contributing basin of Valley Creek. The two most impacted lakes were the tiny West and East Fahlstrom Lakes (sites VC-17 and 18), which are closed-basin lakes that are the terminus of a land-locked drainage area that includes a small residential development and extends to the I-94 corridor.

In the Browns Creek watershed, the lakes did not form an obvious cluster but plotted along a continuum depending on the amount of influence from Na and Cl (Figure 16b). Even the rural lakes were dissimilar to groundwater because of their higher Na and Cl proportions. In the urban lakes (Long Lake and Lake McKusick, BC-5 and 8), Na and Cl composed 52% and 54% of the total cation and anion sums, respectively   the only grouping in which Ca, Mg, and HCO_3 did not dominate the ionic content. The urban lakes in Browns Creek watershed also had a distinctively lower Mg:Ca ratio (0.54) than that of any other group (groundwater, lake water, or stream water in either watershed), which ranged from 0.64 to 0.78. Also as in Valley Creek, concentrations of Ca, Mg, and HCO_3 were much lower in lake water than the corresponding concentrations in groundwater, by about 74-75%.

The lower concentrations of Ca and HCO_3 in lakes relative to groundwater was due to at least two reasons. First, lakes received direct precipitation and possibly overland runoff, which are more dilute than groundwater. Second, the lakes probably precipitated calcite (a $CaCO_3$ mineral) as a consequence of pH changes in the lake caused by algal photosynthesis. This process is ubiquitous in hard-water lakes such as these and was corroborated in Lake Edith by finding carbonates in its sediment. However, this process should increase Mg:Ca ratios in lake water by preferentially removing Ca, yet the Mg:Ca ratios were not consistently higher in lake water compared to groundwater, when group mean values were used.

As with groundwater, the lake-water concentrations of Ca, Mg, and HCO_3 were lower in Browns Creek watershed than in Valley Creek watershed. Lakes in the Browns Creek watershed may be diluted in these ions by runoff from urban impervious surfaces or from soils with lower infiltration rates on steeper slopes. Certainly, the high Na and Cl concentrations in urban lakes in the Browns Creek watershed demonstrated significant input of runoff. In addition, as pointed out above, in-lake precipitation of $CaCO_3$ may lower Ca and HCO_3 concentrations in the groundwater plume downgradient from a lake, thereby diluting groundwater inputs to other lakes in this plume. In other words, lakes in the Browns Creek watershed may be more dilute in part simply because there are more of them (with a greater areal coverage) than in the Valley Creek watershed.

Major Ions in Stream Water

Stream-water samples were categorized *a priori* into either runoff-event (stormflow or snowmelt) samples where flows equaled or exceeded the 90th percentile, or typical-flow samples for all other periods. This categorization matched that used to characterize nutrient and sediment relations in the creeks.

In Valley Creek, typical-flow samples produced nearly identical clusters of ionic content to those of groundwater (Figure 15c and a), again demonstrating the strong control of groundwater discharge on the water quality of Valley Creek. Runoff events had higher percentages of Na and Cl, as expected since these samples came almost exclusively from snowmelt events. However, counterintuitively, Na and Cl concentrations were actually lower during snowmelt events — their percentages increased only because Ca, Mg, and HCO_3 were more diluted than they were. Snowmelt events in Valley Creek appeared to be influenced by runoff over frozen ground of agricultural fields spread with manure, and whether the increase in percentage of Na and Cl was due to road-salt or manure was unclear.

Typical-flow samples in Browns Creek likewise had percentages of major ions similar to those in groundwater, with only slightly higher Na and Cl levels (Figure 16c and a). The major exception was the south branch (site BC-4), with typical-flow percentages that reflected the outflow from urban Long Lake much enriched in Na and Cl. Snowmelt and storm-event samples had not only generally higher percentages of Na and Cl than typical-flow samples did, but higher concentrations as well (Table 7). In contrast, Ca, Mg, and HCO_3 were diluted during runoff events.

Stream water in Browns Creek had lower concentrations of Ca, Mg, and HCO_3 than did Valley Creek during typical-flow periods, probably for the same reason that groundwater in Browns Creek had similarly lower concentrations   however unclear that reason may be. Browns Creek had higher concentrations of Na and Cl under all conditions than did Valley Creek, presumably because of the greater influence of urbanization and roads. A distinctive contrast was that during runoff events Na and Cl concentrations decreased in Valley Creek, but increased in Browns Creek.

Inorganic Trace Constituents

A suite of 23 dissolved trace constituents was determined in 23 stream-water samples; 16 of these samples were baseflow-stormflow pairs from eight sites, and the seven remaining samples were from other sites (Table 8). Most, but not all, of these trace constituents are considered metals. Because of the small sample size, variability and hence statistical significance of differences cannot be realistically assessed, and the patterns discussed below are at most suggestions of hypotheses to be tested.

Some trace constituents appeared to have higher concentration during baseflow conditions than during runoff events: Li (lithium), Mn (manganese), Br (bromine), Sr (strontium), and U (uranium) (Table 8). With the exception of particle-reactive U, most of these constituents are fairly soluble in their ionic species. The observed pattern in concentration could be explained by these constituents being delivered to the streams mostly by groundwater discharge, and being diluted during runoff events.

Most other trace constituents apparently had higher concentrations during runoff events than during baseflow conditions: Al (aluminum), B (boron), Ba (barium), Cd (cadmium), Cs (cesium), Cu (copper), Fe (iron), Mo (molybdenum), Pb (lead), Rb (rubidium), Ti (titanium), W (tungsten), and Zn (zinc) (Table 8). These elements are commonly speciated as particle-reactive cations sequestered in the soil zone and transported to streams by overland runoff that not only carries soil particles but also desorbs some of their bound cations. Of these, Al, Cd, Cu, Pb, and Zn were higher in Valley Creek than in Browns Creek, whereas Fe was higher in Browns Creek than in Valley Creek (Figure 17). No good hypothesis was formulated to explain why Valley Creek, with its generally rural watershed, should have higher concentrations of these metals than did Browns Creek, which has a greater urban component in its watershed. Perhaps these metals are, for some reason, more prevalent in fertilizer or manure applications to the agricultural landscape of Valley Creek. The reader is reminded that our sample size is small.

Organic Pesticides

Eleven samples from Valley Creek and one from Browns Creek were screened for a suite of 26 organic pesticides by the Minnesota Department of Agriculture (Table 9). These pesticides were categorized according to their chemistries as being either base neutral or acid herbicides. No pesticides were detected in the one sample from Browns Creek or the sample from one of the source-water ponds feeding Valley Creek. Most other samples from Valley Creek had detectable levels of base-neutral pesticides, the most common being atrazine and its metabolite deethyl-atrazine (DEA). Their levels (0.05 to 0.12 g L^{-1}) were well below the maximum contaminant level of 3 g L^{-1} set for atrazine. Acetochlor and metolachlor were also commonly suspected or detected but at concentrations too low to be reliably quantified by the screening method. Only one sample, from North Branch Valley Creek, had detectable levels of an acid herbicide, in this case 2,4-D.

Atrazine is widely used across the Midwestern corn belt and is known to be used in the Valley Creek watershed. In Minnesota, atrazine is usually applied in May, and its concentration in runoff commonly peaks with the first major storm event following application. For example, under such conditions Schottler and others (1994) found peak concentrations of about 1—2 g L^{-1} in the Minnesota River. Valley Creek was not sampled under similar conditions for organic pesticides, and so its peak concentrations of atrazine and DEA are as yet unknown. In the Minnesota River, baseflow values of atrazine were about 0.02—0.065 g L^{-1} (Schottler and others, 1994), similar to baseflow values found in Valley Creek. Stormflow concentrations of atrazine and DEA were slightly higher than baseflow concentrations in Valley Creek, but these storms were too small to deliver significant amounts of overland runoff from the basin. The small sample size precluded testing the statistical significance of the difference between baseflow and stormflow concentrations.

Atrazine degrades to DEA rather quickly in the soil zone, but much more slowly in the deeper subsurface, including aquifers. Over time, the DEA-to-atrazine ratio (DAR) tends to increase, as the parent compound degrades into DEA. In Valley Creek, the DAR ranged from 1.25 to 1.67, with an average of 1.53. This was much larger than the baseflow DAR values of about 0.45 found by Schottler and others (1994) in the Minnesota River and suggested a longer travel time in Valley Creek watershed between point of application and discharge. Because Valley Creek is largely fed by groundwater discharge, a longer travel time might be expected compared to the Minnesota River, which has many drainage ditches and subsurface tiles that short-circuit the travel path between fields and the river.

Under baseflow conditions Schottler and others (1994) found that the DAR in the Minnesota River increased slowly over time according to the following model:

$$DAR_t = DAR_0 * e^{tk}$$

where DAR_t = the deethyl-atrazine:atrazine ratio at time t; DAR_0 = the initial DAR (at time zero); t = time in days; and k = 0.0016 day^{-1}, the transformation rate constant. Because Schottler and others (1994) measured DAR in surface waters that may have continued to receive subsurface-tile inputs even during baseflow conditions, the rate constant for the transformation in a deeper aquifer may be substantially smaller (yielding a much slower increase in DAR). If one assumes a DAR_0 of 0.05 to 0.37 (as found in the Minnesota River study), then to reach a DAR of about 1.5 (as found in Valley Creek) would require about 2.4 to 5.8 years. These values likely underestimate the true groundwater travel time in the Valley Creek watershed for two reasons. First, as noted above, the rate constant k is likely overestimated for the hydrologic setting of Valley Creek. Second, because Valley Creek (like most streams) likely receives a mixture of different groundwater ages, even small amounts of "young" groundwater with a low DAR would bias the resulting mixed sample to have a much younger calculated "age" than a true volume-weighted average age. In short, these biases make these travel-time estimates based on the DAR most likely too short, and hence do not contradict the estimated typical Valley Creek groundwater travel times determined from modeling and radioisotope considerations to be on the order of decades.

SUMMARY AND CONCLUSIONS

Physical Hydrology

In their physical hydrologic characteristics, Valley Creek and Browns Creek were generally similar, but with some slight differences that may be attributable to urbanization. Both streams were influenced strongly by groundwater, as shown by annual runoff volumes of both streams being dominated by baseflow (92% for Valley Creek; 87% for Browns Creek). In Valley Creek, this groundwater derived from bedrock aquifers (the Prairie du Chien dolostone, and the Jordan sandstone to the degree that it is hydraulically connected). In contrast, most (about 75%) of the groundwater feeding Browns Creek derived from Quaternary deposits; the remaining 25% discharged in the final 2-km reach as the creek descends its gorge through the Prairie du Chien dolostone and other units. In Valley Creek, the recharge area (groundwatershed) covered at least 60 km^2 and possibly more, considerably larger than, and extending to the north and west of, the surficial watershed. The annual average recharge over this area would have been 24 cm to produce the observed annual baseflow volume. In Browns Creek, the groundwatershed also appeared to cover about 60 km^2, slightly smaller than its surficial watershed, with an annual recharge of 13 cm needed to produce the observed baseflow volume. Recharge in the Valley Creek groundwatershed was larger than is typical in the Twin Cities region because of the high infiltration capacity of its soils. Recharge in the Browns Creek groundwatershed was about typical, with no evidence that urbanization has reduced recharge in any measurable way. Lakes were not shown (nor disproven) to be sites of focused (disproportionately increased) recharge. However, stable isotope analysis indicated substantial exchange of lake and groundwater, as many (nearly half) of the groundwater samples had some component of water that had been influenced by evaporation. Even though groundwater is presumed to derive from infiltration of snowmelt and spring rain, no groundwater sample was nearly as light (depleted in ^{18}O and D) as snowmelt samples were. Tritium analyses showed that essentially all the water in the Valley Creek system was younger than 50 years old, including the deeper aquifers such as the Jordan and Franconia-Ironton-Galesville. Most water samples from the Browns Creek watershed were also younger than 50 years, though results were more variable spatially. Tritiated (and therefore young) water penetrated into the Jordan aquifer near the upgradient divide of the Browns Creek groundwatershed, even though a nearby Prairie du Chien well was devoid of tritium, as was a Jordan well near the watershed mouth.

Quickflow constituted only 3% of the annual volume of Valley Creek and 4% of that of Browns Creek, similar percentages despite the greater perceived urban component in the Browns Creek watershed. Both creeks peaked about 1.5 hours after a rainfall pulse; the rapidity and volume of this peak indicated the source area to be the creek channel and immediately adjacent area. However, Browns Creek had a secondary peak that occurred about 6.25 hr after the rainfall pulse, which was hypothesized to derive from urban runoff delayed by being routed through drainage structures, possibly including Long Lake at the southern end of the watershed. To clarify the influence of land cover differences between the two watersheds on rainfall-runoff relations, unit hydrographs were constructed for each creek, thereby normalizing for differences in precipitation and size of the effective contributing area. Per unit rainfall and per unit area, Browns Creek produced a peak quickflow about 1.35 times larger than Valley Creek. This difference in peak quickflow increased even more (doubled) when contributing area was factored back in, because the contributing area for Browns Creek was about twice that of Valley Creek per unit rainfall, Browns Creek peak quickflow was 2.7 times that of Valley Creek and had double the total volume of quickflow runoff. These differences are consistent with the known effects of urbanization on runoff response of watersheds.

The intermediate flow component was also larger in Browns Creek, constituting 9% of the annual volume, versus only 5% of that in Valley Creek. Peaks in intermediate flows and contributing areas were larger by about a factor of five in Browns Creek relative to Valley Creek. The timing and volume of intermediate flow suggested that it derived from in-channel and floodplain storage areas adjacent to each creek (which would include water delivered to these areas from other parts of the watershed during storm events). However, the intermediate flow component was not as precisely characterized as the baseflow and quickflow components.

Suspended Solids and Nutrients

Suspended solids concentrations and loads were generally similar to or less than other area streams. Browns Creek total suspended solids (TSS) loads were estimated in this report to be 185 metric tons for 1998, with a yield of 4.8 metric tons km^{-2} of directly contributing basin. For the same period, using different methods and a slightly different data set, the Metropolitan Council estimated TSS loads to be 597 metric tons, for a yield of 15.3 metric tons km^{-1}. Either way, the load is greater than that of Valley Creek, estimated at 124 metric tons for 1999, with a yield of 3.4 metric tons km^{-2}. The difference is surprising only in that TSS yields would normally be expected to be larger in an agricultural basin than in an urban basin; however, the Valley Creek watershed has so little overland runoff and sheet erosion that it has an unusually small TSS load. The creeks were different in the source and timing of TSS transport. Most of the TSS load in Valley Creek came from the two tributary branches under baseflow conditions (presumably from channel scour), and sediment was deposited in the main stem below the confluence. In contrast, TSS concentrations increased greatly in the main stem gorge of Browns Creek below the confluence of its two main tributaries, and most of the load at the mouth was carried by stormflows. This suggests that stormwater inputs to the main stem of Browns Creek either carried significant TSS loads or caused scour of channel and bank sediments.

As with TSS, total phosphorus (TP) concentrations and loads were generally similar to or less than other metropolitan area streams. The TP load for Browns Creek was estimated at about 1,025 kg, with a yield of 26 kg km^{-2} from the directly contributing basin; the Metropolitan Council estimated the load at 1,764 kg, for a yield of 45 kg km^{-2}. A smaller TP load was estimated for Valley Creek at 770 kg, with a yield of 21 kg km^{-2}. A somewhat surprising result was that nearly 90% of the TP load in each creek was carried by non-stormflows. In both creeks, the dissolved phosphorus (DP) component was important, composing 49% of the load in Valley Creek and 35% in Browns Creek. While particulate phosphorus, either delivered to or scoured from the channels, was the main source of TP to the creeks, groundwater could have delivered a significant portion of the annual TP load, about 32% in Valley Creek and 22% in Browns Creek.

Total nitrogen concentrations and yields were much higher in Valley Creek than those in Browns Creek, which were similar to those in other metropolitan area streams. The TN load for Valley Creek was about 74.8 metric tons, with a yield of 1,661 kg km^{-2} over the inclusive watershed area. In Browns Creek, the TN load was estimated at 11.5 metric tons, with a yield of 153 kg km^{-2}. In both creeks, most (about 85%) of the TN was in the form of nitrate, and most (about 90%) was carried during non-storm periods of flow. Groundwater was by far the largest contributor of nitrogen (as DN, largely nitrate) to the creeks, about 70% for Browns Creek and at least that much for Valley Creek, based on baseflow volumes and representative DN concentrations in groundwater. The creeks responded differently to storm events: in Browns Creek TN concentrations in baseflow and stormflow samples were similar, whereas in Valley Creek stormflow samples had distinctly lower TN concentrations than baseflow samples because of dilution by quickflow.

Major Ions and Trace Constituents

In both creeks, waters were generally of the Ca-Mg-HCO_3 type, and under typical (non-storm) conditions concentrations in stream water were very similar to those in groundwater, as expected for creeks receiving such direct discharge of groundwater. However, waters of all types (groundwater, lake water, and stream water) were slightly more dilute in the Browns Creek watershed with respect to these major ions. Groundwater from Valley Creek had concentrations of Ca, Mg, and HCO_3 similar to those reported in other studies for the Prairie du Chien-Jordan aquifer; hence, the more dilute waters from the Browns Creek watershed appeared to be the exception. While many factors can affect the concentrations of these ions, the greater coverage of lakes and wetlands in the Browns Creek watershed was hypothesized to be a cause of the reduced concentrations because lakes can trap these ions by precipitation of calcite (and low-Mg calcite).

Browns Creek had generally higher concentrations of Na and Cl, presumably from applications of salt to roads and urban pavements. The ion balances of two urban lakes in the Browns Creek watershed vicinity were dominated by Na and Cl: Long Lake, which feeds South Branch Browns Creek, and Lake McKusick. During snowmelt, concentrations of Na and Cl increased in Browns Creek, but decreased in Valley Creek, indicating roadway and urban runoff into Browns Creek and dilution by non-urban meltwater in Valley Creek.

A few samples were screened for trace metals and organic pesticides in each watershed. In both creeks, most trace metals had higher concentrations during stormflows than during baseflow conditions. Concentrations tended to be higher in Valley Creek than in Browns Creek, notably for Cd, Cu, Pb, and Zn. No pesticides were found in the one sample from Browns Creek. Atrazine and its metabolite deethyl-atrazine were found in most samples from Valley Creek, though far below the maximum contaminant level. Concentrations were comparable to those found in baseflow in the Minnesota River, though the ratio of deethyl-atrazine to atrazine suggested a longer travel time between application and emergence in the stream.

Conclusions

Valley Creek has remained a fine trout stream, mostly because its flow is so dominated by groundwater discharge (producing nearly twice the baseflow of Browns Creek), with virtually no overland runoff delivering eroded sediment to the stream except during extreme events. The waters have remained equably cool and the streambed sufficiently coarse to support the macroinvertebrate food base and spawning habitat required by trout. The pollution of its waters with excessive nitrogen from agricultural activities has apparently had little impact on the macrobiota, though it has negative implications for the receiving water, Lake St. Croix. Recent evidence indicates that Valley Creek was not always such good habitat, and that in the early part of the 20th century it delivered significant quantities of sediment to the St. Croix as a consequence of agricultural activities, especially those in its immediate valley floor (L. Triplett, Univ. of Minnesota, personal communication, 2003). The restoration of its riparian zone to wooded vegetation in the last 50 years, along with improved agricultural practices, has been an important component in reducing erosion and siltation, providing shade, and creating woody debris all of which improve the habitat for trout as well as protecting the receiving water from excessive loadings of sediment and phosphorus. Protection of Valley Creek hinges primarily on three goals: (1) minimize inputs of overland runoff, which could warm the stream, (2) minimize erosional inputs, which could alter streambed substrate required for macroinvertebrates and spawning trout, and (3) maintain the quantity of groundwater-dominated baseflow, which keeps the stream equably cool and can gradually flush out any fine sediment delivered during runoff events.

Browns Creek has been, and can be, a good trout stream along some of its reaches, especially in the lower gorge where groundwater adds 25% to its flow and the riparian zone is wooded and shady. The relatively urbanized South Branch, with its headwaters in Long Lake, certainly adds sediment loads and increases summertime temperatures, both of which degrade trout habitat. Plans by the City of Stillwater to divert stormflows from the South Branch out of the watershed and into Lake McKusick should help reduce sediment loads to the Browns Creek (and to the St. Croix); baseflows may still be allowed to enter Browns Creek, and would still be warmer than optimal for trout during summer, but would help maintain streamflow. The lessons learned at Valley Creek should be applicable to the protection and restoration of Browns Creek: (1) minimize overland stormflow inputs, by diversion if necessary or by infiltration if possible; (2) decrease erosional inputs, by stormwater control and by restoration of the riparian zone; and (3) maintain the dominance of baseflow by groundwater discharge, rather than by release of lake water. Reduction of summertime outflow from Long Lake, if possible, would help reduce temperatures and sediment loading. The outflow is better reduced at the lake outlet rather than downstream, because then groundwater discharge to the South Branch could contribute cool baseflow to the main stem. In particular, sediment delivered or mobilized by urban stormwater inputs to the mainstem should be addressed, as this reach appeared to be a major contributor of the sediment output load from Browns Creek.

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TABLES

Table 1. Land use in Valley Creek and Browns Creek watersheds, 1996.

		(a) Valley Creek			
Category	Land Use	North Branch 20.45 km²	South Branch 20.26 km²	Main Stem 4.32 km²	Basin Total 45.03 km²
Inactive	Water/Wetland	5.18%	0.26%	0.51%	2.52%
	Forest	27.71%	23.96%	67.87%	29.87%
	Grassland	24.99%	18.62%	16.38%	21.30%
Disturbed	Cropland	28.51%	43.64%	3.79%	32.95%
	Mining/Pit	0.48%		0.20%	0.24%
Developed	Lawn	7.89%	9.80%	5.66%	8.54%
	Urban, pervious				
	Impervious	5.24%	3.72%	5.59%	4.59%
	Total	*100%*	*100%*	*100%*	*100%*

		(b) Browns Creek			
Category	Land Use	North Branch 43.18 km²	South Branch 26.07 km²	Main Stem 5.54 km²	Basin Total 74.79 km²
Inactive	Water/Wetland	13.65%	7.02%	8.66%	11.47%
	Forest	21.21%	22.40%	20.01%	21.03%
	Grassland	26.30%	21.95%	28.60%	24.95%
Disturbed	Cropland	21.49%	17.44%	2.58%	18.68%
	Mining/Pit	0.17%	0.72%		0.35%
Developed	Lawn	13.07%	15.36%	28.59%	15.02%
	Urban, pervious		3.06%	0.41%	1.10%
	Impervious	4.11%	12.05%	11.15%	7.40%
	Total	*100%*	*100%*	*100%*	*100%*

NOTES: Data from D. Pitt and R. Bell, University of Minnesota, personal communication (1999).

Table 2. Sample sites and tally in Valley Creek watershed, 1997-99.
Primary sites shaded

Site	UTM Coordinates Easting (m)	Northing (m)	Water Type	Samples (n)	Site Name
1	515716	4973941	stream	163	**Primary site:** South Branch VC at Stagecoach Rd.
1			groundwater	5	Piezometer -- at site 1
2	515705	4974625	stream	137	**Primary site:** North Branch VC near Stagecoach Rd.
3	513196	4973291	stream	18	West Branch VC at Valley Creek Trail (intermittent)
4	513039	4972426	stream	6	South Branch VC at 30th St. (intermittent)
5	516890	4973620	stream	86	**Primary site:** Mainstem VC at Putnam Blvd.
5			groundwater	1	Piezometer -- at site 5
6	515212	4975402	lake	6	Lake Edith
7	514726	4976285	lake	5	Metcalf Pond (outlet)
7			groundwater	1	Piezometer -- at site 7
8	513821	4973229	stream	5	West Branch VC at confluence with South Branch
9	513850	4973193	stream	5	South Branch VC at confluence with West Branch
10	513955	4977130	stream	1	Northeast inlet to Metcalf Pond (intermittent)
11	510819	4973975	stream	1	West Branch VC near Manning (intermittent)
12	513231	4973233	groundwater	3	Piezometer -- West Branch VC at Valley Creek Trail
13	513420	4972816	lake	7	Smith Reservoir
14	513416	4972866	groundwater	4	Piezometer -- South Branch VC below reservoir
15	513420	4972904	stream	2	South Branch VC below reservoir
16	512133	4972426	stream	2	West tributary to South Branch VC at Neal Ave.
17	512610	4976523	lake	2	West Fahlstrom Pond
18	512822	4976484	lake	2	East Fahlstrom Pond
19	515973	4974507	lake	2	Belwin classroom pond
20	516229	4975188	lake	2	Belwin north pond
21	510964	4979550	lake	2	Horseshoe Lake
22	511356	4975780	lake	2	Fahlstrom wetland
23	507665	4979743	groundwater	1	Lake Elmo Park well
24	510576	4974606	groundwater	1	Alberg well
25	511859	4973742	groundwater	1	Dunbar well
26	511194	4973914	groundwater	1	Kruse well
27	513680	4973336	groundwater	1	Scanlon well
28	516168	4974423	groundwater	1	Belwin shop well
29	514281	4973436	stream	1	South Branch VC at Milano residence
30	515287	4973752	stream	1	South Branch VC at Hornickel residence
31	511683	4973639	stream	1	West Branch VC at hwy 22 (intermittent)
32	512431	4973570	stream	1	West Branch VC at Neal Ave. (intermittent)
33	513768	4973291	stream	1	Bahnemann's gully (intermittent)
34	513500	4973095	lake	1	Cliff-base pond
35	513512	4973103	groundwater	1	Piezometer -- Cliff-base pond
36	513401	4973023	groundwater	1	Piezometer -- Main spring-source pond
37	513451	4973153	lake	1	Main pond at Smith residence
38	515059	4973806	groundwater	1	Spring at Snyder residence
39	515976	4973949	groundwater	1	Boiling spring, South Branch VC at Belwin
40	516713	4973672	groundwater	1	Wetland seep along Mainstem VC, above Putnam Blvd.
			Total samples	*488*	

NOTES:
Abbreviations: VC, Valley Creek; UTM, Universal Transverse Mercator; m, meters; n, number of samples.
Sample tally per water type: 431 stream samples; 32 lake samples; 25 groundwater samples.
Samples refer to the total sample set collected for basic water-quality variables, including field variables, nutrients, and suspended sediment.
Smaller subsets of these samples were analyzed for other variables, such as major ions, trace metals, isotopes, and organic pesticides.

Table 3. Sample sites and tally in Browns Creek watershed, 1997-99.
Primary sites shaded

	UTM Coordinates				
Site	Easting (m)	Northing (m)	Water Type	Samples (n)	Site Name
1	515077	4991377	stream	14	**Primary site:** Mainstem BC at hwy 95 (mouth)
1			groundwater	2	Piezometer -- at site 1
2	513351	4991392	stream	14	Mainstem BC above Stonebridge Trail
2			groundwater	1	Piezometer -- at site 2
3	512192	4991009	stream	14	**Primary site:** North Branch BC at McKusick Rd.
3			groundwater	2	Piezometer -- at site 3
4	512161	4990711	stream	13	**Primary site:** South Branch BC at RR track
4			groundwater	2	Piezometer -- at site 4
5	512134	4989433	lake	14	Long Lake (outlet)
5			groundwater	1	Piezometer -- at site 5
6	509872	4995016	stream	9	North Branch BC at hwy 68
6			groundwater	1	Piezometer -- at site 6
7	508398	4997687	lake	2	Goggins Lake
8	514087	4989628	lake	2	Lake McKusick (outlet)
9	506978	4999659	lake	2	Lake Plaisted
10	508540	4995356	lake	2	Benz Lake
11	508421	4994322	lake	2	Pat Lake
12	507622	4991677	lake	2	Lake Masterman
13	512063	4991508	lake	2	South Twin Lake
14	508980	4996119	groundwater	1	Kemp well
15	506141	4993783	groundwater	1	Livesay well
16	507275	4994788	groundwater	1	Erickson well
17	506126	4993897	groundwater	1	Hubman well
18	514111	4991436	groundwater	1	Sinclair well
19	514902	4991214	groundwater	1	O'Laughlin well
20	512334	4990826	stream	2	Mainstem BC at Neal Ave.
			Total samples	*109*	

NOTES:
Abbreviations: BC, Browns Creek; UTM, Universal Transverse Mercator; m, meters; n, number of samples; RR, railroad
Sample tally per water type: 66 stream samples; 28 lake samples; 15 groundwater samples
Samples refer to the total sample set collected for basic water-quality variables, including field variables, nutrients, and suspended sediment. Smaller subsets of these samples were analyzed for other variables, such as major ions, trace metals, isotopes, and organic pesticides.

Table 4. Tritium (bold) and nitrate (square brackets) contents of groundwater and stream water in the Valley Creek and Browns Creek groundwatersheds, 1998-99.

(a) VALLEY CREEK

Stream or Aquifer	***Recharge Zone***		***Discharge Zone***			
Stream				**11.6** [2.5] (VC-2)	**12.0** [6.4] (VC-1)	**12.7** [4.5] (VC-5)
Quaternary			**12.7** [9.3] (VC-12)	**13.3** [0.8] (VC-14)	**15.3** [1.7] (VC-1-GW)	
St. Peter	absent	**11.8** [6.7] (VC-24)	absent	absent	absent	absent
Prairie du Chien	**25.3** [6.2] (VC-23)	**11.4** [5.2] (VC-25)			absent	absent
Jordan		**7.8** [4.0] (VC-26)		**5.9** [4.0] (VC-27)	absent	absent
Franconia/ Ironton-Galesville					**14.0** [0.1] (VC-28)	

(b) BROWNS CREEK

Stream or Aquifer	***Recharge Zone***		***Discharge Zone***			
Stream				**10.3** [1.2] (BC-3)	**12.6** [1.0] (BC-4)	**11.9** [1.1] (BC-1)
Quaternary	**9.5** [1.7] (BC-15)		**3.1** [1.2] (BC-14)	**18.7** [1.2] (BC-3-GW)	**7.8** [0.3] (BC-4-GW)	**3.2** [0.8] (BC-1-GW)
St. Peter			absent	absent	absent	absent
Prairie du Chien	**<0.8** [0.6] (BC-16)		absent	absent	absent	absent
Jordan	**19.9** [2.0] (BC-17)				**3.0** [0.2] (BC-18)	**<0.8** [0.8] (BC-19)

NOTES:
¥ Tritium (**bold**) given in tritium units (TU). All tritium data are from 1999. Average standard deviation due to counting error was 0.94 TU (range 0.4-1.8 TU). Groundwater age interpreted as follows: TU < 1 implies water older than about 50 years; TU > 1 implies water younger than about 50 years or of mixed age.
¥˚Nitrate [square brackets] given in mg/L as N. Data for Quaternary wells and streams are from 1998-99; data for bedrock wells are from 1999. Stream values are for typical baseflow conditions (middle 80% of flows).
¥ Site identification (see Figures 1 and 2) given in parentheses.
¥ Sites arranged approximately from upgradient to downgradient end of assumed flow path, where possible.
¥ Absence of bedrock units estimated from Mossler and Blomgren (1990) for local area near each sample site.

Table 5. Concentrations of suspended solids, total phosphorus, and total nitrogen for typical and high flows in the main branches of Valley Creek and Browns Creek, 1998-99.

	TSS (mg L^{-1})		**TP** (g L^{-1})		**TN** (mg L^{-1})	
	Typical Flow	High Flow	Typical Flow	High Flow	Typical Flow	High Flow
			VALLEY CREEK			
North Branch, VC-2	*$p < 0.001$*		*$p < 0.001$*		*$p = 0.11$*	
Mean	**13**	**43**	**31**	**84**	**2.6**	**2.7**
Median	8	28	25	74	2.3	2.8
IQR	*10*	*63*	*16*	*68*	*1.1*	*0.9*
(N)	(101)	(20)	(80)	(19)	(81)	(18)
South Branch, VC-1	*$p < 0.001$*		*$p < 0.001$*		*$p < 0.001$*	
Mean	**5**	**170**	**19**	**427**	**6.5**	**5.7**
Median	3	27	17	382	6.6	5.6
IQR	*5*	*192*	*10*	*721*	*0.6*	*1.3*
(N)	(95)	(50)	(84)	(41)	(84)	(41)
Main Stem mouth, VC-5	*$p < 0.001$*		*$p = 0.002$*		*$p = 0.29$*	
Mean	**4**	**19**	**30**	**103**	**4.5**	**4.3**
Median	3	9	21	47	4.4	4.4
IQR	*2*	*12*	*16*	*41*	*0.7*	*0.9*
(N)	(64)	(28)	(53)	(27)	(42)	(12)
			BROWNS CREEK			
North Branch, BC-3	*$p = 0.12$*		*$p = 0.01$*		*$p = 0.01$*	
Mean	**13**	**101**	**91**	**174**	**1.4**	**2.4**
Median	10	96	88	138	1.3	2.0
IQR	*5*	*143*	*51*	*83*	*0.4*	*1.0*
(N)	(10)	(3)	(10)	(3)	(9)	(3)
South Branch, BC-4	*$p = 0.02$*		*$p = 0.09$*		*$p = 0.09$*	
Mean	**17**	**142**	**98**	**265**	**1.4**	**1.9**
Median	10	66	99	240	1.3	1.7
IQR	*10*	*243*	*43*	*306*	*0.6*	*1.0*
(N)	(9)	(3)	(8)	(5)	(8)	(4)
Main Stem mouth, BC-1	*$p = 0.01$*		*$p = 0.01$*		*$p = 0.07$*	
Mean	**10**	**344**	**103**	**366**	**1.2**	**2.1**
Median	9	421	96	266	1.1	2.1
IQR	*9*	*371*	*31*	*381*	*0.5*	–
(N)	(10)	(3)	(8)	(3)	(6)	(1)

NOTES: TSS, total suspended solids; TP, total phosphorus; TN, total nitrogen; IQR, interquartile range; N, number of samples; p, 1-tailed alpha error, the probability of incorrectly rejecting the null hypothesis of no difference between typical and high-flow values, according to the Mann-Whitney test. Typical flow refers to flows below the 90th percentile for that year; high flow refers to flows at or above the 90th percentile for that year.

Table 6. Loads and yields of suspended solids, phosphorus, and nitrogen exported by Valley Creek in 1999 and Browns Creek in 1998.

	Load		Yield				Percent Carried by Different Periods of Flow		
			Inclusive Watershed Area		Directly Contributing Area		Non-storm	Storm	Snowmelt
(a) VALLEY CREEK, 1999									
Area basis for calculating yields -->			*45*	*km²*	*36*	*km²*			
TSS	**124,142**	**kg/yr**	**2,759**	**kg/km²/yr**	**3,448**	**kg/km²/yr**	85.5%	4.2%	10.3%
Inorganic	*68,887*	*" "*	*1,531*	*" "*	*1,914*	*" "*			
Organic (VSS)	*55,255*	*" "*	*1,228*	*" "*	*1,535*	*" "*			
TP	**770**	**kg/yr**	**17**	**kg/km²/yr**	**21**	**kg/km²/yr**	88.9%	3.2%	7.9%
Particulate	*464*	*" "*	*10*	*" "*	*13*	*" "*			
Dissolved	*306*	*" "*	*7*	*" "*	*9*	*" "*			
TN	**74,756**	**kg/yr**	**1,661**	**kg/km²/yr**	**2,077**	**kg/km²/yr**	98.0%	1.5%	0.5%
Particulate	*1,794*	*" "*	*40*	*" "*	*50*	*" "*			
Nitrate-N	*64,698*	*" "*	*1,438*	*" "*	*1,797*	*" "*			
Residual dissolved	*8,264*	*" "*	*184*	*" "*	*230*	*" "*			
Runoff	15,826,288	m^3/yr	35	cm/yr	44	cm/yr	97.4%	2.1%	0.5%
(b) BROWNS CREEK, 1998									
Area basis for calculating yields -->			*75*	*km²*	*39*	*km²*			
TSS	**185,694**	**kg/yr**	**2,476**	**kg/km²/yr**	**4,761**	**kg/km²/yr**	47.7%	35.2%	17.1%
Inorganic	*125,258*	*" "*	*1,670*	*" "*	*3,212*	*" "*			
Organic (VSS)	*60,436*	*" "*	*806*	*" "*	*1,550*	*" "*			
TP	**1,025**	**kg/yr**	**14**	**kg/km²/yr**	**26**	**kg/km²/yr**	88.2%	8.5%	3.3%
Particulate	*641*	*" "*	*9*	*" "*	*16*	*" "*			
Dissolved	*384*	*" "*	*5*	*" "*	*10*	*" "*			
TN	**11,491**	**kg/yr**	**153**	**kg/km²/yr**	**295**	**kg/km²/yr**	93.0%	5.3%	1.7%
Particulate	*1,180*	*" "*	*16*	*" "*	*30*	*" "*			
Nitrate-N	*9,708*	*" "*	*129*	*" "*	*249*	*" "*			
Residual dissolved	*603*	*" "*	*8*	*" "*	*15*	*" "*			
Runoff	9,230,332	m^3/yr	12	cm/yr	24	cm/yr	95.0%	4.0%	1.0%

NOTES: TSS, total suspended solids; VSS, volatile suspended solids; TP, total phosphorus; TN, total nitrogen. "Directly contributing area" encompasses only those areas with a direct drainage network to the creek; "inclusive watershed area" includes not only the directly contributing area, but also adjacent topographically closed depressions that would drain to the creek should they flood. Storm and snowmelt periods correspond to times when quickflow exceeded about 15% of total flow in Valley Creek and about 20% of total flow in Browns Creek; non-storm flow periods correspond to times of lower flows.

Table 7. Concentrations of major ions in groundwater, lake water, and stream water in the watersheds of Valley Creek and Browns Creek, 1998-99.

Water Type	Number of Sites	Cations			Anions		
		Ca, mg/L	**Mg**, mg/L	**Na**, mg/L	**HCO_3**, mg/L	**Cl**, mg/L	**SO_4**, mg/L
(a) VALLEY CREEK							
Groundwater	**13**	**60.5**	**25.7**	**5.8**	**233**	**13.2**	**16.3**
Bedrock	7	63.1	24.3	3.9	211	8.0	17.6
In-stream piezometers	6	58.2	26.8	7.5	253	17.7	15.2
Lake Water	**10**	**38.0**	**16.4**	**9.1**	**155**	**20.9**	**8.1**
Rural	6	52.0	22.4	7.1	210	18.2	11.2
Intermediate	4	17.0	7.3	12.0	73	24.9	3.3
Stream Water	**17**	**37.6**	**15.6**	**5.2**	**157**	**12.3**	**10.8**
Typical flows	6	64.0	26.9	6.2	256	15.8	16.7
High flows	11	23.1	9.5	4.7	102	10.4	7.5
(b) BROWNS CREEK							
Groundwater	**12**	**49.4**	**21.0**	**9.2**	**214**	**14.2**	**8.4**
Bedrock	4	52.8	21.5	4.2	206	4.1	6.8
In-stream piezometers and Quaternary wells	8	47.7	20.7	11.7	218	19.3	9.2
Lake Water	**9**	**12.5**	**5.0**	**13.2**	**55**	**21.5**	**1.8**
Rural	3	11.7	4.7	3.3	56	5.3	0.8
Intermediate	3	12.7	5.9	9.7	55	18.6	2.0
Urban	3	13.0	4.2	26.5	55	40.6	2.5
Stream Water	**9**	**33.2**	**13.1**	**9.6**	**146**	**18.3**	**7.1**
Typical flows	5	38.0	14.7	9.1	163	17.6	6.5
High flows	4	27.3	11.1	10.2	125	19.3	7.7

NOTES: Ca, calcium; Mg, magnesium; Na, sodium; HCO_3, bicarbonate; Cl, chloride; SO_4, sulfate; mg/L, milligrams per liter or parts per million. High flows are those at or above the 90th percentile; typical flows are all other flows. For each site, median values were computed for each variable; for each grouping above, this table presents the means of these medians, giving equal weight to each site. The number of sites presented in this table does not match those given in Tables 2 and 3 because not all incidental samples were analyzed for major ions, and because high-flow, typical-flow, and groundwater samples from the same geographic site were considered as functionally different sites in the above summary.

Table 8. Concentrations of inorganic trace constituents in Valley Creek and Browns Creek, 1998-99.
[values in micrograms per liter, or parts per billion (ppb)]

Site ID	Site Name	N	Flow Regime	Al	As	B	Ba	Br	Cd	Co	Cr	Cs	Cu	Fe	Li	Mn	Mo	Ni	Pb	Rb	Se	Sr	Tl	U	W	Zn
	VALLEY CREEK SITES																									
VC-01	South Branch	2	base	2.49	0.55	13.69	30.18	35.59	0.07	0.15	0.88	0.009	0.64	3.11	2.06	6.43	0.60	2.54	0.05	0.77	1.24	72.97	0.17	1.12	0.65	7.03
VC-01	South Branch	1	event	139.95	0.81	28.23	42.13	10.09	0.11	0.22	0.89	0.011	3.16	163.32	0.63	4.21	0.24	1.99	0.13	2.93	1.07	28.80	0.01	0.17	0.00	11.15
VC-02	North Branch	2	base	1.35	0.48	15.50	36.90	36.90	0.05	0.15	0.98	0.005	0.59	0.70	2.56	4.30	0.35	1.70	0.05	0.62	1.02	74.77	0.08	1.08	0.23	8.74
VC-02	North Branch	1	event	1.59	0.60	12.63	26.12	37.70	0.04	0.16	1.11	0.013	0.42	1.60	2.19	5.88	0.59	1.64	0.06	0.54	1.32	70.07	0.25	1.11	0.83	9.86
VC-03	West Branch (int)	1	event	68.07	0.95	27.67	41.82	14.53	1.56	0.23	0.48	0.017	5.90	78.13	0.10	1.34	0.78	2.23	0.25	3.53	0.38	27.43	0.31	0.06	0.92	26.52
VC-04	South Branch at 30th (int)	1	event	238.19	0.45	44.47	58.93	18.33	0.08	0.42	0.65	0.019	5.21	152.86	0.19	2.76	1.12	3.64	0.15	1.58	0.89	32.28	0.08	0.06	0.26	10.74
VC-05	Mainstem (mouth)	1	base	1.76	0.33	13.84	32.66	31.05	0.05	0.16	0.63	0.001	0.96	4.64	1.88	14.32	0.41	1.79	0.06	0.73	0.41	73.71	0.06	1.07	0.19	5.61
VC-05	Mainstem (mouth)	1	event	28.23	0.83	21.94	52.29	20.60	0.15	0.18	0.46	0.015	2.52	69.09	0.59	1.28	0.72	1.85	0.22	2.37	0.73	32.14	0.28	0.26	0.88	11.09
VC-10	NE inlet to Metcalf Marsh (int)	1	event	143.81	0.56	25.20	33.92	5.81	0.26	0.11	0.45	0.008	4.34	122.99	0.07	2.65	0.41	0.98	0.29	1.80	0.23	24.79	0.11	0.03	0.39	101.47
VC-11	West Branch at Manning (int)	1	event	231.75	1.20	25.59	51.89	16.20	0.47	0.12	0.87	0.027	7.36	151.47	0.19	2.90	0.88	2.17	0.39	1.28	0.18	19.26	0.24	0.05	0.92	35.63
	Average, grand			85.72	0.68	22.87	40.68	22.68	0.29	0.19	0.74	0.012	3.11	74.79	1.05	4.61	0.61	2.05	0.16	1.61	0.75	45.62	0.16	0.50	0.53	22.79
	Average, baseflow			1.86	0.45	14.34	33.25	34.51	0.06	0.15	0.83	0.005	0.73	2.82	2.17	8.35	0.45	2.01	0.05	0.70	0.89	73.82	0.10	1.09	0.36	7.13
	Average, event flow			121.65	0.77	26.53	43.87	17.61	0.38	0.21	0.70	0.016	4.13	105.64	0.57	3.00	0.68	2.07	0.21	2.00	0.68	33.54	0.18	0.25	0.60	29.50
	Maximum			238.19	1.20	44.47	58.93	37.70	1.56	0.42	1.11	0.027	7.36	163.32	2.56	14.32	1.12	3.64	0.39	3.53	1.32	74.77	0.31	1.12	0.92	101.47
	Maximum, Site			VC-04	VC-11	VC-04	VC-04	VC-02	VC-03	VC-04	VC-02	VC-11	VC-11	VC-01	VC-02	VC-05	VC-04	VC-04	VC-11	VC-03	VC-02	VC-02	VC-03	VC-01	VC-11	VC-10
	BROWNS CREEK SITES																									
BC-01	Mainstem (mouth)	1	base	2.02	0.79	12.05	32.41	24.22	0.03	0.18	0.37	0.010	0.56	87.09	2.19	46.06	0.55	1.41	0.06	0.58	0.00	71.79	0.17	0.77	0.79	7.53
BC-01	Mainstem (mouth)	1	event	30.24	0.81	15.99	38.92	20.68	0.10	0.19	0.63	0.012	1.91	234.17	1.33	34.08	0.57	1.37	0.23	1.34	0.34	44.63	0.28	0.49	0.81	14.34
BC-02	Mainstem (Stonebridge)	1	base	54.67	0.90	15.53	48.87	20.12	0.04	0.25	0.18	0.007	0.83	108.40	2.44	110.00	0.29	1.42	0.18	0.69	0.19	74.62	0.06	0.85	0.20	9.93
BC-02	Mainstem (Stonebridge)	1	event	42.34	0.78	15.38	35.49	17.39	0.13	0.20	0.52	0.004	2.16	289.94	1.46	47.11	0.37	1.24	0.20	1.56	0.56	45.56	0.09	0.46	0.20	10.58
BC-03	North Branch	1	base	2.46	0.71	13.50	33.84	22.08	0.06	0.17	0.17	0.008	0.29	103.97	2.61	40.66	0.46	1.37	0.07	0.52	0.05	67.58	0.16	0.76	0.83	8.87
BC-03	North Branch	1	event	22.19	0.65	15.18	35.55	22.27	0.07	0.17	0.62	0.011	0.99	236.52	1.74	56.88	0.55	1.41	0.37	1.40	0.30	52.24	0.24	0.58	0.75	8.13
BC-04	South Branch	1	base	4.57	1.06	17.18	40.74	24.80	0.01	0.24	0.12	0.005	0.44	54.47	2.25	166.23	0.30	1.56	0.07	0.69	0.79	79.01	0.05	1.06	0.21	8.85
BC-04	South Branch	1	event	49.73	0.90	19.91	44.19	18.42	0.14	0.22	0.52	0.005	2.14	568.26	0.96	122.38	0.31	1.37	0.24	2.83	0.39	40.33	0.11	0.33	0.22	13.54
BC-05	Long Lake (outlet)	1	base	4.63	0.90	25.30	37.11	18.32	0.02	0.08	0.19	0.003	0.81	23.47	0.50	2.99	0.16	0.50	0.12	1.43	0.00	37.05	0.12	0.00	0.33	13.88
BC-05	Long Lake (outlet)	1	event	126.11	0.99	26.89	47.31	15.33	0.21	0.12	0.62	0.015	3.99	118.94	0.36	8.76	0.54	0.87	0.22	1.30	0.00	20.88	0.31	0.03	0.91	21.70
BC-06	North Branch at hwy 68	1	base	2.60	0.56	11.74	28.68	19.98	0.02	0.17	0.15	0.004	0.35	105.19	2.50	62.64	0.25	1.29	0.12	0.45	0.57	74.21	0.06	0.34	0.20	7.29
	Average, grand			31.05	0.82	17.15	38.46	20.33	0.08	0.18	0.37	0.008	1.32	175.49	1.67	63.44	0.40	1.25	0.17	1.16	0.29	55.26	0.15	0.51	0.50	11.33
	Average, baseflow			11.83	0.82	15.88	36.94	21.59	0.03	0.18	0.20	0.006	0.55	80.43	2.08	71.43	0.34	1.26	0.10	0.73	0.27	67.38	0.10	0.63	0.43	9.39
	Average, event flow			54.12	0.83	18.67	40.29	18.82	0.13	0.18	0.58	0.009	2.24	289.56	1.17	53.84	0.47	1.25	0.25	1.69	0.32	40.73	0.20	0.38	0.58	13.66
	Maximum			126.11	1.06	26.89	48.87	24.80	0.21	0.25	0.63	0.015	3.99	568.26	2.61	166.23	0.57	1.56	0.37	2.83	0.79	79.01	0.31	1.06	0.91	21.70
	Maximum, Site			BC-05	BC-04	BC-05	BC-02	BC-04	BC-05	BC-04	BC-01	BC-05	BC-05	BC-04	BC-03	BC-04	BC-01	BC-04	BC-03	BC-04	BC-04	BC-04	BC-05	BC-04	BC-05	BC-05

NOTES: BC, Browns Creek; hwy, highway; int, intermittent; N, number of samples; VC, Valley Creek. Site names abbreviated in this table; for full site names see Tables 2 and 3. For site locations, see Figures 1 and 2.

Table 9. Organic pesticide detections and concentrations in Valley Creek and Browns Creek watersheds, 1999.

Date and Time	Flow Conditions	Detection: Base Neutrals	Detection: Acid Herbicides	Concentrations (µg/L): Atrizine (Atr)	Concentrations (µg/L): Deethyl-atrazine (DEA)	DEA:Atr Ratio (DAR)
(a) VALLEY CREEK						
Site 1: South Branch						
18-May-1999 06:00	baseflow	D	ND	suspect	0.08	
11-Jun-1999 01:00	storm	D	ND	0.08	0.12	1.50
11-Jun-1999 04:00	storm	D	ND	0.07	0.11	1.57
11-Jun-1999 05:00	storm	D	D	0.07	0.11	1.57
Site 2: North Branch						
18-May-1999 06:00	baseflow	D	ND	0.05	0.08	1.60
06-Jun-1999 05:00	storm	D	ND	0.06	0.1	1.67
06-Jun-1999 16:00	storm	ND	ND	suspect		
06-Jun-1999 22:00	storm	D	ND	0.08	0.1	1.25
11-Jun-1999 02:00	storm	D	ND	suspect	0.11	
11-Jun-1999 04:00	storm	ND	ND			
Site 37: Main pond, Smith res.						
14-Jun-1999 13:30	na	ND	ND			
(b) BROWNS CREEK						
Site 1: Mainstem (mouth)						
14-Jun-1999 12:00	baseflow	ND	ND			

NOTES: D, detect; ND, non-detect; suspect, probably present; µg/L, micrograms per liter. See Figures 1 and 2 for site locations. Base neutrals pesticides included acetochlor, alachlor, atrazine, chlorpyrifos, chlorothalonil, cyanazine, deethyl-atrazine, deisopropyl-atrazine, diazinon, dimethoate, EPTC, fonofos, malathion, metolachlor, metribuzin, methyl-parathion, pendimethalin, phorate, terbufos, and trifluralin. Acid herbicides included 2,4-D, dicamba, dichlorprop, MCPA, MCPP, and triclopyr. Minimum reporting limits ranged from 0.05 to about 0.2 µg/L. Maximum contaminant level for atrazine is 3 µg/L.

FIGURES

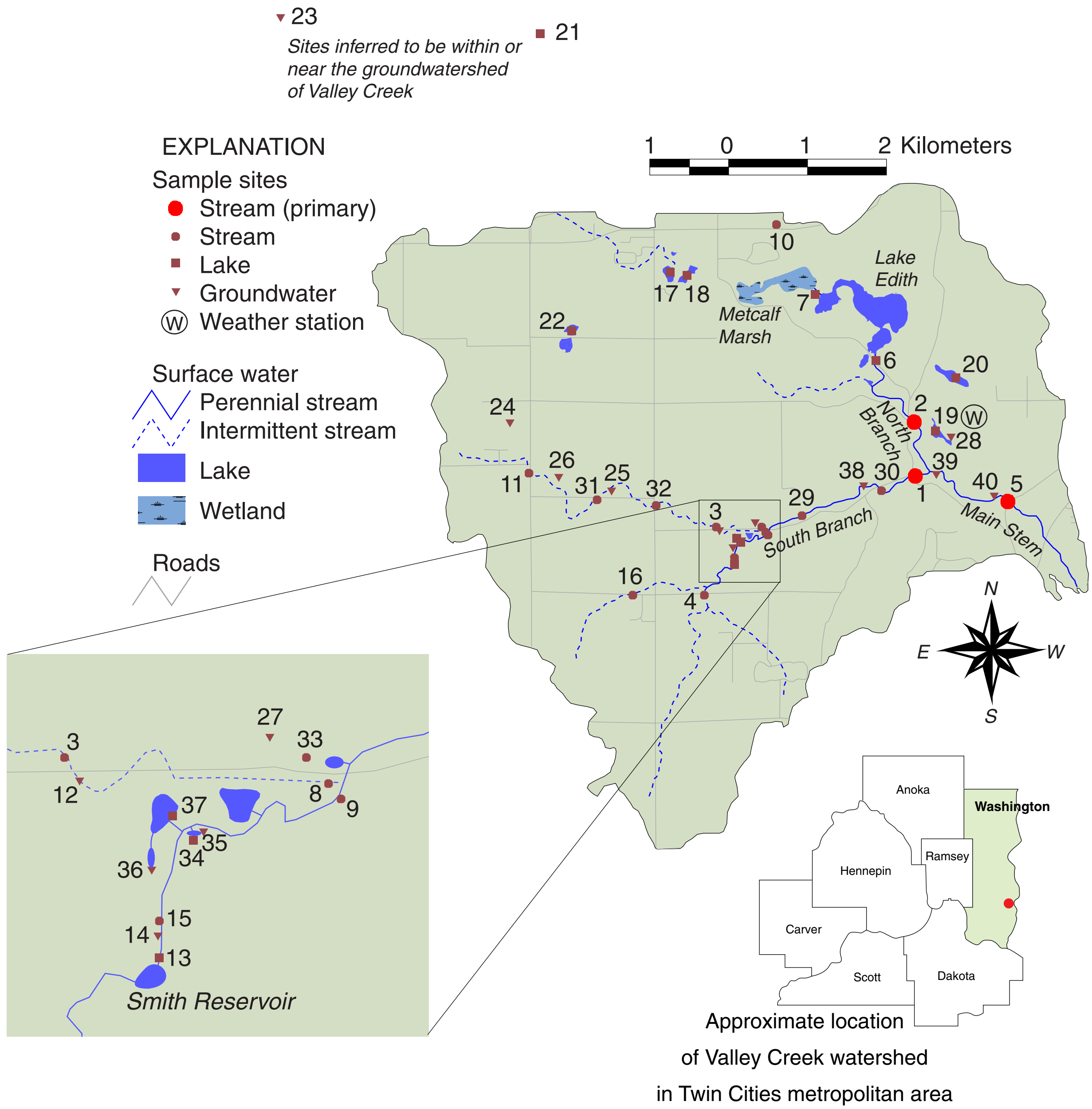


Figure 1.--Valley Creek watershed and sampling sites, 1997-99

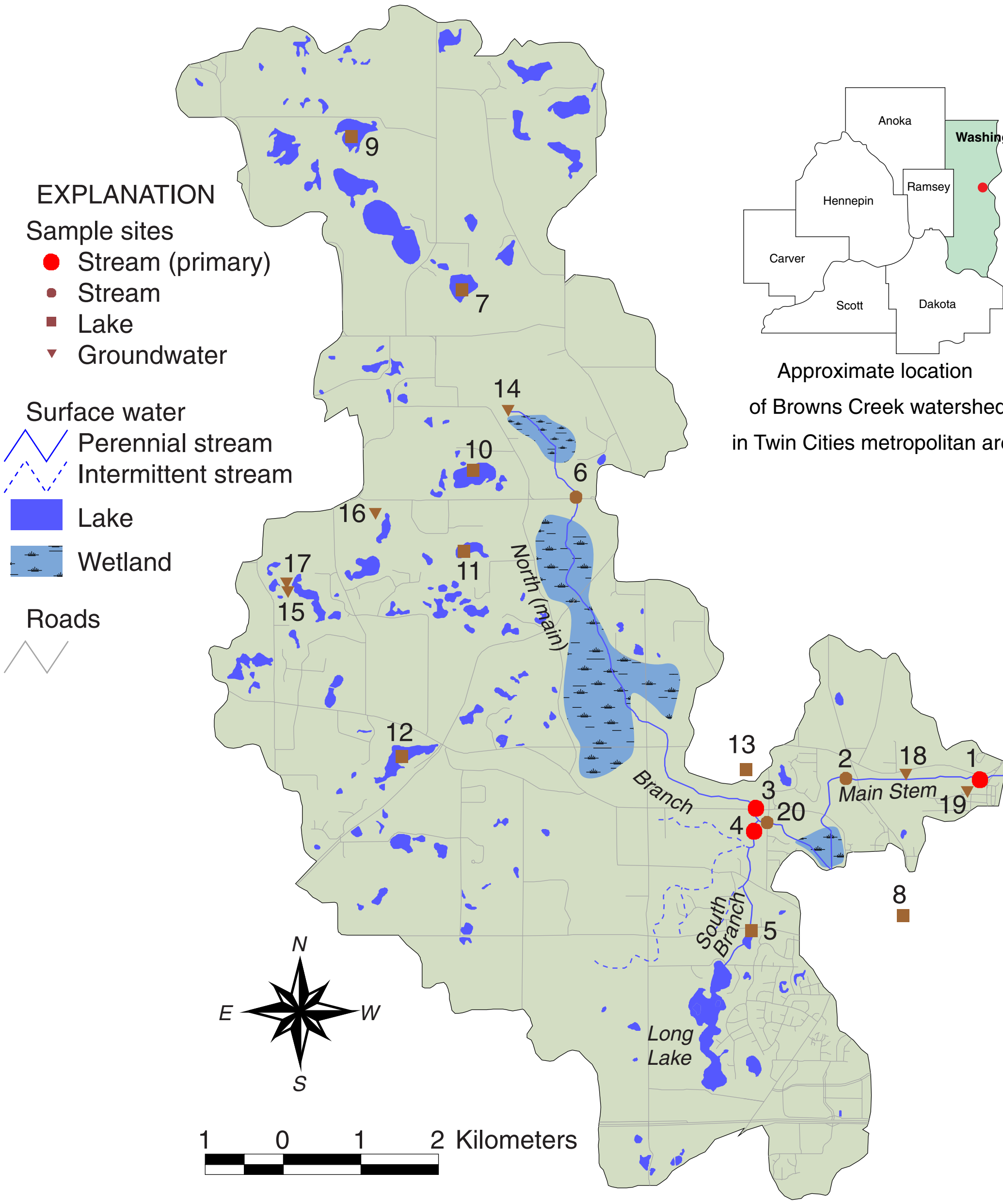


Figure 2.--Browns Creek watershed and sampling sites, 1997-99

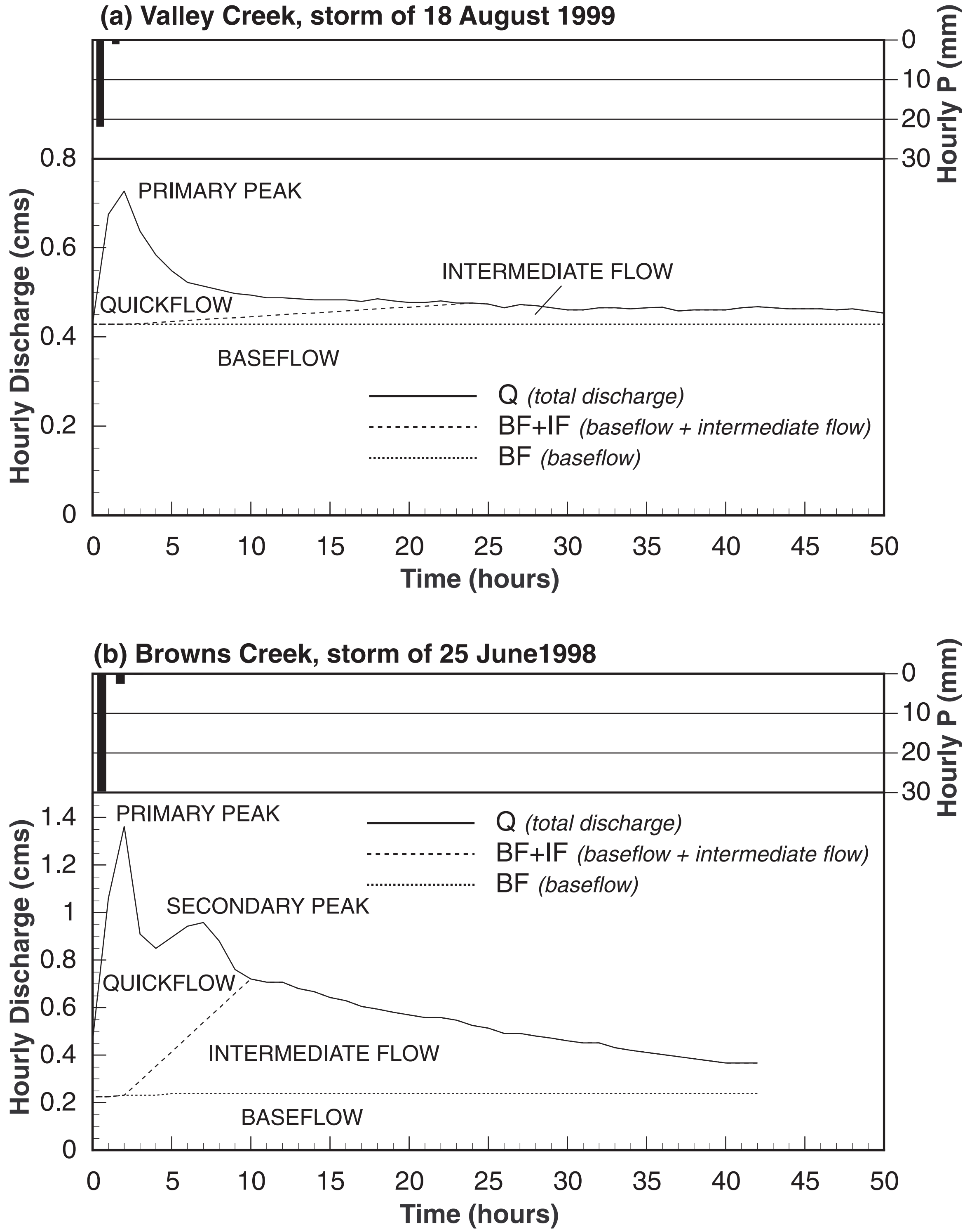
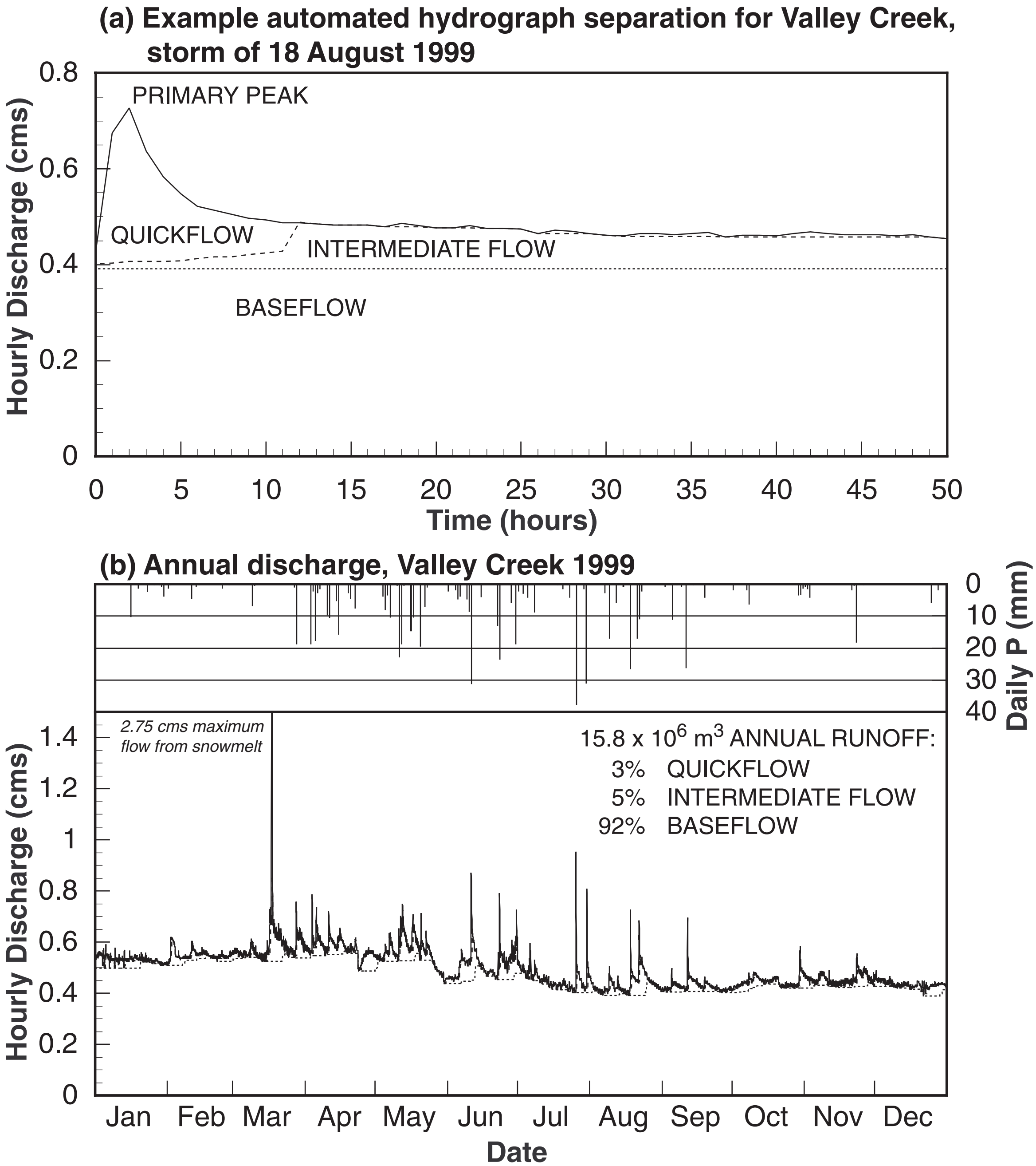


Figure 3.--Example stormflows and manual hydrograph separations, Valley Creek and Browns Creek, 1998-99



EXPLANATION

—— BF + IF + QF = Q   - - - - BF + IF   ········ BF

NOTES

Units: cms, cubic meters per second; m, meters; mm, millimeters

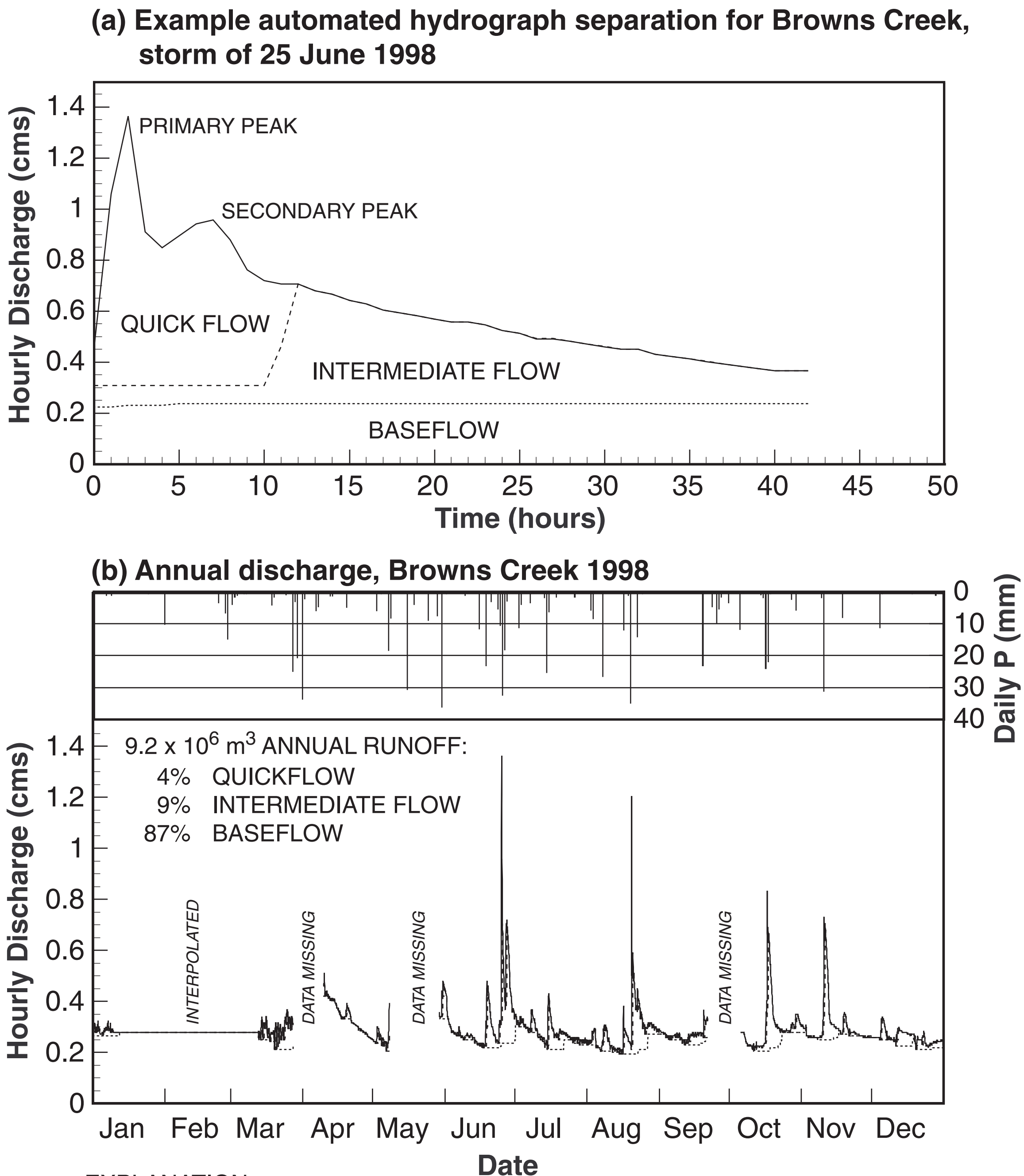
Q, total discharge; BF, baseflow; IF, intermediate flow; QF, quickflow; P, precipitation

BF determined as hourly running minimum of previous 7 days.

BF + IF determined as hourly running minimum of previous 12 hours.

P from Belwin Center weather station, 1 km northwest of gauging station.

Figure 4.--Discharge at mouth of Valley Creek, 1999



EXPLANATION

—— BF + IF + QF = Q   - - - - - BF + IF   ········· BF

NOTES

Units: cms, cubic meters per second; m, meters; mm, millimeters

Q, total discharge; BF, baseflow; IF, intermediate flow; QF, quickflow; P, precipitation

BF determined as hourly running minimum of previous 7 days.

BF + IF determined as hourly running minimum of previous 12 hours.

P from SCWRS weather station, 13 km north of gauging station.

Figure 5.--Discharge at mouth of Browns Creek, 1998

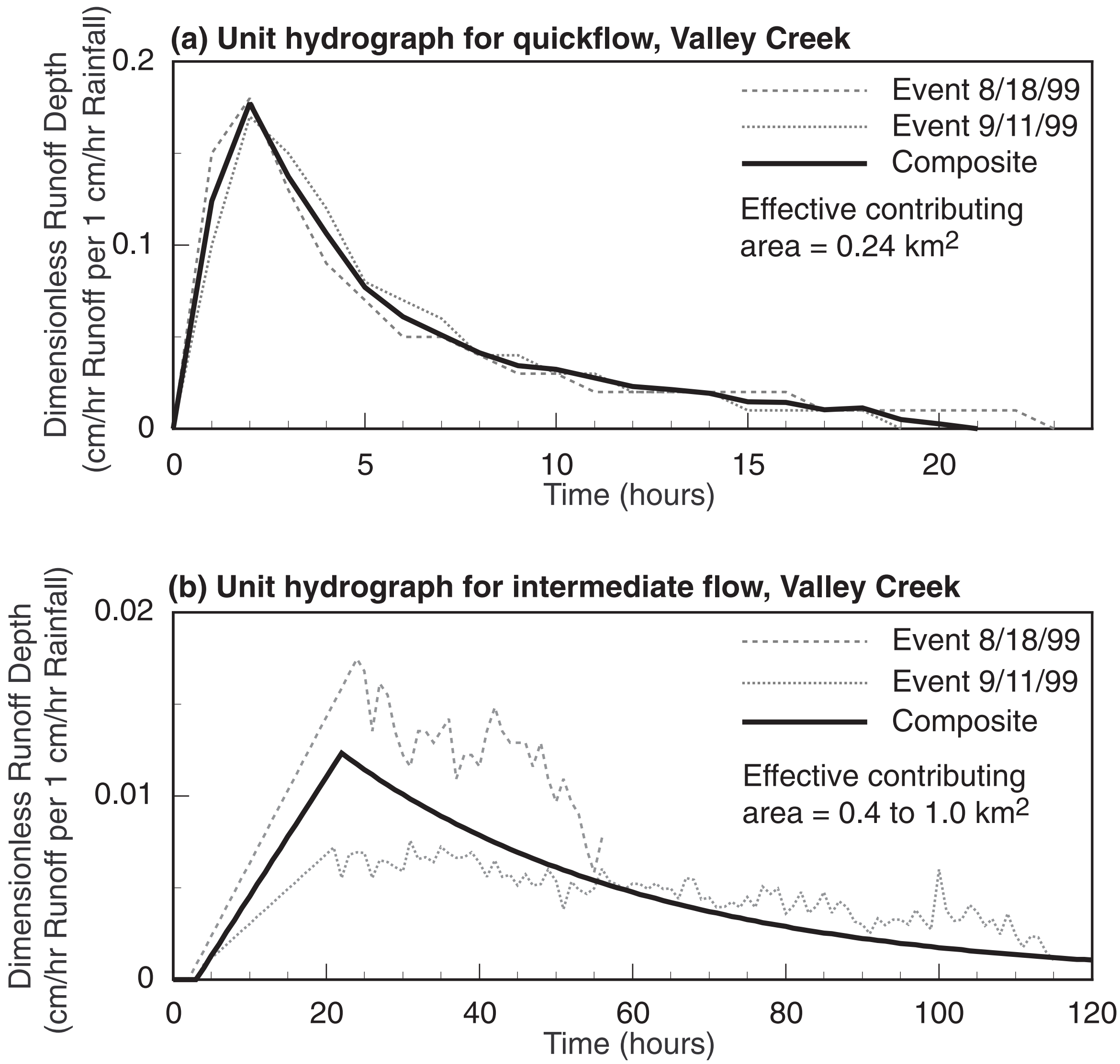


Figure 6.--Unit hydrographs for quickflow and intermediate flow at mouth of Valley Creek, 1999

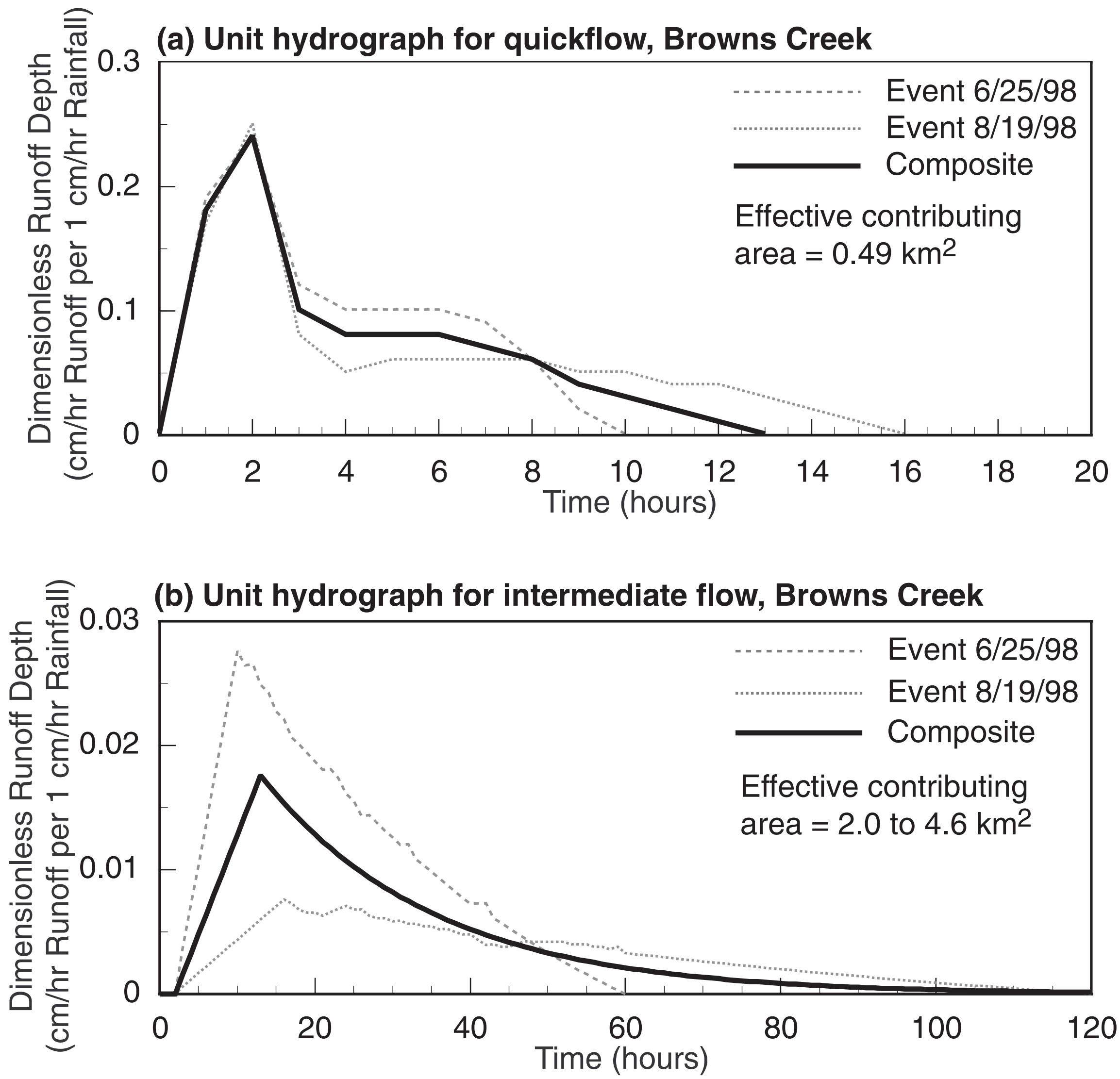
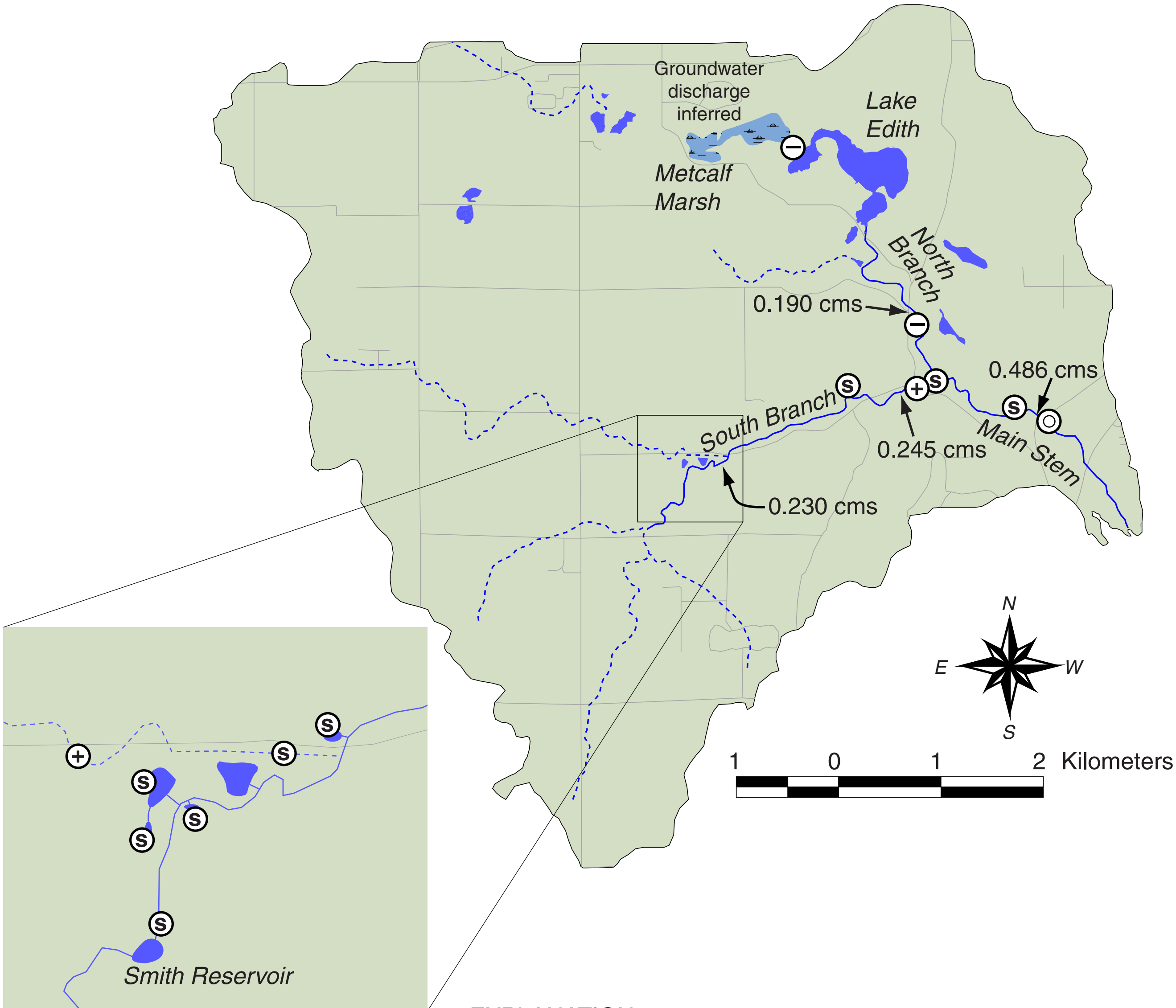


Figure 7.--Unit hydrographs for quickflow and intermediate flow at mouth of Browns Creek, 1998



EXPLANATION

Ⓢ Spring
⊕ Piezometer with positive head (groundwater seeping into stream)
⊖ Piezometer with negative head (water seeping out of stream)
◎ Piezometer with small or ambiguous head (little groundwater interaction)
← Median stream flow, 1999

For base map symbol interpretation, see Figure 1

Figure 8.--Valley Creek local stream/groundwater interactions and incremental stream flows, 1999

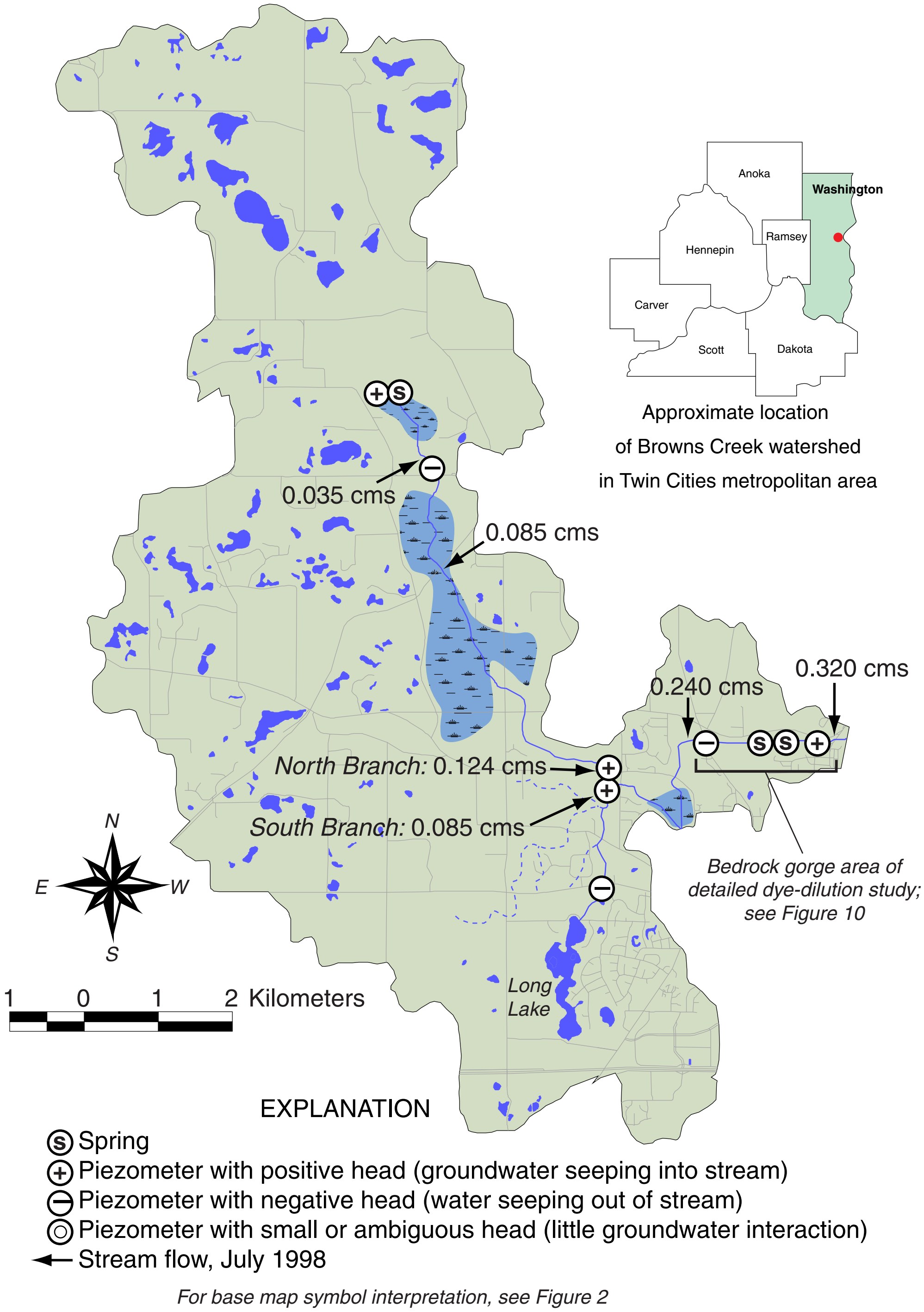
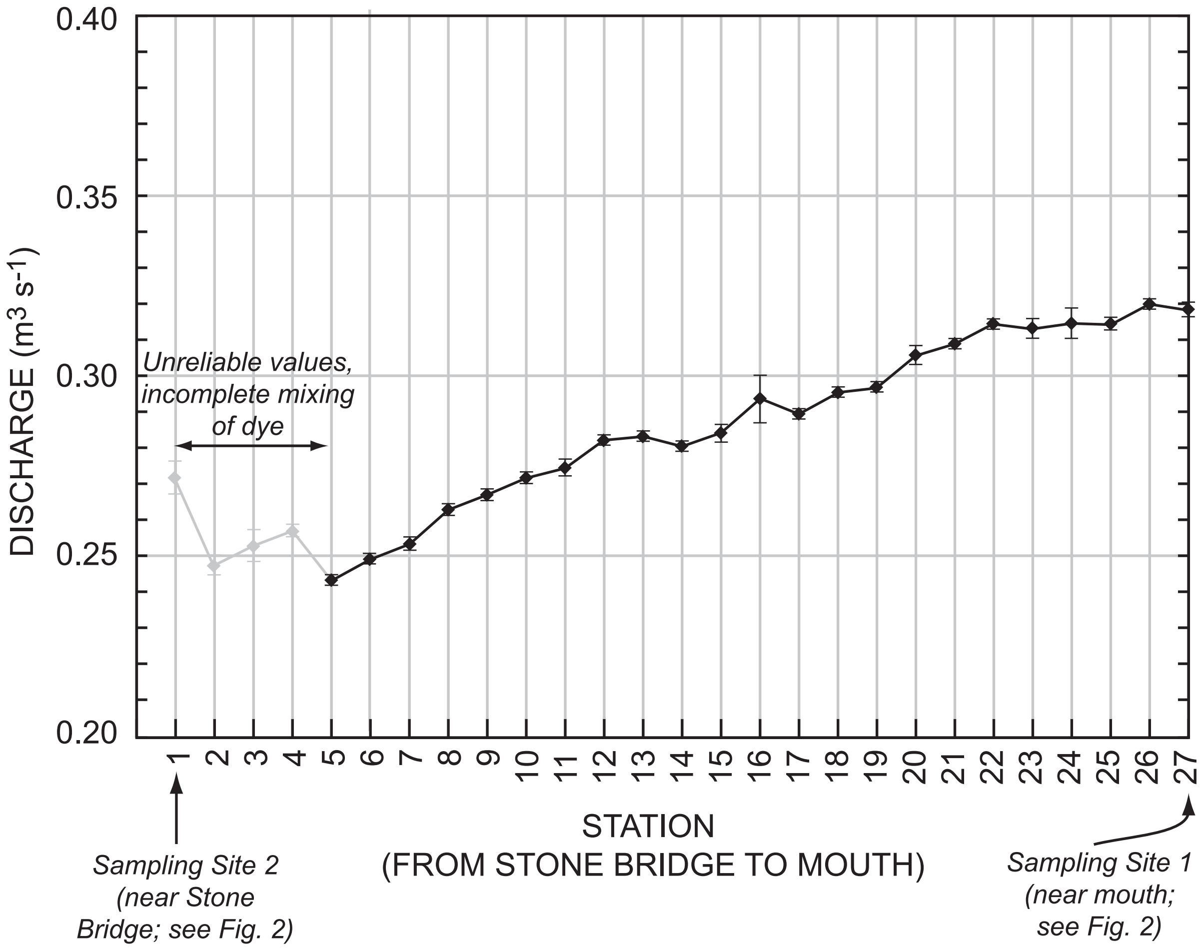


Figure 9.--Browns Creek local stream/groundwater interactions and incremental stream flows, 1998



NOTES:

- Discharge determined by dye-dilution method
- Small decreases in flow not feasibly detectable by this method and must be due to small errors
- Error bars show range of three samples
- Sampling stations were about 75 m apart
- Flow increased about 0.08 $m^3 s^{-1}$ from station 5 to 27, or about 0.0048 $m^3 s^{-1}$ per 100 m

Figure 10.--Incremental discharge along lowermost reach of Browns Creek, 17 July 1998

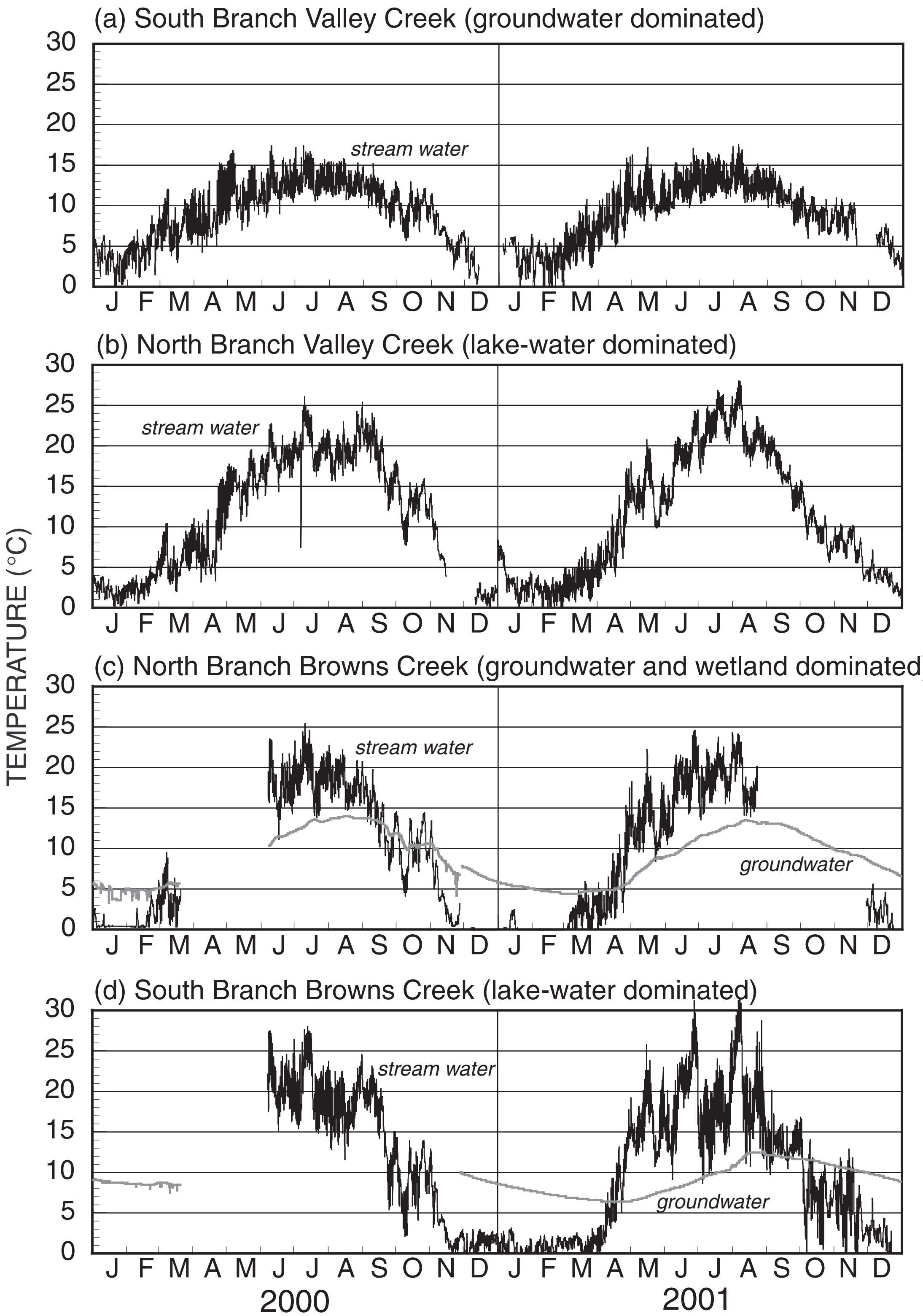


Figure 11--Water temperatures in Valley Creek and Browns Creek, 2000-01

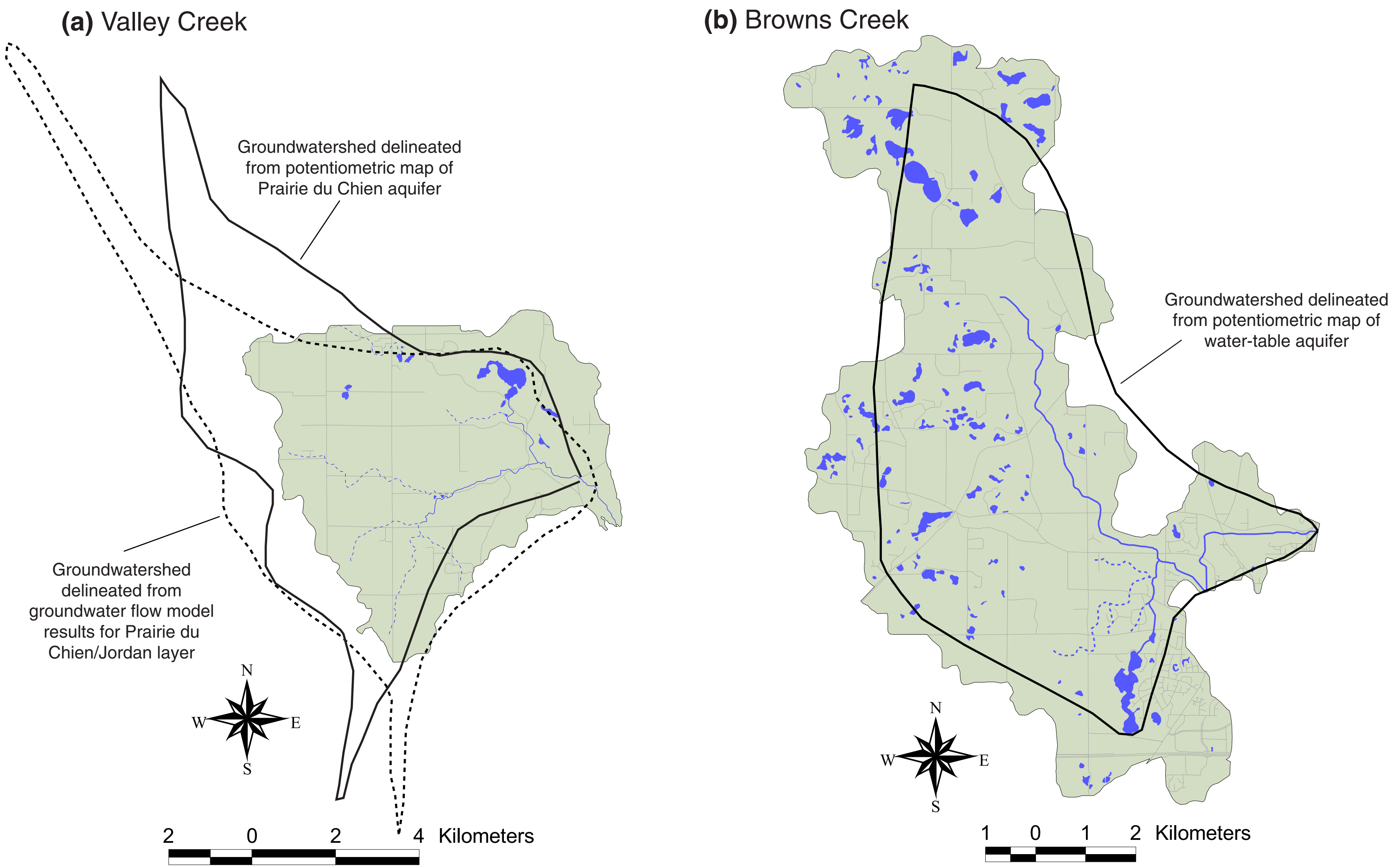


Figure 12.--Groundwatersheds of Valley Creek and Browns Creek

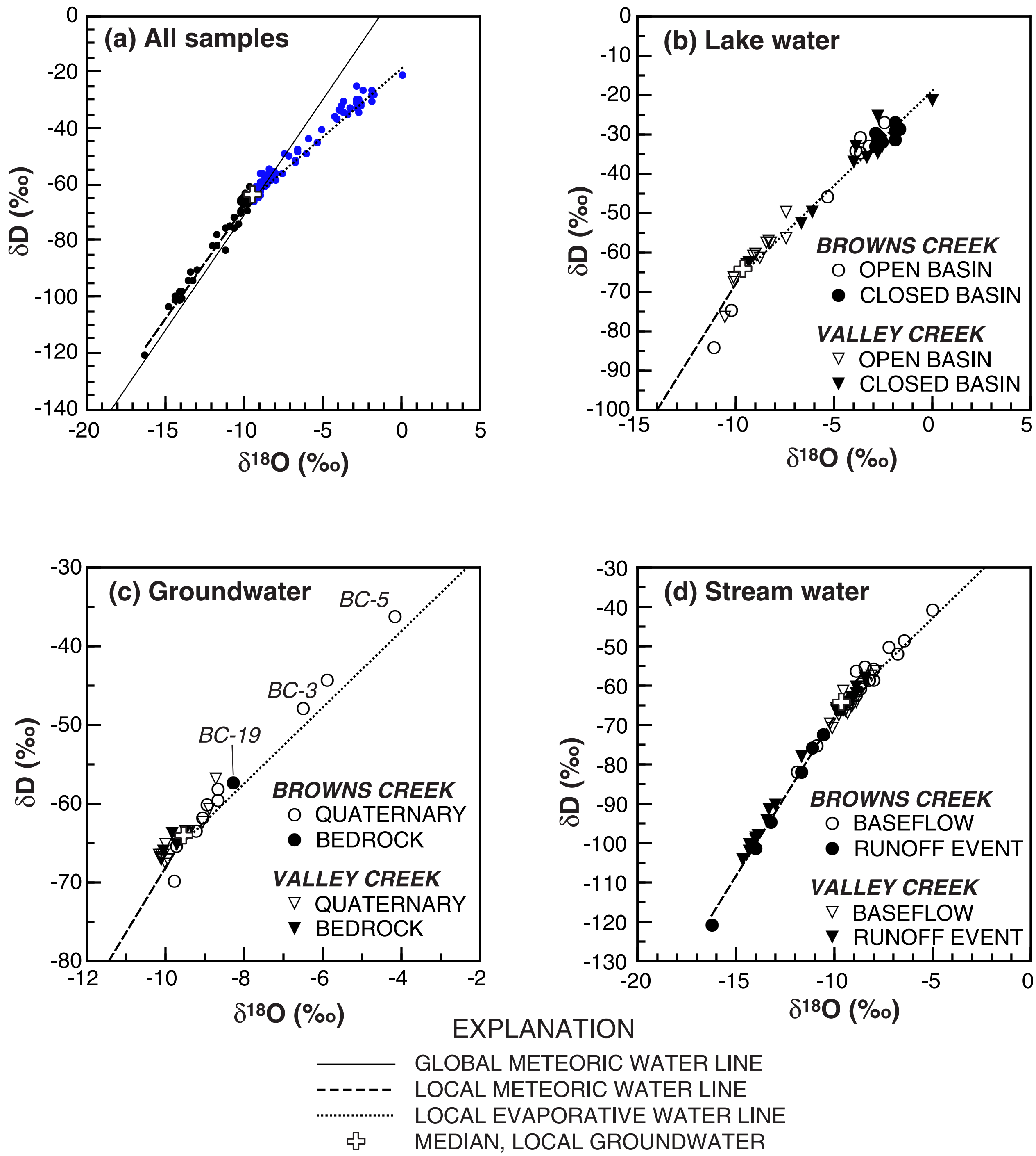


Figure 13.--Stable isotope composition of water from Valley Creek and Browns Creek watersheds, 1998-99

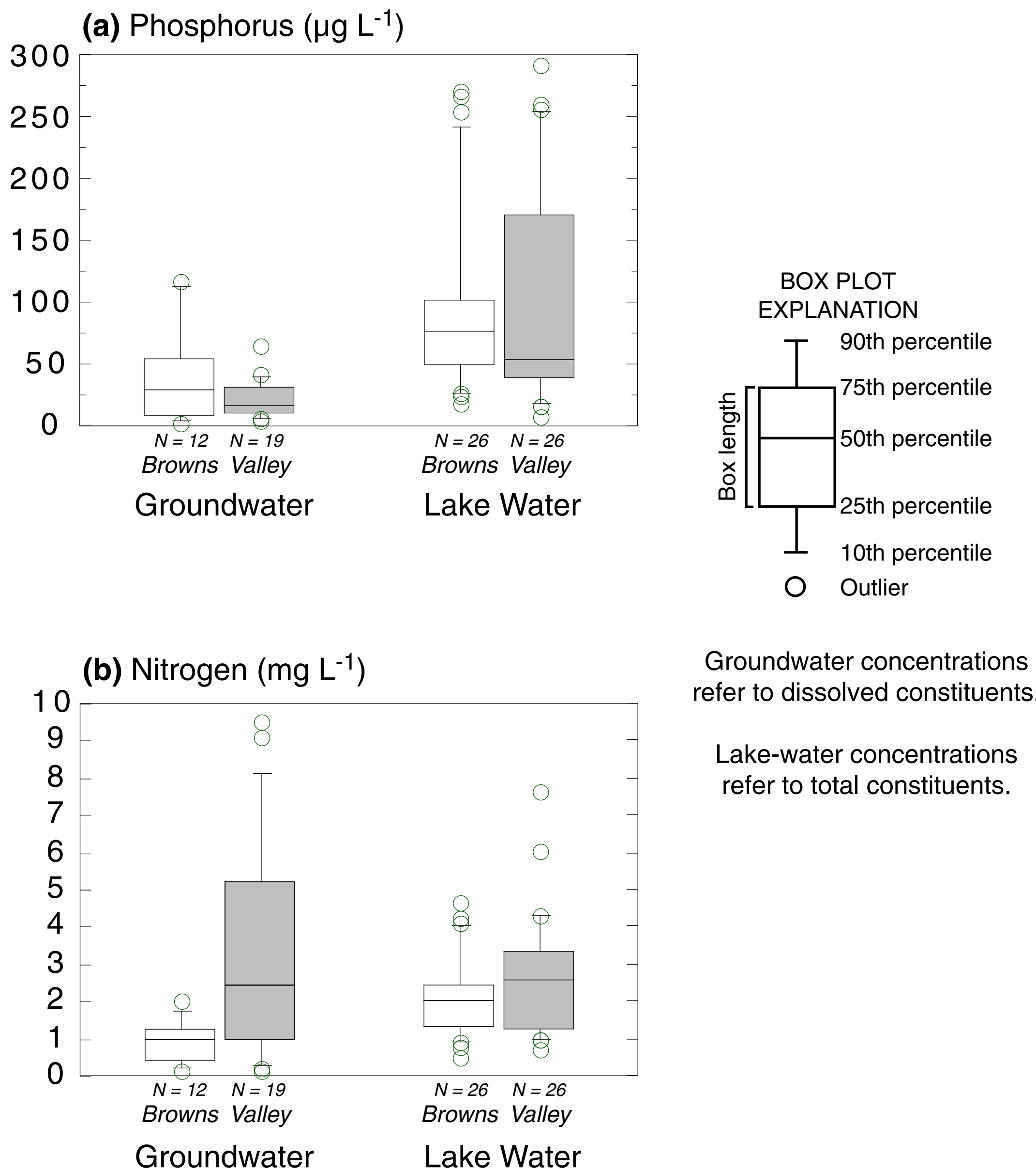
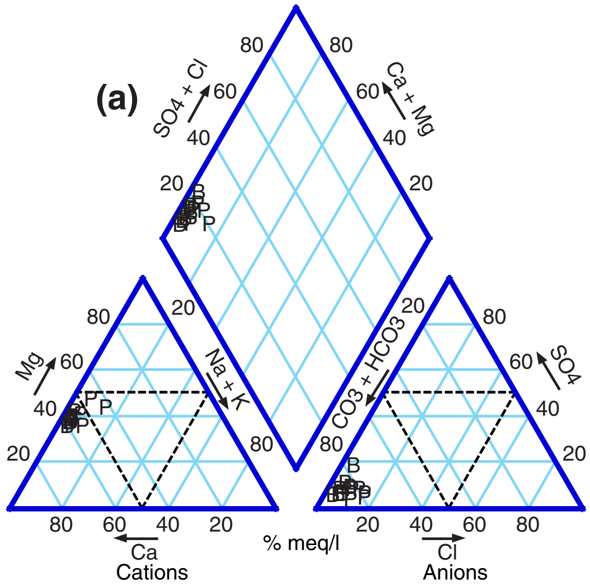


Figure 14.--Phosphorus and nitrogen concentrations in groundwater and lake water from Browns Creek and Valley Creek watersheds, 1998-99



VALLEY CREEK

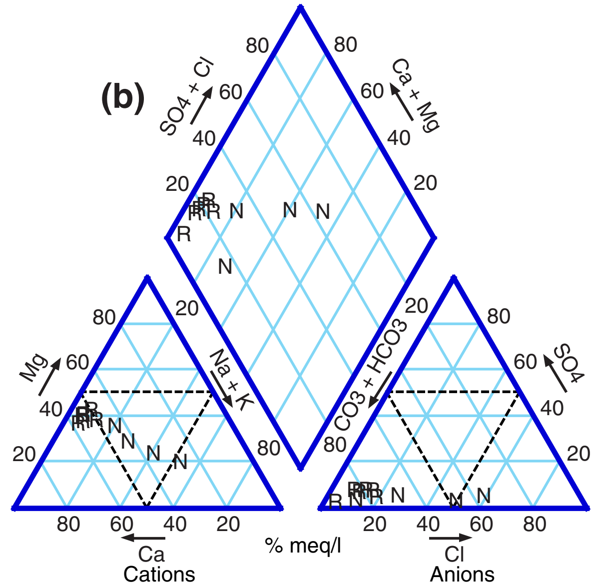
GROUNDWATER CHEMISTRY

Major ions

EXPLANATION

P — Piezometer in stream bed or spring (VC-1, VC-5, VC-7, and four headwater springs: VC-12, VC-14, VC-35, and VC-36)

B — Bedrock well (VC-23, VC-24, VC-25, VC-26, VC-27, and VC-28)



VALLEY CREEK

LAKE-WATER CHEMISTRY

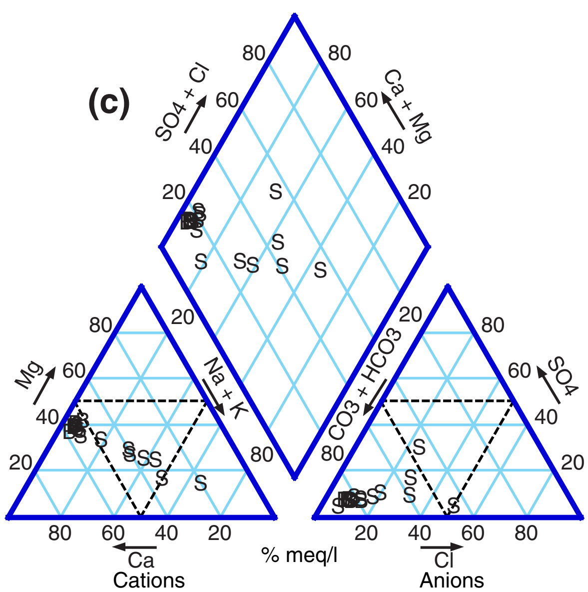
Major ions

EXPLANATION

U — Urban lakes (None in this study)

N — Intermediate lakes (West and East Fahlstrom Ponds, Horseshoe, and Fahlstrom Wetland; sites VC-17, VC-18, VC-21, and VC-22)

R — Rural lakes (Edith, Metcalf Marsh, Smith Reservoir, Belwin Classroom, and Belwin North; sites VC-6, VC-7, VC-13, VC-19, and VC-20)



VALLEY CREEK

STREAM-WATER CHEMISTRY

Major ions

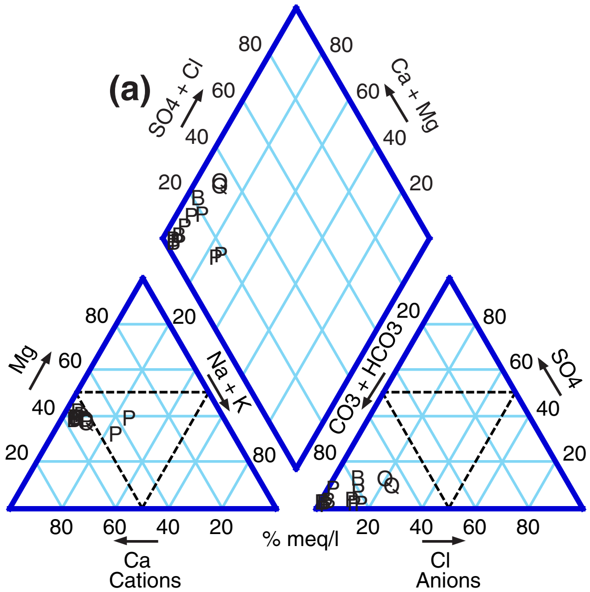
EXPLANATION

B — Typical flow ("Baseflow") (VC-1, VC-2, VC-5, VC-9, and VC-10)

S — Snowmelt or storm flow (VC-1, VC-2, VC-3, VC-4, VC-5, VC-8, VC-9, VC-10, VC11, VC-32, and VC-33)

Figure 15.--Major ion chemistry in the Valley Creek Watershed: (a) groundwater, (b) lake water, and (c) stream water.

Units are percentage of each ion or pair of ions, relative to total cation or anion sum, in terms of meq/L (milleqivalents per liter). Each plotted point represents the median value for a site, with stream-water sites split into typical and high-flow categories.



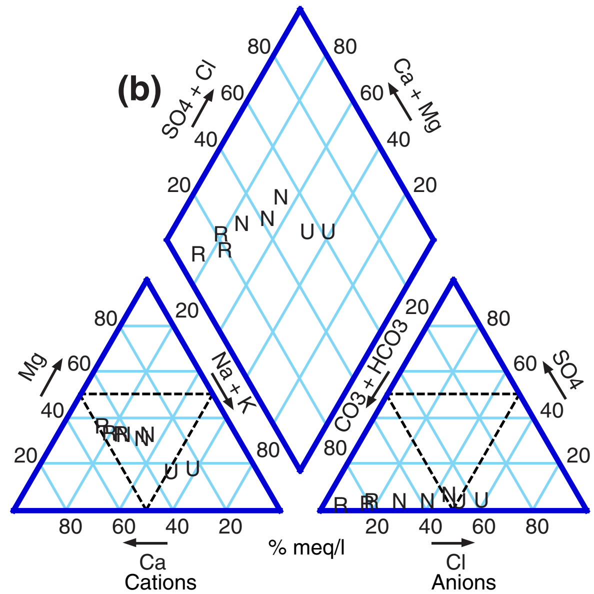
BROWNS CREEK
GROUNDWATER CHEMISTRY
Major ions

EXPLANATION

P Piezometer in stream bed (BC-1, BC-2, BC-3, BC-4, BC-5, and BC-6)

Q Quaternary well (BC-14 and BC-15)

B Bedrock well (BC-16, BC-17, BC-18, and BC-19)



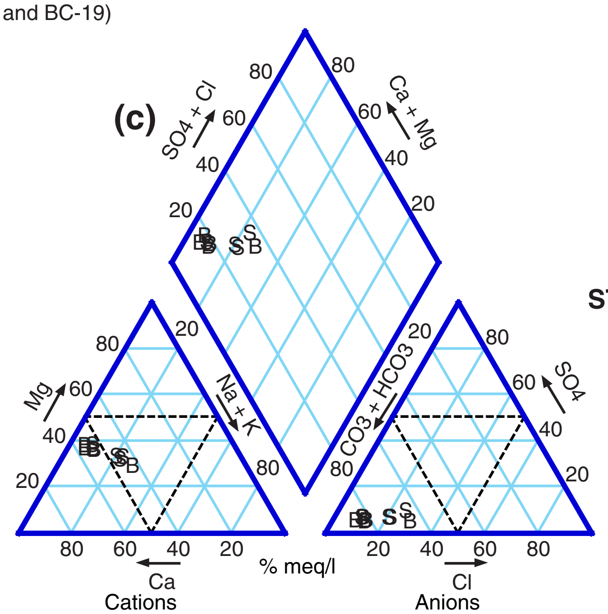
BROWNS CREEK
LAKE-WATER CHEMISTRY
Major ions

EXPLANATION

U Urban lakes (Long and McKusick; BC-5 and BC-8)

N Intermediate lakes (Goggins, Masterman, and South Twin; BC-7, BC-12, and BC-13)

R Rural lakes (Plaisted, Benz, and Pat; BC-9, BC-10, and BC-11)



BROWNS CREEK
STREAM-WATER CHEMISTRY
Major ions

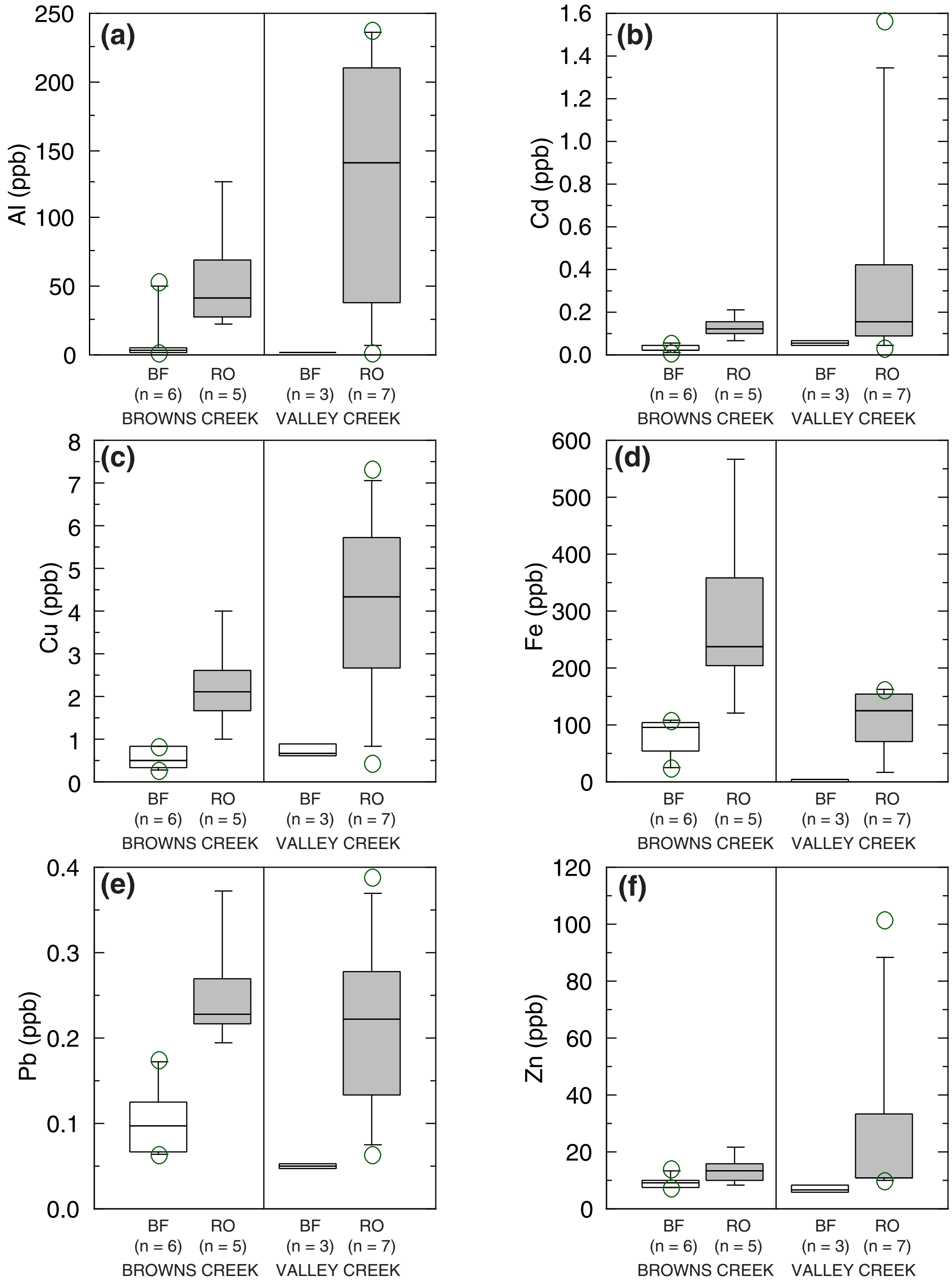
EXPLANATION

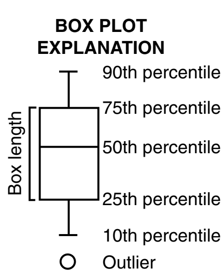
B Typical flow ("Baseflow") (BC-1, BC-2, BC-3, BC-4, and BC-6)

S Snowmelt or storm flow (BC-1, BC-2, BC-3, and BC-4)

Figure 16.--Major ion chemistry in the Browns Creek Watershed: (a) groundwater, (b) lake water, and (c) stream water.

Units are percentage of each ion or pair of ions, relative to total cation or anion sum, in terms of meq/L (milleqivalents per liter). Each plotted point represents the median value for a site, with stream-water sites split into typical and high-flow categories.





NOTES:
BF, baseflow (white boxes); RO, runoff event (shaded boxes);
ppb, parts per billion; n = number of sites

Figure 17.--Selected trace-metal concentrations for Browns Creek and Valley Creek, 1998-99