

# Seasonal and Short-Term Variability in Chlorinated Solvent Concentrations in Two Karst Springs in Middle Tennessee: Implications for Sampling Design

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## Abstract

The U.S. Geological Survey in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund is evaluating volatile organic compound sampling strategies for karst springs. Water-quality signatures for two contaminated karst springs in Middle Tennessee were determined by continuously monitoring selected water-quality properties through one complete hydrologic cycle. High-frequency flow-controlled sampling was used to characterize chlorinated solvent concentrations. The results indicate that discharge from and contaminant concentrations in Wilson Spring near Lewisburg, Tennessee, are flashy as indicated by rapid fluctuations in water quality and discharge in response to storm events. During one storm event, chloroform concentrations in discharge from this spring increased to 33 milligrams per liter, which represents a 60-fold increase over the concentration before the storm. The increased chloroform concentrations were correlated with a decrease in specific conductance and peak discharge. The maximum chloroform concentrations detected during this storm, represents a sixfold increase over the maximum concentrations measured at any other time during the study period. Big Spring at Rutledge Falls shows little change in water-quality properties indicating a large recharge area and diffuse-flow aquifer conditions. Results from the study demonstrate the need to develop site-specific sampling strategies for karst springs. Results also indicate that evaluating water-quality signatures of karst springs is helpful in designing a site-specific sampling strategy.

## INTRODUCTION

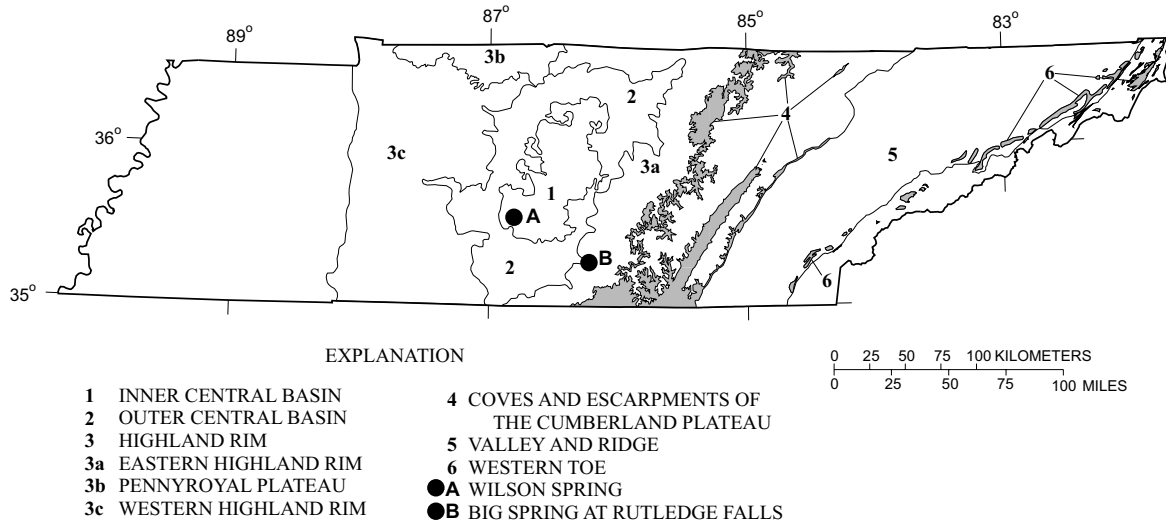
Karst springs are important sampling points that are commonly used as monitoring locations to collect water-quality data at contaminated sites in karst hydrogeologic regimes (Quinlan and Ewers, 1985). Abrupt changes in water quality in karst springs in response to rainfall events are well documented (Hess and White, 1988, Quinlan and Alexander, 1987; Dreiss, 1989; Brown and Ewers, 1991; Ryan and Meiman, 1996). Quinlan and Alexander (1987) published guidelines for water-quality sampling frequency in karst terranes. The importance of high-frequency flow-dependent sampling in accurately determining concentrations of fecal bacteria, chloride, and pesticides in water from a karst spring has been documented (Meiman, 1991). Cretella (1985) showed that volatile organic compound (VOC) concentrations in a karst spring could vary as much as tenfold throughout a storm cycle. Despite these findings, little consideration has been given to the design of sampling programs for monitoring water quality in karst springs. Quarterly and semi-annual samplings are still conducted at many contaminated karst sites.

Depending on the maturity of karst development and the nature of a rainfall event, each spring has a distinctive water-quality and discharge signature (Quinlan and Ewers, 1985). Hydrographs of

continuous water-quality data are needed to reveal these signatures. The U.S. Geological Survey, in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund, is studying three contaminated springs in karst areas of Middle Tennessee to evaluate VOC sampling strategies. The springs were continually monitored for specific water-quality properties; and during selected storm events, high-frequency sampling was conducted for VOC analysis. This report presents preliminary data from two of these springs, Wilson Spring near Lewisburg, Tennessee, and Big Spring at Rutledge Falls near Tullahoma, Tennessee.

## DESCRIPTION AND HISTORY OF WILSON SPRING

Wilson Spring is located in the Central Basin karst region of Tennessee (fig. 1), as described by Wolfe and others (1997). The hydrogeology of the Central Basin is characterized by ground-water flow in massive Ordovician limestones. This type of massive limestone alternates through out the geologic section with thin-bedded, shaly, limestones (Farmer and Hollyday, 1999). Uplift of the Nashville Dome has resulted in the development of extensive fracturing in this karst region. Dissolution of the limestone has enlarged these fractures resulting in karst development in the massive



**Figure 1.** Location of study springs and karst regions of Tennessee. (Modified from Wolfe and others, 1997.)

formations. The thin-bedded shaly formations generally act as confining units. The thin-bedded Ordovician-age Lebanon Limestone caps the hills in the study area and retards the downward movement of water. Surface streams that run off the Lebanon Limestone onto the massive Ridley Limestone (Ordovician age) can sink into the upper Ridley karst aquifer as described by Crawford and Ulmer (1994). A 10-foot-thick thin-bedded unit is present within the Ridley Limestone approximately 100 feet below the stratigraphic top of this unit (Wilson, 1990). The thin-bedded unit restricts downward flow, and cave streams are developed on the top of this unit. Wilson Spring is the surface discharge point of one of these cave streams (Crawford and Ulmer, 1994). Land use in the area is predominantly agricultural.

In October 1990, a train derailment near Wilson Spring resulted in the release of more than 15,000 gallons of chloroform, a dense nonaqueous phase liquid. The chloroform sank into the upper Ridley aquifer at the site. According to Crawford and Ulmer (1994), the chloroform pooled on top of the thin-bedded unit of the Ridley Limestone, and then moved southwest downdip along weathered bedding planes until being trapped by low permeability, less weathered rock. Water containing chloroform is transported along the strike of the bedding planes through a cave stream southeast to Wilson Spring. Since 1992, Ogden Environmental and Energy Services (a consultant for the railroad) have been continuously monitoring discharge and rainfall at the site and analyzing samples on a monthly bases for VOC's. Based on this monitoring, chloroform concentrations typically range from 1 to 5 milligrams per liter (mg/L) seasonally.

Water from the spring is impounded and treated before being released into Big Rock Creek.

## DESCRIPTION AND HISTORY OF BIG SPRING

Big Spring at Rutledge Falls is located in Middle Tennessee on the escarpment of the Highland Rim (fig. 1). The spring discharges approximately 3.5 cubic feet per second (ft<sup>3</sup>/s) from the Manchester aquifer into Crumpton Creek. The discharge occurs near the contact between the Late Devonian-age and Early Mississippian-age Chattanooga Shale and the overlying Mississippian-age Fort Payne Formation. The Chattanooga Shale ranges from 20 to 30 feet in thickness and is generally considered to be a major confining unit in Tennessee (Burchett, 1977). The Fort Payne Formation ranges from 20 to 230 feet in thickness and is predominantly soluble dolomitic limestone. The Manchester aquifer is a regional aquifer comprised of gravel in the residuum of the upper part of the Fort Payne Formation and solution openings in the bedrock of the Fort Payne Formation (Burchett and Hollyday, 1974). Numerous springs and seeps are present along the Highland Rim where the contact between the Fort Payne Formation and the Chattanooga Shale crops out. Land use in the area of the spring is mixed residential and agriculture. Chlorinated solvents including perchloroethylene (PCE) and trichloroethylene (TCE) have been detected in water samples collected from the spring at concentrations of approximately 2 and 9 micrograms per liter (µg/L), respectively. The general direction of ground-water

flow in the area near the spring is from the southeast (Mahoney and Robinson, 1993).

## METHODS

In February 2000, gaging stations were established at both springs according to the procedures described by Carter and Davidian (1982). Continuous stage-recorders described by Buchanan and Somers (1968) were used to collect stage data in 0.01-foot increments at 15-minute intervals. On October 1, 2000, the recording interval was changed to 10 minutes at Wilson Spring to correspond with frequency of data collection by the consultant for the railroad. Discharge measurements were made at both springs for a range of stages according to procedures described by Buchanan and Somers (1969), and discharge ratings were developed following procedures described by Kennedy (1983). These ratings were applied to the continuous-stage data to produce continuous-discharge records using techniques described by Kennedy (1983).

Field measurements of water quality were made at both springs according to the general procedures described by Wood (1976) and Wilde and Radtke (1998). Field measurements of specific conductance, pH, dissolved oxygen (DO), and water temperature were made using a Hydrolab DataSonde 4. At Wilson Spring, the instrument was placed in a tub just below the lip of a flume because of the shallow water depth inside the flume. During field visits, a specific conductance and temperature meter was used to compare measurements made in the tub with measurements in the flume. Measurements were made at 15-minute intervals at both springs until October 1, 2000, when Wilson Spring measurements were changed to 10-minute intervals to coincide with the consultant's data-collection interval. Instruments were calibrated before deployment by using standard reference solutions and following the procedures recommended by the manufacturer (Hydrolab Corporation, 1997). At approximately 3-week intervals, data were downloaded from the instruments and calibration was checked. Recalibration was performed as necessary. Rainfall data collected at Wilson Spring were obtained from the consultants for the railroad.

VOC samples were collected and processed using methods described by Wilde and others (1998a and 1998b). Forty-milliliter VOC vials were dipped in the water body by hand to collect grab samples at both springs. At Wilson Spring during a storm event in November 2000, an ISCO model 6100 automatic VOC sampler was used to collect samples at 1-hour intervals from the tub. Several grab samples were collected during this storm event to verify the accuracy of the

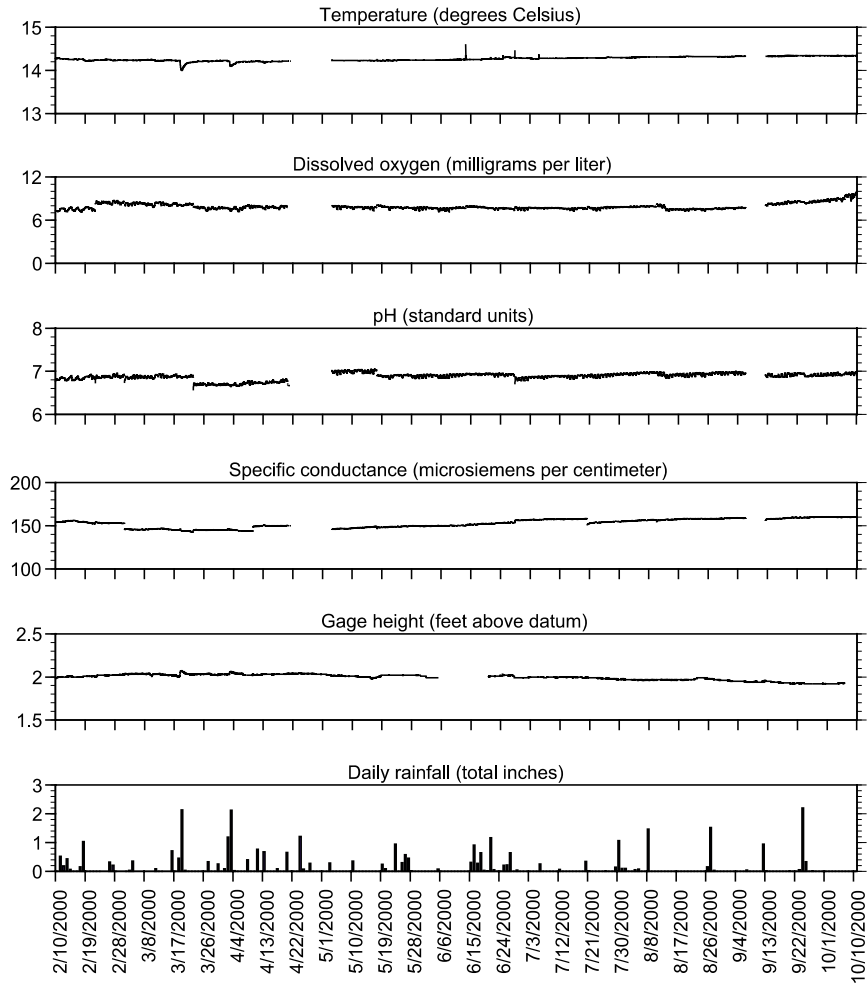
results obtained from the automatically collected samples.

Samples were analyzed for VOC's using a Scentograph PLUS II portable gas chromatograph (GC) equipped with a purge-and-trap unit. Purge-and-trap procedures similar to those described by U.S. Environmental Protection Agency (U.S. EPA) Method 5030B (1992) were used. Periodic duplicate samples were collected and sent to the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Denver, Colorado, to validate the results obtained using the portable GC.

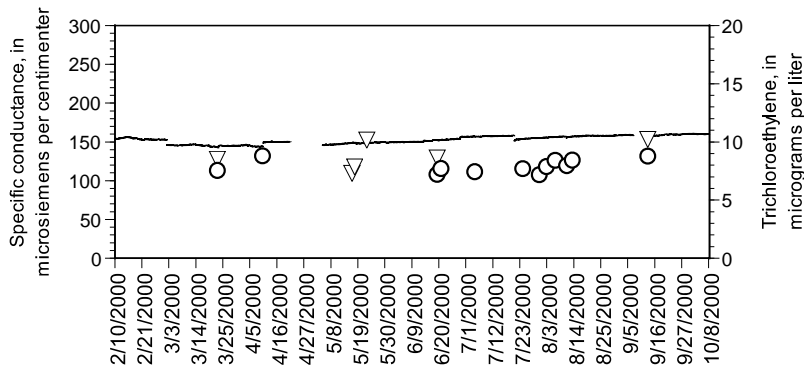
## DISCUSSION

Continuous water-quality data collected at Big Spring show little variation from February through October 2000 (fig. 2). Storm events that occurred during the study period appeared to have only slight effects on measured water-quality properties. Gage height showed little variation, therefore, a rating curve was not established. Temperature, DO, and pH remained constant with mean values of approximately 14 °C, 8 mg/L, and 7.0, respectively. Specific conductance averaged about 150 microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ ), with a slight increase in the summer and fall months (fig. 2). TCE concentrations reflect a similar pattern of little variation, with values ranging between 7 and 10  $\mu\text{g}/\text{L}$  (fig. 3). The flashy water-quality signature (characterized by large variations in concentrations of chemical constituents and values of physical properties) normally associated with conduit-type karst springs is not present at Big Spring. The constant discharge implies that this spring discharges from an aquifer with a large recharge area, a large amount of storage, and in which diffuse flow is dominant—all characteristics that correlate with the Manchester aquifer.

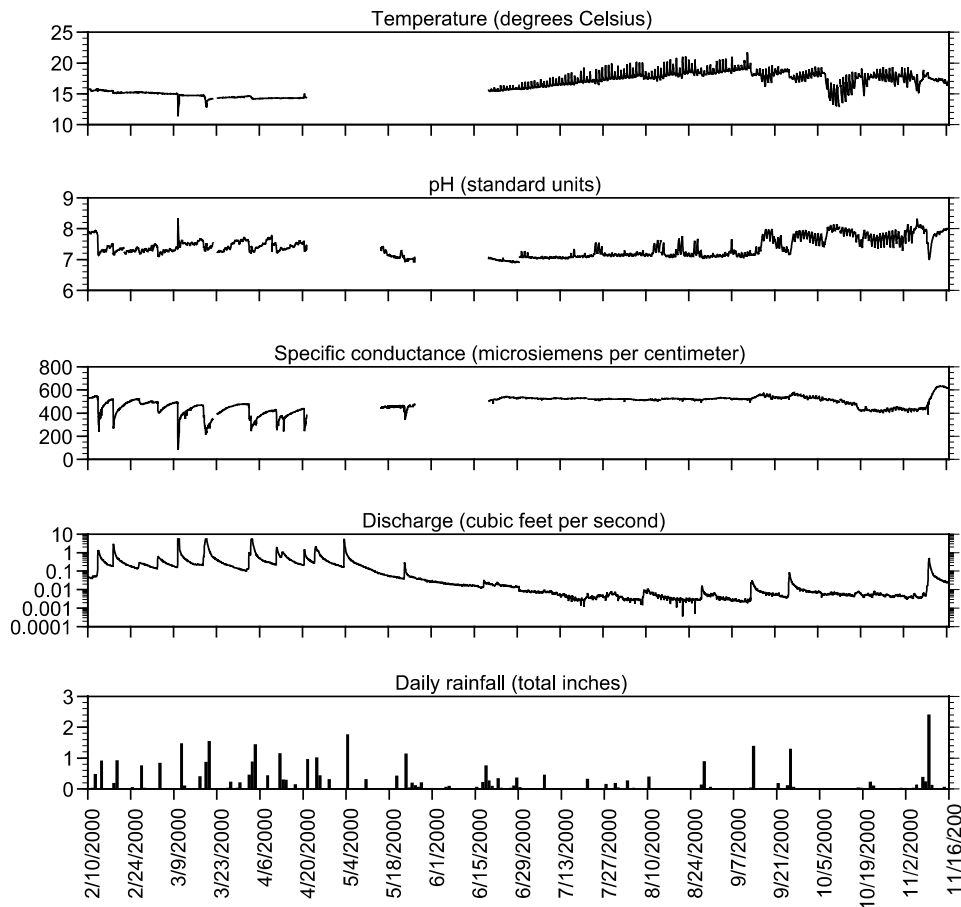
In contrast, Wilson Spring has a flashy water-quality signature. During spring the 2000 storm season, storm events resulted in dramatic changes in discharge and specific conductance, and smaller fluctuations in pH and temperature. During storms, discharge increased from less than 0.1  $\text{ft}^3/\text{s}$  to greater than 5  $\text{ft}^3/\text{s}$  and specific conductance commonly decreased from a high of about 550 to as low as 100  $\mu\text{S}/\text{cm}$  (fig. 4). The higher pre-storm specific conductance may be attributed to a long residence time of water in the aquifer. This long residence time allows for increased dissolution of the limestone resulting in an increased ionic content and resultant specific conductance of the water. The lower specific conductance during the storm event is attributed to the rapid influx of water with ionic content that has had only a short period of



**Figure 2.** Continuous water-quality and gage-height data from Big Spring at Rutledge Falls at 15-minute intervals, Feb. 10 through Oct. 10, 2000. Daily rainfall data from U.S. Geological Survey gaging station located 19 miles west-northwest of Big Spring. (Line gaps indicate missing data.)



**Figure 3.** Trichloroethylene and specific conductance data from Big Spring at Rutledge Falls, Feb. 10 through Oct. 8, 2000. Water samples were analyzed by the U.S. Geological Survey National Water Quality Laboratory (USGS NWQL) or using a portable gas chromatograph (GC). (Line gaps indicate missing data.)



**Figure 4.** Water-quality, discharge, and rainfall data collected from Wilson Spring, Feb. 10 through Nov. 16, 2000 (discharge and rainfall data collected by Ogden Environmental and Energy Services). (Line gaps indicate missing data.)

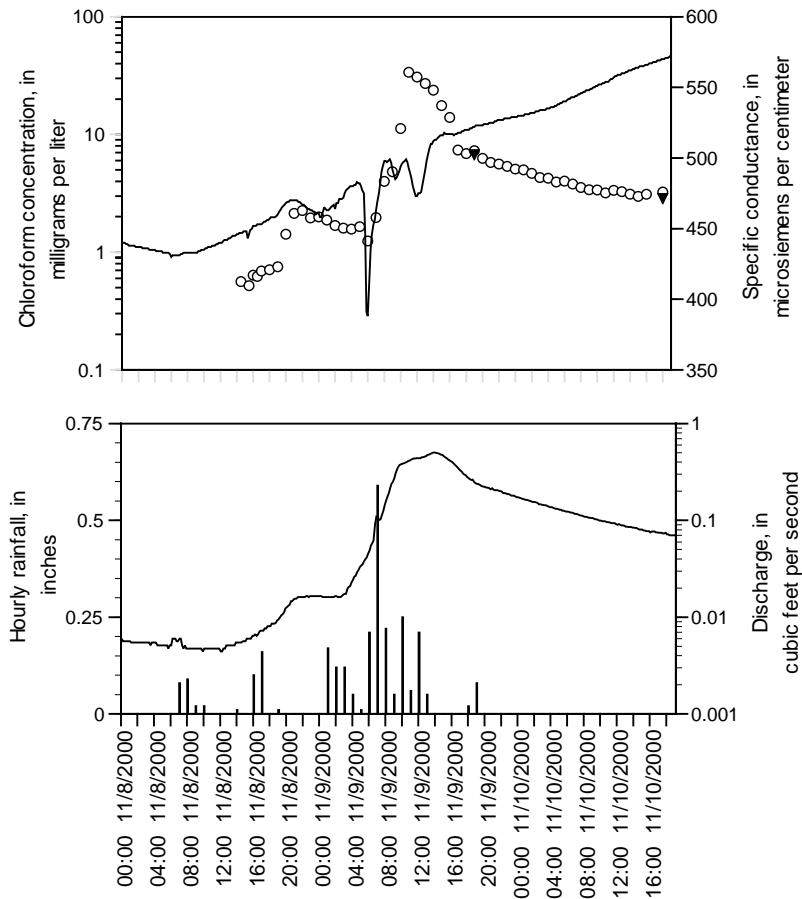
time to interact with the limestone. During summer 2000, discharge declined and specific conductance remained stable at approximately 580  $\mu\text{S}/\text{cm}$ . Daily cycles in values of pH and temperature in the summer may be the consequence of biological activity in the tub and solar radiation (fig. 4).

During the sampling period, six grab samples were collected from the tub that corresponded with samples collected by the automatic sampler. Chloroform concentrations detected in the samples collected by the automatic sampler were consistently within 15 percent of the concentrations detected in the grab samples.

On November 8, 2000, the first major storm occurred following a dry summer. The data from this storm elucidated some important characteristics about the hydrology of the spring. The storm produced 2.61 inches of rain beginning on November 8 and lasting until 1800 hours Greenwich Mean Time (GMT) on November 9 (fig. 5). At approximately

1500 hours GMT on November 8, discharge began to increase from a base-flow level of about 0.005  $\text{ft}^3/\text{s}$  to a peak of 0.5  $\text{ft}^3/\text{s}$  at 1350 hours GMT on November 9 (fig. 5). As discharge increased, specific conductance started to rise, reaching a maximum value of 630  $\mu\text{S}/\text{cm}$  at 1500 hours GMT on November 13, approximately 4 days after the peak discharge occurred. This peak is 205  $\mu\text{S}/\text{cm}$  higher than the value of 425  $\mu\text{S}/\text{cm}$  observed on November 8, 2000 (fig. 4).

Dreiss (1989) concluded that fluctuations in dissolved solids and other water-quality properties, as well as contaminant concentrations that do not coincide with peak discharge, are common in mature karst systems. Temporary increases in specific conductance after the start of storm events are believed to be the result of more mineralized water that is driven from the diffuse-flow parts of the aquifer by increases in head in the conduits (Hess and White, 1988). During the period of increasing

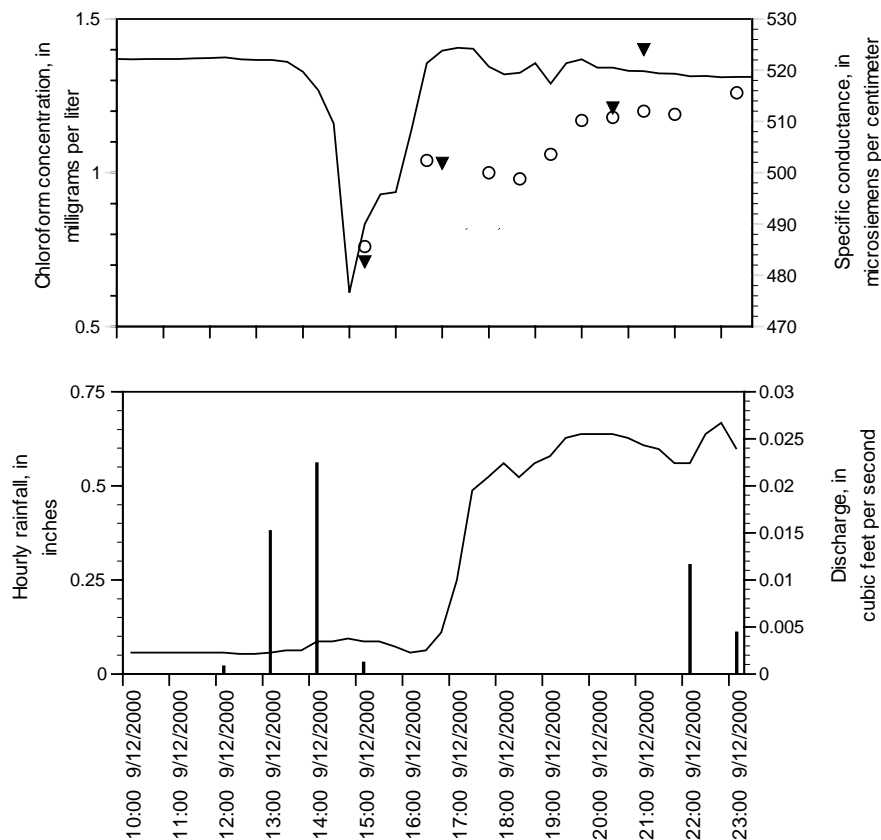


**Figure 5.** Chloroform, specific conductance, rainfall, and discharge data collected from Wilson Spring during a November 2000 storm (discharge and rainfall data collected by Ogden Environmental and Energy Services). Water samples were analyzed by the U.S. Geological Survey National Water Quality Laboratory (USGS NWQL) or using a portable gas chromatograph (GC).

discharge in Wilson Spring on November 9, 2000, an abrupt decline in specific conductance was observed and correlated with a decrease in chloroform concentrations (fig. 5). During a minor storm on September 12, 2000, a similar decrease in specific conductance occurred. During the latter part of this storm as specific conductance increased, VOC concentrations increased from 0.76 to 1.27 mg/L (fig. 6). VOC data were not collected during the first part of the storm. On September 21 and on August 14, 2000, chloroform concentrations of 1.38 and 0.86 mg/L, respectively, were detected in water samples from the spring. The decrease in specific conductance on

September 12 and November 9, 2000, are both interpreted to be the results of direct recharge of water to the aquifer from a nearby sinkhole or sinkholes. Hess and White (1988), in studies of other karst springs, interpreted these types of events to indicate arrival of water from specific solution channels to the main spring.

During the November 2000 storm, a second distinct specific conductance decrease occurred, coinciding with peak discharge. During this part of the storm, chloroform concentrations increased to 33 mg/L (fig. 5), which represents a 60-fold increase over the concentration before the storm. Dye traces performed



**Figure 6.** Chloroform, specific conductance, rainfall, and discharge data collected at Wilson Spring during a September 2000 storm (discharge and rainfall data collected by Ogden Environmental and Energy Services). Water samples were analyzed by the U.S. Geological Survey National Water Quality Laboratory (USGS NWQL) or using a portable gas chromatograph (GC).

by Crawford and Ulmer (1994) indicate the main source of water to Wilson Spring to be a cave stream that flows approximately 2,200 feet from near the contaminant source area to the spring. This cave stream appears to be transporting high concentrations of chloroform to the spring under certain hydrologic conditions. The maximum chloroform concentrations detected during the November 2000 storm, represents a sixfold increase over the maximum concentrations measured at any other time during the study period. Data collected during subsequent storms will determine if increased chloroform concentrations occur during storms throughout the year or only during specific hydrologic events, such as the first major storm after extended dry periods.

## CONCLUSIONS

Because of the low probability of successfully drilling wells that intersect karst conduits, springs are commonly used to monitor ground-water contamination in karst terrane. Literature is replete with studies documenting large water-quality variations in karst springs in response to storm events. Studies have addressed the need for specially designed sampling methodologies to detect peak contaminant concentrations in karst springs. Knowledge of the complete range in contaminant concentrations is necessary to calculate accurate contaminant loads in discharge from karst springs. In addition, pulses of high contaminant concentrations could exceed toxicity levels for aquatic organisms. Lack of awareness of the

occurrence of pulses could result in undetected risk to the aquatic community in and downstream of these springs. Despite the previous work, sampling programs for monitoring karst springs rarely implement the special techniques needed to accurately characterize contaminant concentrations and loads. The wide range in concentrations present in the storm samples from Wilson Spring indicates the need for sampling strategies to be developed for karst springs on a site-specific basis. The water-quality signature of a given spring can be determined by continuously monitoring selected water-quality properties through one complete hydrologic cycle. This signature can be used to develop long-term sampling strategies that best characterize contaminant levels. In springs such as Big Spring, quarterly or semi-annual sampling may be adequate, but in flashy springs such as Wilson Spring, a more comprehensive program including the collection of high-frequency flow-controlled VOC samples is necessary.

The springs evaluated in this study contain VOC's. Only one other study was found in the literature that addressed sampling for these types of compounds in a karst system. Additional research is needed to evaluate the differences in contaminant signatures that may exist for the various classes of chemicals in karst springs. This study further emphasizes the need to re-evaluate sampling methodology in karst aquifer systems.

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