

# Variability of Isotope and Major Ion Chemistry in the Allequash Basin, Wisconsin

by John F. Walker<sup>1</sup>, Randall J. Hunt<sup>2</sup>, Thomas D. Bullen<sup>3</sup>, David P. Krabbenhoft<sup>4</sup> and Carol Kendall<sup>5</sup>

---

## Abstract

As part of ongoing research conducted at one of the U.S. Geological Survey's Water, Energy, and Biogeochemical Budgets sites, work was undertaken to describe the spatial and temporal variability of stream and ground water isotopic composition and cation chemistry in the Trout Lake watershed, to relate the variability to the watershed flow system, and to identify the linkages of geochemical evolution and source of water in the watershed. The results are based on periodic sampling of sites at two scales along Allequash Creek, a small headwater stream in northern Wisconsin. Based on this sampling, there are distinct water isotopic and geochemical differences observed at a smaller hillslope scale and the larger Allequash Creek scale. The variability was larger than expected for this simple watershed, and is likely to be seen in more complex basins. Based on evidence from multiple isotopes and stream chemistry, the flow system arises from three main source waters (terrestrial-, lake-, or wetland-derived recharge) that can be identified along any flowpath using water isotopes together with geochemical characteristics such as iron concentrations. The ground water chemistry demonstrates considerable spatial variability that depends mainly on the flowpath length and water mobility through the aquifer. Calcium concentrations increase with increasing flowpath length, whereas strontium isotope ratios increase with increasing extent of stagnation in either the unsaturated or saturated zones as waters move from source to sink. The flowpath distribution we identify provides important constraints on the calibration of ground water flow models such as that undertaken by Pint et al. (this issue).

---

## Introduction

As one of five sites in the U.S. Geological Survey's Water, Energy, and Biogeochemical Budgets (WEBB) Program, the objectives of the Trout Lake WEBB project are to (1) describe processes controlling water and solute fluxes in the Trout Lake watershed, (2) examine interactions among those processes, and (3) improve the capability to predict changes in water and solute fluxes for a range of spatial and

temporal scales (Elder et al. 1992). Previous work has included modeling of ground water systems, investigations of water sources and flowpaths, comparisons of carbon processes at the watershed scale, and detailed investigations of biogeochemical processes at the sediment-water interface (references cited in Walker and Bullen 2000). From this previous work, it became clear that to understand the underlying mechanisms and estimate solute fluxes out of the basin, a better understanding of the watershed-scale hydrology and hydrogeochemistry is needed.

Past research in small watersheds has taken two approaches to understanding flowpaths and geochemical evolution within the watershed. The first, sometimes termed the "small watershed approach," monitors flow, isotopic, and chemical characteristics of the stream at the watershed outlet, and attempts to recreate the observed stream characteristics by mixing different proportions of two or more end members, representing various sources of water contributing to the stream. In many cases, flow is divided into "new" water corresponding to precipitation inputs and "old" water corresponding to water from previous events stored within

---

<sup>1</sup>U.S. Geological Survey, 8505 Research Way, Middleton, WI 53562; (608) 821-3817; jfwalker@usgs.gov

<sup>2</sup>U.S. Geological Survey, 8505 Research Way, Middleton, WI 53562; (608) 821-3847; rjhunt@usgs.gov

<sup>3</sup>U.S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94025; (650) 329-4577; tdbullen@usgs.gov

<sup>4</sup>U.S. Geological Survey, 8505 Research Way, Middleton, WI 53562; (608) 821-3843; dpkrabbe@usgs.gov

<sup>5</sup>U.S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94025; (650) 329-4576; ckendall@usgs.gov

Published in 2003 by the National Ground Water Association.

the watershed (Sklash and Farvolden 1979; Hooper and Shoemaker 1986; Rose 1996). To better explain the stream water characteristics, researchers have added additional source waters and tracers, and improved the mixing models (Brown et al. 1999; Burns et al. 2001). Recently, novel approaches have examined the underlying principles of the basic hydrograph separation technique using experimental watersheds (Kendall et al. 2001), and used years of experience at the Panola Research Watershed to examine the small watershed approach within the context of the scientific method and concepts of hypothesis testing (Hooper 2001). These and other studies suggest a shift in the focus of field studies from the chemical dynamics of the stream to a more in-depth understanding of the combined hydrologic and geochemical processes occurring within watersheds (Hooper 2001).

The second approach used in small watershed research has taken a more direct look at processes occurring within the watershed. In general, this has involved a more concerted effort to examine the spatial variability of water sources within the watershed, and interpret that data in the context of physical ground water flowpaths (Huddart et al. 1999; McGlynn et al. 1999; Abbott et al. 2000; Ojiambo et al. 2001; Welsch et al. 2001). Similar to the idea of using detailed measurements to constrain plausible mixing models (Kendall et al. 2001), it is possible to use detailed obser-

vations within a watershed to constrain physically based watershed models (Chen and Beschta 1999; Pint et al., this issue).

Several single-lake basin hydrogeologic studies conducted in the North Temperate Lakes (NTL) area (Kenoyer 1986; Marin 1986; Krabbenhoft 1988; Wentz and Rose 1989; Krabbenhoft and Babiarz 1992; Rose 1993) have led to detailed descriptions of the ground water flow network around three of the long-term ecological research (LTER) lakes (Sparkling Lake, Crystal Lake, and Crystal Bog) and three non-LTER lakes in the area (Little Rock, Palette, and Vandercook lakes). At the basin scale, Krabbenhoft et al. (1995) found that the ground water basin is 50% larger than the surface topography would suggest, which is important for basin-yield calculations. A common conclusion of all of these studies was that the unconsolidated aquifer is hydraulically conductive, providing good connection between the aquifer and the lakes. Because precipitation readily percolates into the sandy soils of the region, overland-flow runoff is negligible as a hydrologic input to the lakes.

Walker and Krabbenhoft (1998) demonstrated that as one moves from the headwaters of Allequash Creek watershed (Figure 2, site 1) to its basin outlet (Trout Lake) (Figure 2, site 70), the sources of water progress from a relatively homogeneous meteoric source (ground water and local precipitation falling on the stream) to a mixture of

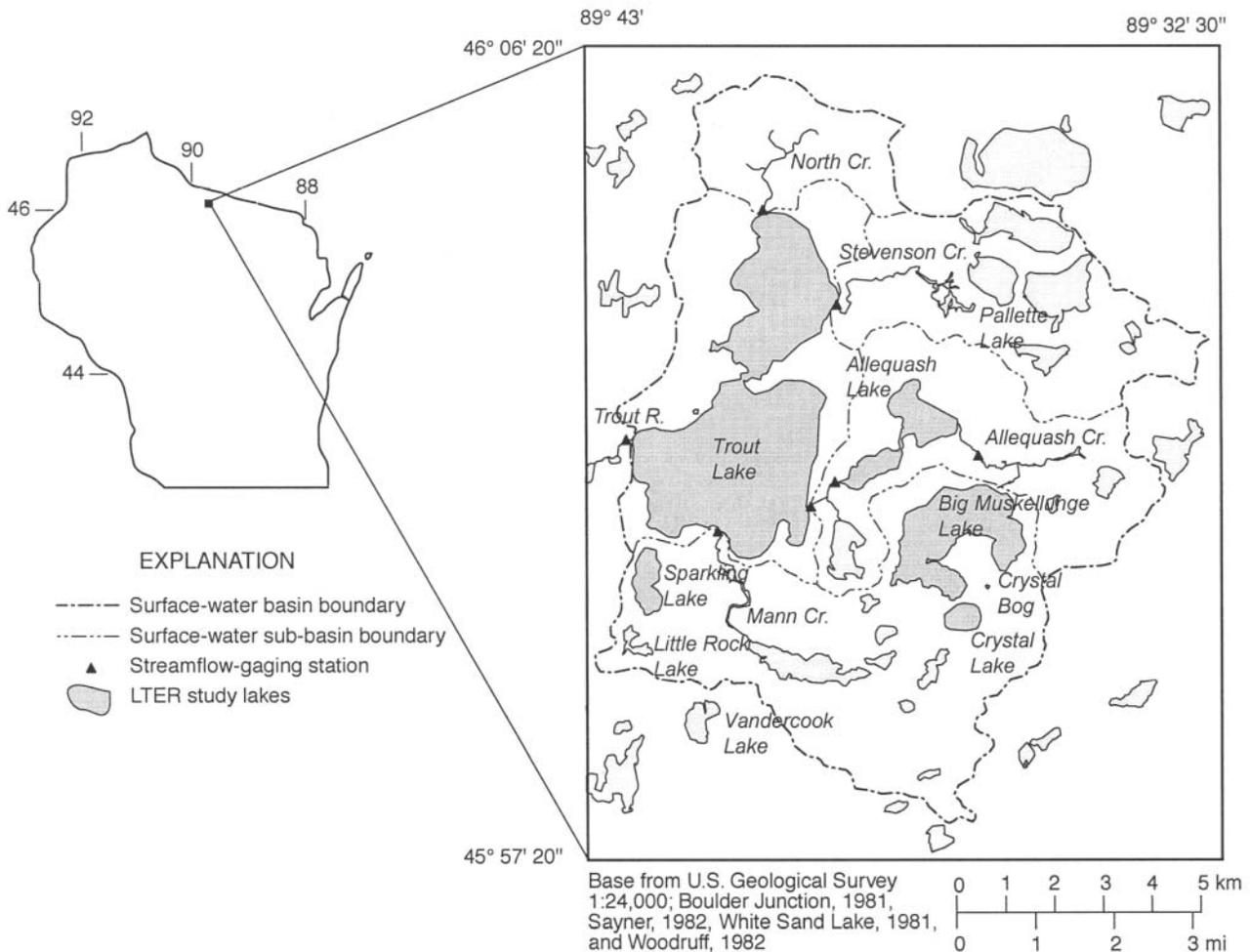


Figure 1. Map showing location of the study area in Wisconsin.

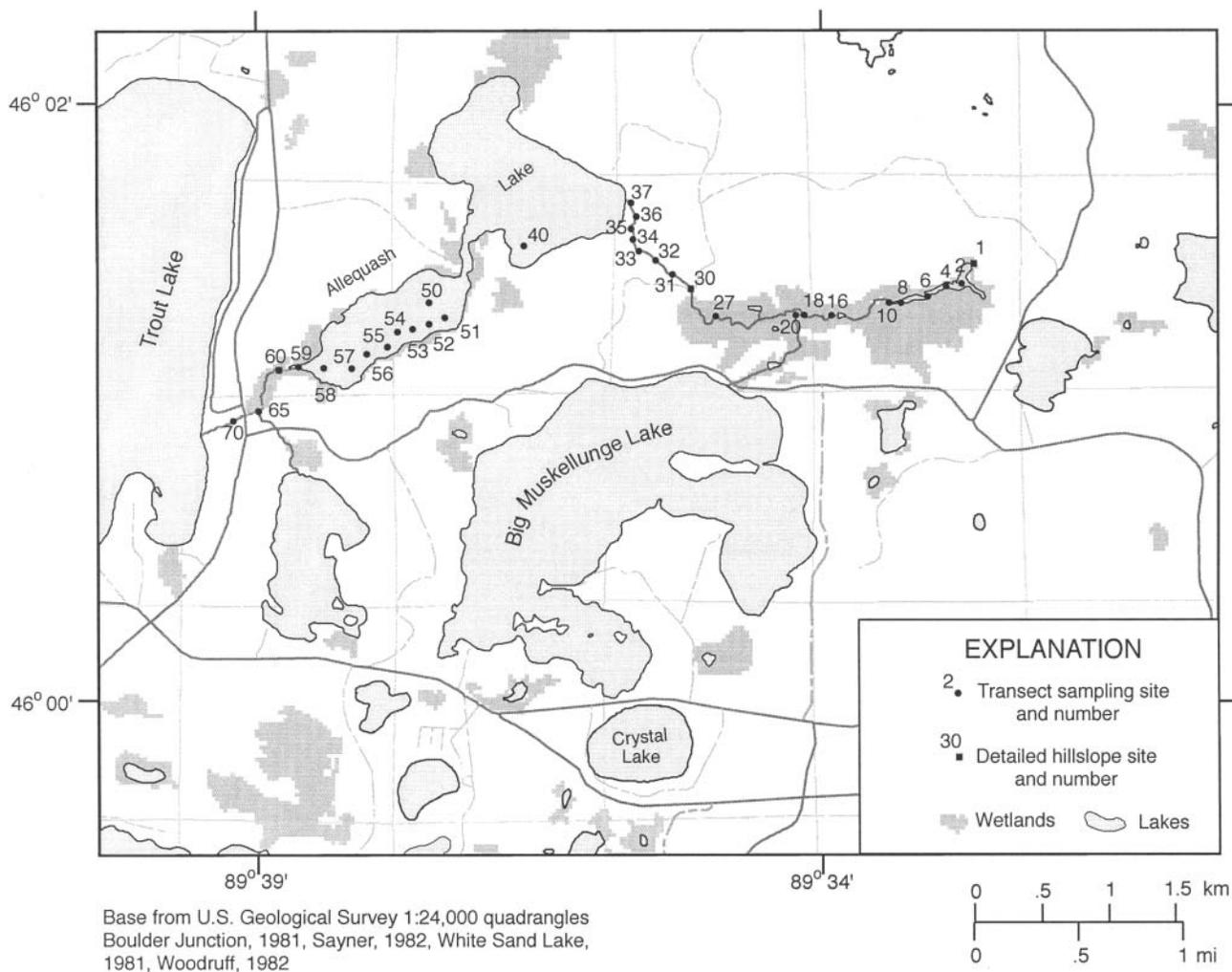


Figure 2. Map showing sampling locations along Allequash Creek.

ground water, precipitation, and evaporated surface water sources. Chemical evolution of ground water in a basin, in contrast to changes in water source, might be expected to be more complex due to a variety of factors such as water source, redox state, and mineral-water contact time along any specific flowpath.

Watershed research often assumes that the ground water system is sufficiently homogeneous to be characterized by two or more chemical end members (Hooper et al. 1990). While the determination of overall chemical evolution over long (e.g., >10 km) flowpaths is relatively straightforward (Plummer et al. 1990), it becomes less straightforward for shorter (e.g., 0.1 to 10 km) flowpaths as the need to consider small-scale physical and mineralogic heterogeneities increases. Moreover, the individual influences of multiple water sources become more evident at smaller scales, and it is important to recognize that geochemical evolution along a flowpath depends in large part on the chemistry and chemical state of the source water (Bullen et al. 1996). Clearly, our ability to assess watershed processes and changes in process resulting from future stress to the system will stem from an understanding of the hydrogeochemical heterogeneity.

The purpose of this paper is to assess the spatial and temporal variability of stream and ground water isotopic

composition and cation chemistry in the Trout Lake watershed, to relate the variability to the watershed flow system, and to identify the importance of geochemical evolution and source of water to the flow system and solute chemistry of the watershed. Results from this paper are then evaluated in the context of a deterministic ground water flow model in a companion paper (Pint et al., this issue).

### Study Area and Previous Results

The WEBB study area is located within the Trout Lake watershed, in the Northern Highlands Lake District of north-central Wisconsin. Watershed research efforts have focused primarily on Allequash Creek, a subwatershed of the Trout Lake watershed (Figure 1). The Trout Lake WEBB study area is co-located with one of the National Science Foundation's LTER sites. The North Temperate Lakes LTER site is operated by the Center for Limnology at the University of Wisconsin (Magnuson et al. 1984), and focuses primarily on in-lake processes at seven lakes in the Trout Lake area.

One of the predominant features of the Northern Highlands area is the presence of thousands of kettle lakes, formed 10,000 years ago at the end of the last continental glaciation. The lakes range in size from 0.1 to more than

1500 hectares, in depth from 1 to 33 m, and in fertility from oligotrophic to eutrophic. The lake district is sparsely settled by humans and lies within two state forests that include 80% of the land area and 60% of the lake frontage. Many lakes have completely forested watersheds and no private frontage. The forest vegetation consists of a mixture of coniferous and deciduous species.

The Allequash Creek watershed has a surface water drainage area of 2200 hectares and ranges in elevation from ~490 to 520 m above mean sea level. Mean monthly temperatures are minimum in January, ranging from  $-17^{\circ}$  to  $-6^{\circ}\text{C}$ , and are maximum in August, ranging from  $+13^{\circ}$  to  $+26^{\circ}\text{C}$ . Precipitation averages 79 cm/year (Cheng and Anderson 1994), while recharge to the ground water system averages 27 cm/year (Hunt et al. 1998); thus evapotranspiration and canopy interception combined averages 52 cm/year. The lakes in the area are ice free about seven months each year. Located ~70 km southeast of Lake Superior, and 200 km northwest of Lake Michigan, the Trout Lake WEBB site is climatically influenced by the Great Lakes.

Geologic features of the area are dominated by a sandy outwash plain consisting of 30 to 50 m of unconsolidated sand and gravel overlying Precambrian igneous bedrock (Okwueze 1983; Attig 1985). The predominant soils are thin and poorly developed sands, loams and silts (loamy sand, sandy loam, loamy fine sand, and sand make up 86% of the soils) with high-organic content in the upper horizon. The area is representative of the glacial lake districts common to the Upper Midwest and Canada, but has some individual characteristics that distinguish it from other nearby lake areas. Among the most important of these features is the fact that the glacial drift is believed to be essentially carbonate free; therefore the ground water chemistry is largely controlled by silicate hydrolysis (Kenoyer and Bowser 1992; Bullen et al. 1996).

The relatively straightforward hydrogeology of the region provides the opportunity to test multiple techniques of ground water flowpath identification. For example, Kenoyer and Bowser (1992) and Bullen et al. (1996) used different approaches to determine the flowpath taken by lake water recharge beneath a narrow isthmus that had been instrumented with multipiezometer nests just to the south of Big Muskellunge Lake (Figure 1). Kenoyer and Bowser (1992) relied on the traditional approach based on physical measurements of ground water head across the isthmus. Bullen et al. (1996) relied on the nearly ideal conservative nature of water isotopes ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ) for use with ground water systems and that the source lake water was greatly enriched in  $\delta^{18}\text{O}$  relative to regional ground water because of evaporation at the lake surface. Thus, to identify the flowpath, they tracked the enriched  $\delta^{18}\text{O}$  signal of the lake water through the aquifer. The flowpaths obtained by the two methods differed significantly given the scale of the study, pointing to the value of using the isotopic approach, which tracks the water molecule itself to accurately identify the lake water recharge flowpath and to constrain the necessary assumptions of physically based ground water flow models (Bullen et al. 1996).

Regardless of the flowpath determined by these two approaches, the results of these two studies indicated that dissolution of both plagioclase feldspar and a calcium-mag-

nesium silicate, such as hornblende, were the principal reactions required to account for the chemistry along both terrestrial- and lake-recharge flowpaths. Dissolution of each of these minerals causes dissolved calcium to increase, and thus the amount of calcium produced through weathering is a useful indicator of water-mineral contact time. In addition, Bullen et al. (1996) combined laboratory experiments and field observations to suggest that strontium isotopes provide an effective surrogate for water mobility through the aquifer, in that  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of ground water tend to decrease along flowpaths through highly conductive portions of the aquifer, but increase as a result of stagnation in either the unsaturated zone or in less conductive portions of the aquifer. Thus, by using the combined information of calcium concentrations, strontium isotopes, and water isotopes, it should be possible to characterize the geochemical evolution of various water sources in terms of mineral-water contact time and water mobility along any flowpath through this aquifer. Finally, strontium and oxygen isotope compositions of large lakes in the study area appear to be determined largely by mixing of two water sources: terrestrial recharge having relatively radiogenic strontium and meteoric  $\delta^{18}\text{O}$ , and evaporated meteoric water having relatively unradiogenic strontium and enriched  $\delta^{18}\text{O}$  (Bullen et al. 1996). On a plot of  $\delta^{18}\text{O}$  vs.  $\delta^{87}\text{Sr}$ , the lakes describe a mixing array between these two proposed end-members. As we will discuss, the compositions of many of the ground waters sampled within the Allequash Creek basin diverge from this simple mixing array, and thus have experienced additional chemical modifications along their flowpaths.

## Field Methods

One objective of the Trout Lake WEBB study is to examine processes at several spatial scales to explore possible predictive capabilities of scaling up from smaller to larger catchments. Therefore, sampling and data collection were carried out at two spatial scales. At the smaller spatial scale, detailed monitoring sites have been installed on three hillslopes starting at the headwaters and ending at the outlet from Allequash Lake (Figure 2, sites 1, 30, and 60). At each of these three sites, transects of nested piezometers were installed from near the top of the hillslope to the base of each hill. Additional nested sampling points extended from the base of the hill to the other side of the stream, including well nests under the streambed. In all, more than 100 wells were installed with depths ranging from 0.5 to 7.5 m below the land surface. Samples were collected from the nested wells monthly from June through September 1993, resulting in five samplings for each well. The samples were analyzed for major cations and stable isotopes ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$ ). Associated with the small-scale sampling, continuous records of instantaneous throughfall, stream discharge, and water levels in the hillslope piezometer nests were collected.

The large-scale sampling of stream and ground water along the Allequash Creek transect was conducted during August 1994. Beginning with the headwaters (Figure 2, site 1), sites were chosen at ~100 to 200 m intervals throughout the length of the creek, and stream samples were collected.

For a subset of the stream-sampling sites, a temporary piezometer was installed in the center of the stream and sampled at a depth of ~1 m into the sand in the streambed; in some wetland areas (e.g., sites 2 through 10 in Figure 2), the depth to sand through the overlying organic sediments and peat deposits exceeded 10 m. This sampling resulted in 22 stream samples and 17 streambed samples. Near the headwaters (Figure 2, sites 1 through 10), the width of the active stream channel ranged from 5 to 10 m; in this section the stream is essentially a wide pond, created by several beaver dams. In the middle portion of the creek (Figure 2, sites 16 through 27), the active stream-channel width ranged from 2 to 5 m; the stream flows through a series of smaller beaver ponds and an extensive riparian wetland. In the downstream portion of the creek (Figure 2, sites 30 through 37), the active stream-channel width ranged from 1 to 4 m; in this portion the stream is better defined, and generally consists of a relatively stable sand bed. More detailed sampling in the bed of Allequash Lake was conducted in June 1997 and May 1998.

For Allequash Creek, the hydrologic conditions for the two main sampling years (1993 and 1994) were similar; the average flow for the two water years was nearly identical, and the average flows during the sampling period June through September were within 20% of one another (the average flow for the period in 1993 was 20% less than the same period in 1994). For the two periods of detailed lakebed sampling, average flow for the 1997 water year was ~30% higher than the main sampling years, and average flow in 1998 was roughly the same as the main sampling years. For the sampling periods, flow in 1997 was ~30% higher than the main sampling periods, and roughly 20% lower in 1998 compared to the main sampling periods.

## Geochemical Techniques

Water samples were collected using a peristaltic pump (for mini-piezometers and deep wells) or by sampling the stream water ~0.5 m below the water surface. Samples were analyzed for calcium, magnesium, iron, and strontium concentrations and stable isotopes ( $\delta D$ ,  $\delta^{18}O$ ,  $^{87}Sr/^{86}Sr$ ). Samples collected for calcium, magnesium, iron, and strontium concentrations and strontium isotopes were filtered with a 0.45  $\mu m$  cellulose nitrate filter and acidified with nitric acid; samples for oxygen and deuterium isotope analyses were collected in glass bottles and were unfiltered and untreated.

Analyses of water and strontium isotopes were performed at the U.S. Geological Survey National Research Program Laboratory in Menlo Park, California. Oxygen-18 values were measured using  $CO_2-H_2O$  equilibration (Epstein and Mayeda 1953) on a Finnigan-Mat 251 mass spectrometer. Deuterium values were determined using the zinc oxidation method (Kendall and Coplen 1985) and analyzed on a Finnigan Delta E mass spectrometer. Oxygen-18 and deuterium values are reported in standard delta notation relative to Vienna Standard Mean Ocean Water (VSMOW). Analytic error ( $2\sigma$ ) is estimated at  $\pm 0.1$ /mil and  $\pm 2.0$ /mil for  $^{18}O$  and deuterium, respectively.

Water samples were also analyzed for strontium isotopic composition. Teflon labware and Teflon-distilled

reagents were used throughout the sample preparation procedure. Strontium in the waters was separated from other cations on an HCl cation exchange column using BioRad AG50X8 resin. Approximately 125 mL of the water samples were loaded directly onto the column without pretreatment. The strontium fraction was taken to dryness with 40  $\mu L$  of 0.15N  $H_3PO_4$ , converted to nitrate form and loaded onto a tantalum ribbon for mass spectrometric analysis.

Strontium isotopes were measured on a Finnigan MAT 261 mass spectrometer. Strontium isotope values are reported in this study as a ratio of  $^{87}Sr$  to  $^{86}Sr$ . All reported values of  $^{87}Sr/^{86}Sr$  have been corrected for mass fractionation to  $^{88}Sr/^{86}Sr = 8.37521$ . The machine used in this study routinely reports a value of 0.71023 for the NIST 987 strontium metal. At the 95% confidence level ( $2\sigma$ ), values associated with  $^{87}Sr/^{86}Sr$  analyses are estimated to be precise to within  $\pm 0.04$ /mil ( $^{87}Sr/^{86}Sr \pm 0.00003$ ) or better. We also report the strontium isotope ratios in terms of delta values, calculated relative to the NIST 987 strontium metal and reported as  $\delta^{87}Sr$ . Delta values relative to the average composition of the source water along any flowpath are reported as  $\delta_r^{87}Sr$ . Total dissolved calcium, magnesium, strontium, and iron concentrations were analyzed using a Perkin-Elmer Elan 6000 inductively coupled plasma mass spectrometer. Error associated with these measurements is estimated to be  $\pm 2\%$ . Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. government.

## Results and Discussion

### Transverse Transect $\delta^{18}O$ Results Near Stream

Similar to results noted by Walker and Krabbenhoft (1998), the two main end member sources of water in the Allequash Creek watershed are meteoric water that recharges through the ground surface (terrestrial recharge, average  $\delta^{18}O$  value of approximately 11.3‰) and evaporatively fractionated water from lakes (lake recharge,  $\delta^{18}O$  ranging from 4.4‰ to 5.5‰) that re-enters the ground water system through the lakebed. Water that recharges the aquifer from wetlands is intermediate to these end member compositions in terms of  $\delta^{18}O$ , and results from variable evaporative fractionation of meteoric water that has short residence time on the surface. We note here that because the meteoric water in the surface and subsurface waters shows a narrow range of  $\delta D$  and  $\delta^{18}O$  values due to mixing of the seasonal meteoric signal (Walker and Krabbenhoft 1998) and because lakes in the region tend to have well-averaged water isotope compositions (Krabbenhoft et al. 1992), subsequent discussion will rely on the value for  $\delta^{18}O$  alone to discriminate waters of meteoric or evaporated origin.

At hillslope sites 30 and 60, there is considerable spatial and temporal variation of isotopic composition (Figures 3 and 4, respectively). At site 30, the shallow ground water beneath the north bank (1.4 m from the center of the stream) represents meteoric-recharge water, which originates from the adjacent hillslope and upland recharge areas. Beneath the south bank (0.9 m from the center of the stream) and streambed (Figure 3), the highly evaporated water at depth is a plume of lake water originating from Big

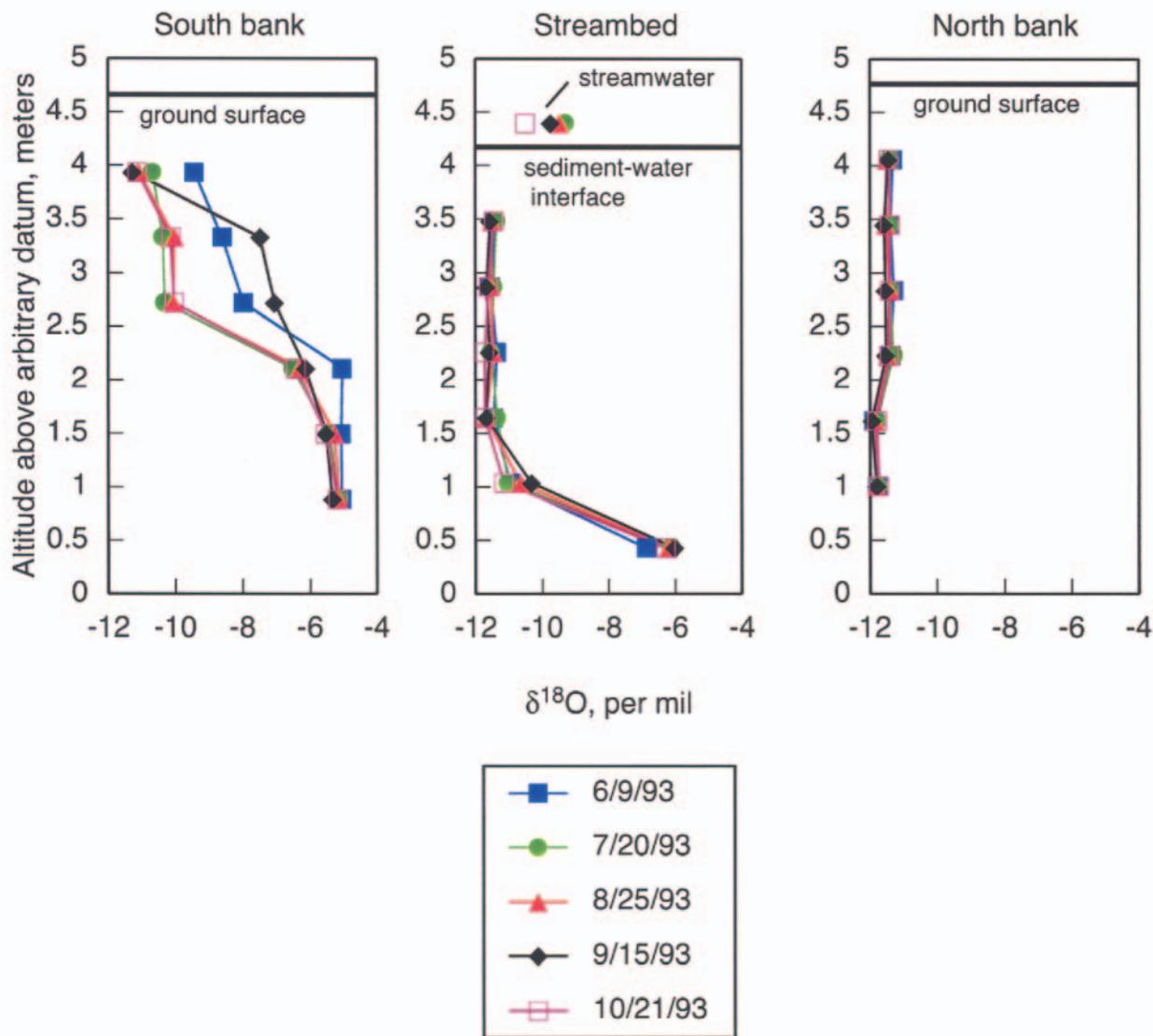


Figure 3. Profiles of  $\delta^{18}\text{O}$  beneath the streambed and banks at site 30 for various sampling times.

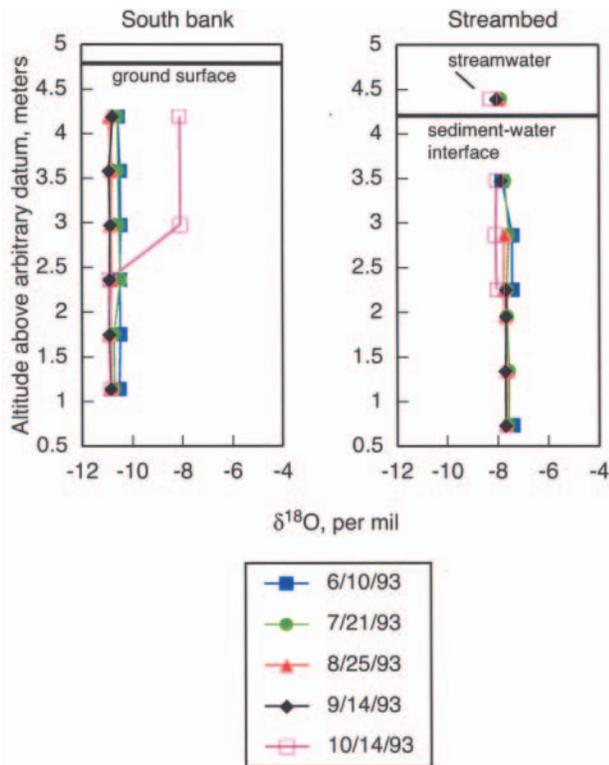
Muskellunge Lake (Figure 2), over 1 km away from the site that is converging toward its discharge point (Walker and Krabbenhoft 1998). At site 30, the south bank is adjacent to a local wetland, and the area up to the bank remains saturated close to the surface for most of the year. Thus, the shallow ground water beneath the south bank demonstrates temporal variability corresponding to a mixing of terrestrially derived recharge, locally derived wetland water, and Big Muskellunge water; the latter two are enriched in  $\delta^{18}\text{O}$  due to evaporation. Because the relatively shallow water beneath the streambed is most similar to the north bank, it appears that the stream is receiving water primarily from the north bank at this site.

At site 60, beneath the streambed, the  $\delta^{18}\text{O}$  value is intermediate between the end member compositions and represents a mixture of terrestrial recharge and evaporated water recharged from upland lakes (Figure 4). Beneath the south bank (10 m from the center of the stream), one might expect to see evaporated water recharged from upgradient lakes; however, the predominant isotopic signature represents well-mixed meteoric recharge from either the hillslope or upland recharge areas. With the exception of the

October sampling, the temporal variability at both locations is quite small, demonstrating a high degree of mixing of the two water sources. The October sampling is much different from the other sampling events. Periodic observations of water levels in piezometers near the south bank and in the stream (USGS unpublished data) have indicated that the gradient between the stream and the south bank occasionally will reverse, resulting in infiltration of stream water into the bank (the predominant direction is from the bank to the stream). A gradient reversal occurred in mid-September 1993, and persisted for several months. Thus, the  $\delta^{18}\text{O}$  enriched (less negative) waters on the south bank represent stream water that has moved into the bank.

#### Longitudinal Transect $\delta^{18}\text{O}$ Result

The  $\delta^{18}\text{O}$  results from the stream and subsurface sampling along the length of Allequash Creek are depicted in Figure 5. Because the headwaters originates as a pond that receives discharge from a series of springs, the first few surface water sampling locations are slightly more evaporated than terrestrial recharge water (values ranging from  $-11\text{‰}$  to  $-12\text{‰}$ ), which is present in the subsurface just



**Figure 4. Profiles of  $\delta^{18}\text{O}$  beneath the streambed and south bank at site 60 for various sampling times.**

below the streambed for the first 600 m (through site 10 on Figure 2). Thus the headwater portion of the creek is a spring pond/creek system that receives mostly terrestrial recharge, and becomes slightly more evaporated in the downstream direction due to evaporation from the pond. This agrees with field observations of a large stream width and slow moving current from the headwaters to a large beaver dam at site 10. The creek then flows slowly through a series of beaver dams, ending at ~1.4 km downstream (site 18 on Figure 2). From site 10 to site 30 at a distance of ~2.7 km, the stream water becomes  $\delta^{18}\text{O}$  enriched (more evaporated) as it receives more discharge from ground water that was recharged at an upgradient lake.

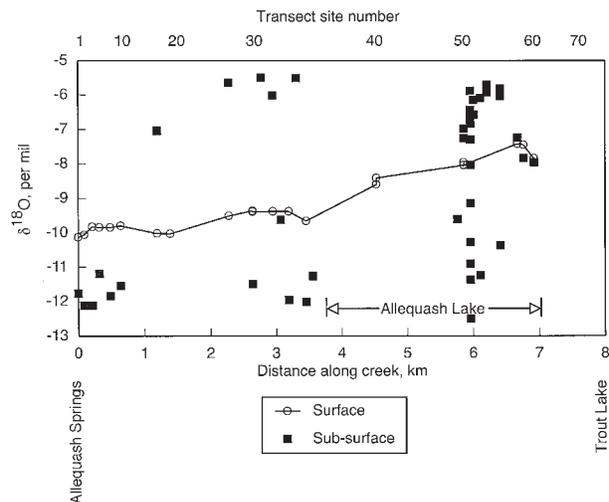
Downstream of site 30, the  $\delta^{18}\text{O}$  signature in the stream remains fairly constant relative to the  $\delta^{18}\text{O}$  signature in the subsurface samples despite localized transitions from lake-derived recharge to terrestrial-derived recharge in the subsurface waters (2.7 to 3.4 km, or sites 31 through 37 on Figure 2), indicating that there is not enough flow from the subsurface to the stream to change the stream composition until just before the stream enters Allequash Lake (3.4 to 3.7 km). As one might expect from increased residence time of a lake, samples from Allequash Lake show increasingly more evaporated surface water, mostly due to evaporation within the lake and partly due to input of subsurface water with a lake- or wetland-derived origin (5.8 to 6.8 km, or sites 50 through 59 on Figure 2). Although it is likely that this is primarily caused by evaporation within the lake, there might be some contribution from input of subsurface water with a lake- or wetland-derived origin (5.8 to 6.8 km, or sites 50 through 59 on Figure 2), based on the combination of isotope and dissolved iron data. Water leaving the

lake downstream retains the lake composition until enough terrestrial recharge is captured by the stream to change the bulk stream composition (last site sampled in Figure 5). The flow is relatively large at this location (average daily flow of 35,000  $\text{m}^3/\text{day}$ ); thus the terrestrial-derived recharge component must be relatively large in the immediate upstream reach to appreciably change the bulk composition of the stream.

This underscores the importance of evaluating potential surface water sampling locations used in a watershed study. Ground water samples collected in the area of the surface water site may not reflect the character of the ground water-derived water present in the stream. Moreover, the magnitude of ground water discharge along the stream is not expected to be equal at all locations. Thus, upscaling processes measured at a subset of sites could contain artifacts that obscure the process operating at the basin scale.

#### Longitudinal Transect Cation Chemistry

Because the local aquifers are carbonate-poor and calcium can be considered a generally conservative ion in circumneutral pH aquatic systems (Stauffer 1985) such as in the Allequash Basin (USGS unpublished data), calcium concentrations in the Allequash transect should provide a useful geochemical index of water-mineral contact time and thus of flowpath length at a given velocity. We note that dissolved calcium is ~5 mg/L in Big Muskellunge Lake water (the “lake-recharge” water source) and somewhat less than 5 mg/L in water from the unsaturated zone and water table wells on the hillslopes (the “terrestrial recharge” source). Based on the range of calcium concentrations observed in waters from the Trout Lake region (USGS unpublished data), we suggest that calcium values up to 10 mg/L would indicate relatively short flowpaths (perhaps up to a few hundred meters), values from 10 to 20 mg/L would indicate intermediate-length flowpaths (perhaps on the order of a

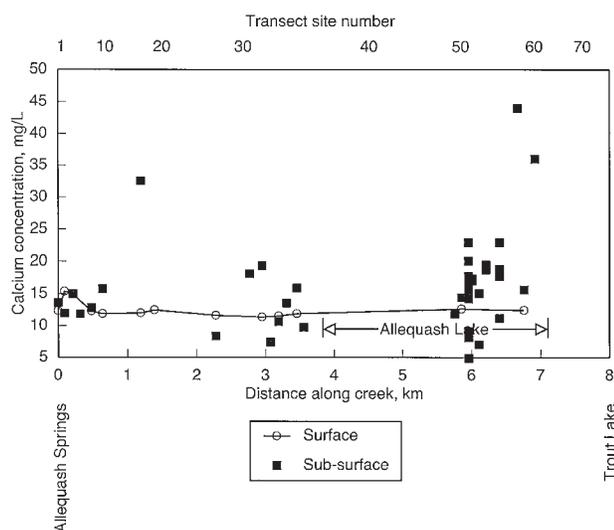


**Figure 5. Distribution of  $\delta^{18}\text{O}$  in surface waters and subsurface samples collected 1 m into the sand in the streambed. Distance along the creek is measured along the centerline of the channel beginning at the headwaters (Allequash Springs) and increasing in a downstream direction. Transect site numbers refer to sites shown in Figure 2.**

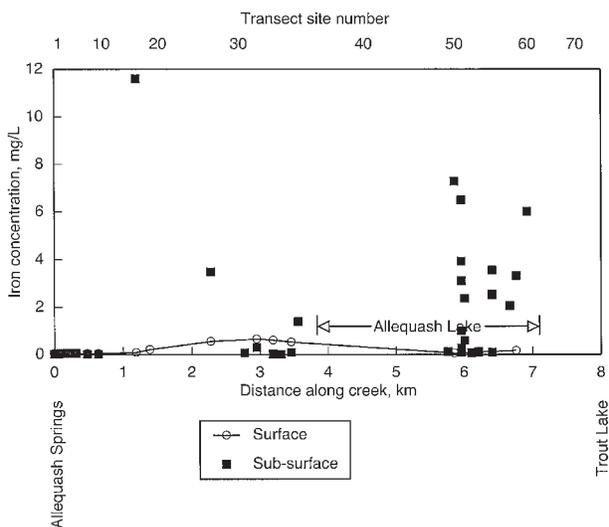
kilometer), and values in excess of 20 mg/L would indicate relatively long flowpaths (perhaps several kilometers). It should be noted that calcium concentration alone is a measure of water-mineral contact time and cannot be used to distinguish relatively short, slow-velocity flowpaths from relatively long, fast-velocity flowpaths. To infer flowpath length and velocity relations, we combine calcium concentration information with strontium isotope composition that serves as a geochemical index of relative flowpath velocity as reflected in the relative mobility or stagnation along the flowpath.

Calcium concentrations in waters from the transect sampling are shown in Figure 6. Based on the ranges given previously, the first portion of the creek from the headwaters to the large beaver dam (site 10, Figure 2) consists of intermediate and short flowpaths. The next section, through the wetlands and up to site 30, consists of a mixture of relatively short and long flowpaths that apparently originate from a lake water source (as evidenced by the isotopically enriched  $\delta^{18}\text{O}$  in Figure 5). From site 30 to the lake, the flowpaths are generally short; however, calcium concentrations measured in and downstream of the lower basin of Allequash Lake are among the highest measured in the basin, indicating very long flowpaths. The stream chemistry in the lower reach generally reflects these changes in subsurface chemistry.

An examination of dissolved iron is also useful in this watershed because it can distinguish between sources of evaporated water that experience reducing conditions (wetland-derived or deep lake recharge, both of which move through organic-rich sediments) from those that do not (littoral zone lake-derived recharge). This difference in lake-derived ground water is observed by comparing Figures 5 and 7; samples that are clearly lake-derived (with enriched  $\delta^{18}\text{O}$  in Figure 5) can have high to very low iron concentrations (Figure 7). With a few exceptions, there is very lit-



**Figure 6.** Distribution of dissolved calcium concentrations in surface waters and subsurface samples collected 1 m into the sand in the streambed. Distance along the creek is measured along the centerline of the channel beginning at the headwaters (Allequash Springs) and increasing in a downstream direction. Transect site numbers refer to sites shown in Figure 2.



**Figure 7.** Distribution of dissolved iron concentrations in surface waters and subsurface samples collected 1 m into the sand in the streambed. Distance along the creek is measured along the centerline of the channel beginning at the headwaters (Allequash Springs) and increasing in a downstream direction. Transect site numbers refer to sites shown in Figure 2.

tle dissolved iron in the stream and lake samples (Figure 7), suggesting that the oxidizing conditions are limiting iron levels through the formation of iron hydroxides. There are a few locations where iron is present in the subsurface, most notably above site 30, which is likely associated with dissolved organic matter derived from the upstream wetlands. Further downstream, iron is once again present in ground water beneath the lakebed in the lower basin, and probably originates from wetlands off the northwest shore of Big Muskellunge Lake (Pint et al., this issue).

#### Longitudinal Transect Strontium Isotopes

Bullen et al. (1996) noted that the stable-isotope pair  $^{87}\text{Sr}/^{86}\text{Sr}$  can be used to discern differences in water-mineral contact time, thus allowing us to further distinguish the source of the ground water and flowpath dynamics. In terrestrial recharge areas with short flowpaths, the geochemical conditions (i.e., low pH, high  $p\text{CO}_2$ ) and long contact time within the unsaturated zone facilitate the weathering of K-feldspar and biotite in addition to plagioclase and calcium-magnesium silicate, resulting in a more radiogenic strontium isotope composition (more positive or enriched in  $\delta^{87}\text{Sr}$ ). In the Allequash Creek watershed, the unsaturated zone waters are characterized by a  $\delta^{87}\text{Sr}$  around +2‰ in thin unsaturated zones (<2 m) to greater than +20‰ in thick unsaturated zones (>5 m). The average  $\delta^{87}\text{Sr}$  for terrestrial-recharge water in the Allequash Creek basin has been estimated to be +15‰ (Bullen et al. 1996). As ground water with this  $\delta^{87}\text{Sr}$  composition travels through the saturated zone for an appreciable distance, the  $\delta^{87}\text{Sr}$  may either decrease or increase, depending on flowpath dynamics that largely depend on grain size. In contrast, lake-derived recharge is always characterized by lower  $\delta^{87}\text{Sr}$  ( $\delta^{87}\text{Sr} < 0\text{‰}$ ) relative to the originating composition in the lake.

These contrasting trends in strontium isotope evolution develop in large part due to differences in ground water

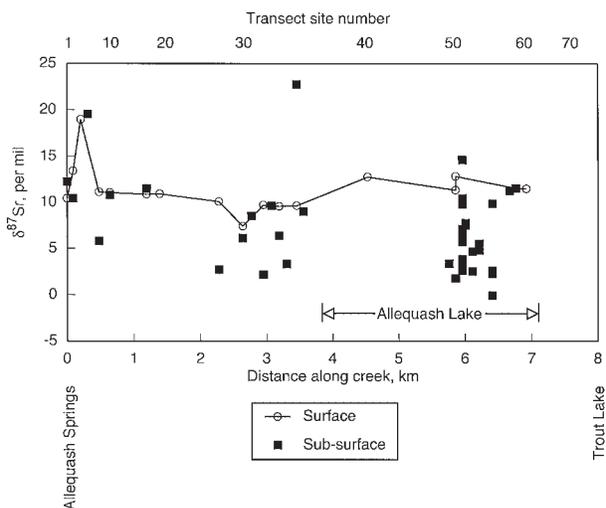
mobility along terrestrial- and lake-recharge flowpaths (Bullen et al. 1996). In cases where water velocities are slow (such as in the unsaturated zone or in poorly transmissive, fine-grained portions of the aquifer), the  $\delta^{87}\text{Sr}$  becomes more positive relative to that of the source water regardless of whether the ground water is derived from terrestrial, lake, or wetland recharge. Under such transport-limited conditions, the slow-moving water is more likely to reach thermodynamic equilibrium (i.e., at the water-mineral interface) with respect to both plagioclase and calcium-magnesium silicate that contain relatively unradiogenic strontium, and evolve toward the more enriched  $\delta^{87}\text{Sr}$  derived from biotite and K-feldspar. In contrast, given sufficient travel distance in the saturated zone (on the order of hundreds of meters) at relatively fast velocities such as along lake water recharge flowpaths and in general through highly transmissive portions of the aquifer, ground waters will be characterized by  $\delta_r^{87}\text{Sr} < 0\text{‰}$  when normalized to the composition of the water just prior to its introduction to the saturated zone. This trend probably results from both protracted dissolution of plagioclase and calcium-magnesium silicate and the suppression of dissolution of biotite and K-feldspar along such pathways.

In the headwaters, where the predominant source of water is terrestrial recharge, the relatively radiogenic strontium isotope values apparently indicate slow flow rates or, more likely, long contact times in the unsaturated zone (Figure 8). From site 16 (1.2 km from the headwaters) through site 30, where the source of water is primarily lake derived, the less radiogenic strontium isotope values apparently indicate faster flow rates as well as a lack of evolution in the unsaturated zone. From site 30 through Allequash Lake, the strontium isotope values indicate a return to slower flow rates and/or an increasing role for evolution in the unsaturated zone. These observations are also supported by the calcium distribution described previously, to the extent that calcium is a useful measure of water-aquifer contact time (Figure 6).

Given the relative mineralogic homogeneity of the glacial outwash sand that comprises the aquifer, less complex relations between ground water chemistry, stream chemistry, and associated solute budgets and basin yields might be expected. However, the spatial variability in source water and chemistry depicted in Figures 5 through 7 was considerably higher than expected, particularly for the shallow subsurface samples. Much of the variability can be related to geochemical differences at the start of the flowpath for each source water; however, flowpath length and differing velocities through the subsurface are also important drivers. The variability within this watershed is striking, and has important implications for watershed research. The wide variability in chemistry underscores the inadequacy of assigning single values of concentrations to subsurface water and residence times used to simulate weathering reactions.

#### Longitudinal Transect Use of Multiple Isotopes

In many cases, analysis of multiple isotopes can improve the understanding of a flow system. Simple two-member mixing models using two isotopes can be used to describe the chemical evolution of the chemistry of the

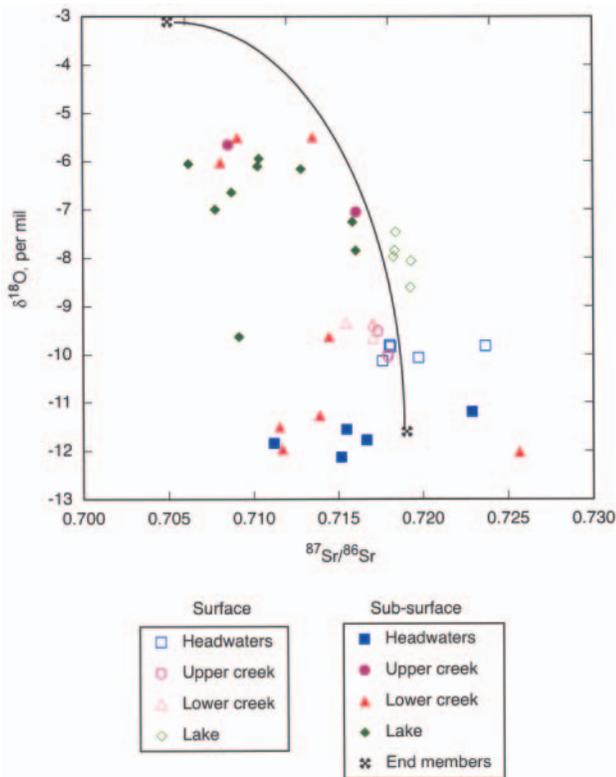


**Figure 8.** Distribution of  $\delta^{87}\text{Sr}$  in surface waters and subsurface samples collected 1 m into the sand in the streambed. Distance along the creek is measured along the centerline of the channel beginning at the headwaters (Allequash Springs) and increasing in a downstream direction. Transect site numbers refer to sites shown in Figure 2.

watershed stream system. If we consider  $\delta^{18}\text{O}$  as an indicator of source water (terrestrial-derived versus lake-derived recharge) and  $\delta^{87}\text{Sr}$  as a general indicator of some combination of velocity, water-mineral contact time, and/or water mobility along a flowpath, then a plot of  $\delta^{18}\text{O}$  versus  $\delta^{87}\text{Sr}$  should result in samples falling along a mixing line between the two extremes (Figure 9). Bullen et al. (1996) demonstrated that several of the lakes from the region lie along such a mixing array between the compositions of evaporated meteoric water and average terrestrial recharge in this region. Because the Allequash Creek samples deviate significantly from the mixing hyperbola drawn between these two end members, use of a simple two-component mixing model is clearly not valid. However, the deviations from the ideal mixing line can be explained in terms of along-flowpath processes that modify the mixing relationship. For example, lake water that originally falls along the two-component mixing line (e.g., Big Muskellunge Lake) can be transformed in  $\delta^{87}\text{Sr}$  as it moves along a flowpath from Big Muskellunge Lake toward Allequash Creek and the ultimate sink in the system, Trout Lake. Thus, using oxygen and strontium isotopes together helps to discern deviations from the simple two-component mixing scenario that are likely to arise from along-flowpath processes on the local scale. It is important to recognize that even though such local-scale processes can variably modify the original composition of the recharge water along individual flowpaths, the stream itself generally acts as an integrator except along portions where subsurface inputs are not sufficiently large to effect a change in stream chemistry.

#### Implications for Watershed Research

Sampling surface water and ground water along the Allequash Creek transect provides a great deal of information regarding water sources and flowpaths within the watershed. Assuming subsurface samples collected 1 m



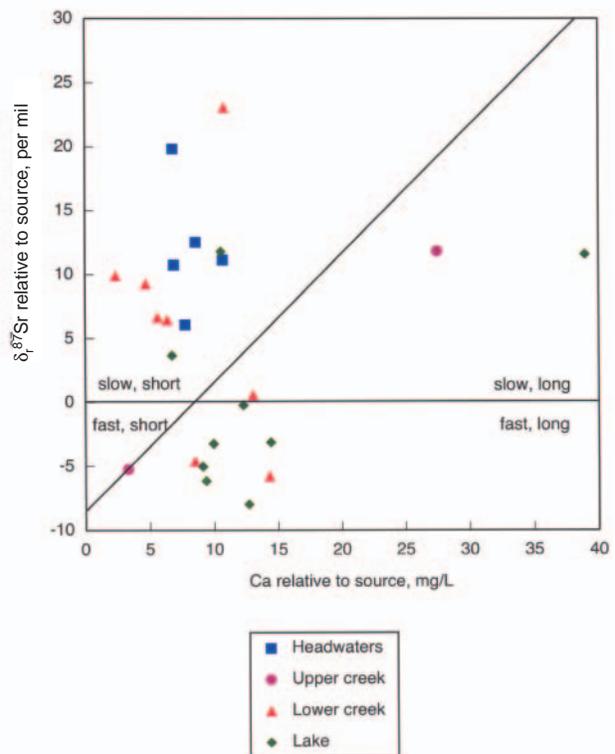
**Figure 9. Relationship between  $\delta^{18}\text{O}$  and  $\delta^{87}\text{Sr}$  for surface and subsurface samples collected 1 m into the sand in the streambed for sections of Allequash Creek and in the lakebed of the lower basin of Allequash Lake. The curve drawn represents a simple two-member mixing between radiogenic meteoric waters and unradiogenic evaporated lake waters.**

below the streambed are representative of the ground water system prior to interacting with the stream, then it is possible to determine in a qualitative way where different source waters and various types of flowpaths enter the stream system. The values of  $\delta^{18}\text{O}$  can be used to distinguish terrestrial-derived sources (11‰ to 12‰) from lake- and wetland-derived sources (5‰ to 6‰). Calcium concentrations can be used to discern relative differences in the length of, or mineral-aquifer contact time along, flowpaths. Strontium isotope ratios can be used as a measure of relative differences in the overall mobility of water along flowpaths and express the differences developed during residence in contrasting environments, such as the unsaturated zone and highly transmissive portions of the aquifer. Because  $^{87}\text{Sr}/^{86}\text{Sr}$  trends differ along flowpaths originating from terrestrial and lake water recharge (Bullen et al. 1996), values of  $\delta^{87}\text{Sr}$  should be computed relative to the particular source water as determined based on  $\delta^{18}\text{O}$ . A generalized plot of  $\delta_r^{87}\text{Sr}$  versus calcium for subsurface samples collected along Allequash Creek is shown in Figure 10. Based on values for numerous wells along a flowpath (USGS unpublished data), the plot has been divided into four regions that distinguish between relative flowpath length and relative water mobility along the flowpath. Note that the line distinguishing between short and long flowpaths is sloped, reflecting the fact that both flowpath length and water mobility are needed to determine the relative increase in calcium downstream from a given source water. Note

additionally that there are no easily distinguished patterns between position within the watershed (reflected by the grouping of the sites) and the length and velocity of the flowpaths. The results in Figure 10 are consistent with the ground water flow model presented in the following paper (Pint et al., this issue).

## Conclusions

Our studies at Allequash Creek have allowed us to make several site-specific observations on the factors controlling the linkages between ground water and surface water chemistry, many of which are probably extendable to many other watersheds. There are distinct water isotopic and geochemical differences observed at a smaller hillslope scale and the larger Allequash Creek scale. The variability was larger than expected for this geologically homogeneous simple watershed, and is likely to be seen in more complex basins. The flow system arises from one of three main source waters (terrestrial-, lake-, and wetland-derived recharge). Depending on the flowpath length, integrated water mobility through the aquifer, and the proximity of the creek to water sources, the weathering rates and resulting chemical signature demonstrate considerable spatial variability. High calcium concentrations result from long flowpaths or protracted mineral-aquifer contact time; high  $\delta^{87}\text{Sr}$



**Figure 10. Values for  $\delta_r^{87}\text{Sr}$  and calcium concentrations for subsurface samples collected 1 m into the sand in the streambed for sections of Allequash Creek and in the lakebed of the lower basin of Allequash Lake. The  $\delta_r^{87}\text{Sr}$  values are computed relative to source water (based on the value of  $\delta^{18}\text{O}$ ), and the calcium concentrations are computed by subtracting the average value for each source water from the sampled concentration.**

in the saturated zone results from reduced mobility of water at some point along the flowpath from recharge source to discharge sink, either in the unsaturated zone or along poorly transmissive portions of the aquifer. In addition, the use of multiple isotopes and chemistry were vital to understanding the spatial variability of water source and flowpaths.

At the scale sampled, all the parameters investigated in this study showed spatial variability, even though they are often considered “conservative” in a watershed setting. Contrary to using simple relations for a baseline or background solute concentrations for a watershed, knowledge of where the water originates in the watershed is crucial for understanding the processes that are responsible for ground water ion and isotope chemistry that dictates subsequent stream chemistry. For example, a chemical hydrograph separation using “new” and “old” water would be complicated in that these signature compositions can be dependent on where the stream and ground water samples are taken. Moreover, in order to have predictive power in addition to simple descriptive power, an understanding of the watershed processes, not only stream processes, is needed. That is, where it is conceivable that a solute basin yield may be obtained using an estimated average ground water concentration, a prediction of the timing and magnitude of what will happen to the basin yield if some change within the basin were to occur (clear-cutting, fire, development, climate change) requires a conceptual understanding of which processes, where, and at what magnitude these processes are occurring in the basin. Moreover, a deterministic modeling framework is needed to quantify the change.

Much of the variability in this watershed is due to the effects of multiple water sources; this concept will be explored in the companion paper by Pint et al. (this issue). It should also be noted that the degree of variability, and insights gained therein, would not have been revealed without the relatively large number of subsurface sampling locations within the watershed. Clearly, the variability could not have been identified had a more traditional approach of sampling only the stream near the basin outlet been employed. Only with the combined approach of stream and ground water sampling was the more complex and interesting system elucidated. It is our belief that the findings from this “simple” watershed will also likely hold true in other watersheds. Finally, accurate knowledge of the watershed boundaries is critical for calculating solute budgets and basin yields.

## References

Abbott, M.D., A. Lini, and P.R. Bierman. 2000.  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and  $^3\text{H}$  measurements constrain groundwater recharge patterns in an upland fractured bedrock aquifer, Vermont, USA. *Journal of Hydrology* 228, no. 1: 101–112.

Attig, J. Jr. 1985. *Pleistocene Geology of Vilas County, Wisconsin*. Madison, Wisconsin: Wisconsin Geological and Natural History Survey Informational Circular 50.

Brown, V.A., J.J. McDonnell, and C. Kendall. 1999. The role of event water, a rapid shallow flow component, and catchment size in summer stormflow. *Journal of Hydrology* 217, no. 3/4: 171–190.

Bullen, T.D., D.P. Krabbenhoft, and C. Kendall. 1996. Kinetic and mineralogic controls on the evolution of groundwater chemistry and  $^{87}\text{Sr}/^{86}\text{Sr}$  in a sandy silicate aquifer, northern

Wisconsin, USA. *Geochimica et Cosmochimica Acta* 60, no. 10: 1807–1821.

Burns, D.A., J.J. McDonnell, R.P. Hooper, N.E. Peters, J.E. Freer, C. Kendall, and K. Beven. 2001. Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA). *Hydrological Processes* 15, no. 10: 1903–1924.

Chen, H., and R. Beschta. 1999. Dynamic hydrologic simulation of the Bear Brook Watershed in Maine (BBWM). *Environmental Monitoring and Assessment* 55, no. 1: 53–96.

Cheng, X., and M.P. Anderson. 1994. Simulating the influence of lake position on groundwater fluxes. *Water Resources Research* 30, no. 7: 2041–2049.

Clark, I.D., and P. Fritz. 1997. *Environmental Isotopes in Hydrogeology*. Boca Raton, Florida: Lewis Publishers.

Elder, J.F., D.P. Krabbenhoft, and J.F. Walker. 1992. Water, energy, and biogeochemical budgets (WEBB) program: Data availability and research at the northern temperate lakes site, Wisconsin. Madison, Wisconsin: U.S. Geological Survey Open-File Report 92–48.

Epstein, S., and T. Mayeda. 1953. Variation of  $^{18}\text{O}$  of waters from natural sources. *Geochimica et Cosmochimica Acta* 4, 213–224.

Gat, J.R. 1970. Environmental isotope balance of Lake Tiberias. In *Isotope Hydrology*. Vienna: International Atomic Energy Agency.

Hooper, R.P. 2001. Applying the scientific method to small catchment studies: A review of the Panola Mountain experience. *Hydrological Processes* 15, no. 10: 2039–2050.

Hooper, R.P., N. Christophersen, and N.E. Peters. 1990. Modeling streamwater chemistry as a mixture of soil-water end members: An application to the Panola Mountain catchment, Georgia, USA. *Journal of Hydrology* 116, 321–343.

Hooper, R.P., and C.A. Shoemaker. 1996. A comparison of chemical and isotopic hydrograph separation. *Water Resources Research* 22, no. 10: 1444–1454.

Huddart, P.A., F.J. Longstaffe, and A.S. Crowe. 1999.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  evidence for inputs to groundwater at a wetland coastal boundary in the southern Great Lakes region of Canada. *Journal of Hydrology* 214, no. 1: 18–31.

Hunt, R.J., T.D. Bullen, D.P. Krabbenhoft, and C. Kendall. 1998. Using stable isotopes of water and strontium to investigate the hydrology of a natural and a constructed wetland. *Ground Water* 36, no. 3: 434–443.

Kendall, C., and T.B. Coplen. 1985. Multisample conversion of water to hydrogen by zinc for stable isotope determination. *Analytical Chemistry* 57, 1437–1440.

Kendall, C., J.J. McDonnell, and W. Gu. 2001. A look inside ‘black box’ hydrograph separation models: A study at the Hydrohill catchment. *Hydrological Processes* 15, no. 10: 1877–1902.

Kenoyer, G.J. 1986. Evolution of groundwater chemistry and flow in a sandy aquifer in northern Wisconsin. Ph.D., diss., Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin.

Kenoyer, G.J., and C.J. Bowser. 1992. Groundwater chemical evolution in a sandy silicate aquifer in northern Wisconsin, I. Patterns and rates of change. *Water Resources Research* 28, no. 2: 579–589.

Krabbenhoft, D.P., and C.L. Babiarez. 1992. The role of groundwater transport in aquatic mercury cycling. *Water Resources Research* 28, no. 12: 3119–3128.

Krabbenhoft, D.P. 1988. Hydrologic and geochemical investigations of aquifer-lake interactions at Sparkling Lake, Wisconsin. Ph.D. diss., Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin.

Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarez, J.P. Hurley, and A.W. Andren. 1995. Mercury cycling in the Allequash Creek Watershed, northern Wisconsin. *Water, Air, and Soil Pollution* 80, 425–433.

Magnuson, J.J., C.J. Bowser, and T.K. Kratz. 1984. Long-term ecological research (LTER) on north temperate lakes of the

- United States. *Verhandlungen Internationale Vereinigung Limnologie* 22, 533–535.
- Marin, L.E. 1986. Spatial and temporal patterns in the hydrogeochemistry of a bog-wetland system, Northern Highlands Lake District, Wisconsin. M.S. thesis, Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin.
- McDonnell, J.J., T. Tanaka, M.J. Mitchell, and N. Ohte. 2001. Hydrology and biogeochemistry of forested catchments. *Hydrological Processes* 15, no. 10: 1673–1674.
- McGlynn, B.L., J.J. McDonnell, J.B. Shanley, and C. Kendall. 1999. Riparian zone flowpath dynamics during snowmelt in a small headwater catchment. *Journal of Hydrology* 222, no. 1: 75–92.
- Ojiambo, B.S., R.J. Poreda, and W.B. Lyons. 2001. Ground water/surface water interactions in Lake Naivasha, Kenya, using  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ , and  $^3\text{H}/^3\text{He}$  age-dating. *Ground Water* 39, no. 4: 526–533.
- Okwueze, E. 1983. Geophysical investigations of the bedrock and the groundwater-lake flow system in the Trout Lake region of Vilas County, northern Wisconsin. Ph.D. diss., Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin.
- Pint, C.N., R.J. Hunt, and M.P. Anderson. 2003. Flow path delineation and ground water age, Allequash Basin, Wisconsin. *Ground Water* 41, no. 7, 895–902.
- Plummer, L.N., J.F. Busby, R.W. Lee, and B.B. Hanshaw. 1990. Geochemical modeling of the Madison Aquifer in parts of Montana, Wyoming, and South Dakota. *Water Resources Research* 26, no. 9: 1981–2014.
- Rose, S. 1996. Temporal environmental isotopic variation within the Falling Creek (Georgia) watershed: Implications for contributions to streamflow. *Journal of Hydrology* 174, no. 3: 243–261.
- Rose, W.J. 1993. Hydrology of Little Rock Lake in Vilas County, north-central Wisconsin. Madison, Wisconsin: U.S. Geological Survey Water Resources Investigations Report 93–4139.
- Sklash, M.G., and R.N. Farvolden. 1979. The role of groundwater in storm runoff. *Journal of Hydrology* 43, no. 1/4: 45–65.
- Stauffer, R.E. 1985. Use of solute tracers released by weathering to estimate groundwater inflow seepage to lakes. *Environmental Science and Technology* 19, 405–411.
- Walker, J.F., and T.D. Bullen. 2000. Trout Lake, Wisconsin: A water, energy, and biogeochemical budgets program site. Reston, Virginia: U.S. Geological Survey Fact Sheet 161–99.
- Walker, J.F., and D.P. Krabbenhoft. 1998. Groundwater and surface-water interactions in riparian and lake-dominated systems. In *Isotope Tracers in Catchment Hydrology*, ed. J.J. McDonnell and C. Kendall. Amsterdam: Elsevier.
- Welsch, D.L., C.N. Kroll, J.J. McDonnell, and D.A. Burns. 2001. Topographic controls on the chemistry of subsurface stormflow. *Hydrological Processes* 15, no. 10: 1925–1938.
- Wentz, D.A., and W.J. Rose. 1989. Interrelationships among hydrologic-budget components of a northern Wisconsin seepage lake and implications for acid-deposition modeling. *Archives of Environmental Contamination and Toxicology* 18, 147–155.