Volatile Organic Compound Data from Three Karst Springs in Middle Tennessee, February 2000 to May 2001

By Shannon D. Williams *and* James J. Farmer

ABSTRACT

The U.S. Geological Survey (USGS), in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund, collected discharge, rainfall, continuous water-quality (temperature, dissolved oxygen, specific conductance, and pH), and volatile organic compound (VOC) data from three karst springs in Middle Tennessee from February 2000 to May 2001. Continuous monitoring data indicated that each spring responds differently to storms. Water quality and discharge at Wilson Spring, which is located in the Central Basin karst region of Tennessee, changed rapidly after rainfall. Water quality and discharge also varied at Cascade Spring; however, changes did not occur as frequently or as quickly as changes at Wilson Spring. Water quality and discharge at Big Spring at Rutledge Falls changed little in response to storms. Cascade Spring and Big Spring at Rutledge Falls are located in similar hydrogeologic settings on the escarpment of the Highland Rim.

Nonisokinetic dip-sampling methods were used to collect VOC samples from the springs during base-flow conditions. During selected storms, automatic samplers were used to collect water samples at Cascade Spring and Wilson Spring. Water samples were collected as frequently as every 15 minutes at the beginning of a storm, and sampling intervals were gradually increased following a storm. VOC samples were analyzed using a portable gas chromatograph (GC). VOC samples were collected from Wilson, Cascade, and Big Springs during 600, 199, and 55 sampling times, respectively, from February 2000 to May 2001.

Chloroform concentrations detected at Wilson Spring ranged from 0.073 to 34 mg/L (milligrams per liter). Chloroform concentrations changed during most storms; the greatest change detected was during the first storm in fall 2000, when chloroform concentrations increased from about 0.5 to about 34 mg/L. Concentrations of cis-1,2-dichloroethylene (cis-1,2-DCE) detected at Cascade Spring ranged from 0.30 to 1.8 µg/L (micrograms per liter) and gradually decreased between November 2000 and May 2001. In addition to the gradual decrease in cis-1,2-DCE concentrations, some additional decreases were detected during storms. VOC samples collected at weekly intervals from Big Spring indicated a gradual decrease in trichloroethylene (TCE) concentrations from approximately 9 to 6 µg/L between November 2000 and May 2001. Significant changes in TCE concentrations were not detected during individual storms at Big Spring.

Quality-control samples included trip blanks, equipment blanks, replicates, and field-matrix spike samples. VOC concentrations measured using the portable GC were similar to concentrations in replicate samples analyzed by the USGS National Water Quality Laboratory (NWQL) with the exception of chloroform and TCE concentrations. Chloroform and TCE concentrations detected by the portable GC were consistently lower (median percent differences of –19.2 and –17.4, respectively) than NWQL results. High correlations, however, were observed between concentrations detected by the

portable GC and concentrations detected by the NWQL (Pearson's $r > 0.96$). VOC concentrations in automatically collected samples were similar to concentrations in replicates collected using dip-sampling methods. More than 80 percent of the VOC concentrations measured in automatically collected samples were within 12 percent of concentrations in dip samples.

INTRODUCTION

Approximately 40 percent of the United States east of the Mississippi River is underlain by various types of karst aquifers (Quinlan, 1989), and more than two-thirds of the State of Tennessee is underlain by carbonate rocks and can be classified as karst (Wolfe and others, 1997). In karst settings, ground-water levels, discharge, and water-quality conditions can fluctuate widely and rapidly (Hess and White, 1988; Dreiss, 1989; Brown and Ewers, 1991; Ryan and Meiman, 1996). These fluctuations create a potential for temporal variability in contaminant concentrations that may not be discerned by periodic sampling. Yet for investigations of chlorinated solvents and other volatile organic compounds (VOCs) in ground water, periodic sampling generally remains the accepted approach for monitoring contaminant concentrations.

Passive sorption samplers may be effective in evaluating the presence or absence of chlorinated solvents, are simple to deploy and retrieve, and are economical to analyze (Einfeld and Koglin, 2000); however, the basic information needed to quantitatively interpret the response of passive samplers to systems with fluctuating flow and concentrations has not been collected and published. Closely spaced storm samples are an effective means to characterize variable concentrations (Quinlan and Alexander, 1987), but few detailed data sets have been collected and published that adequately document VOC concentrations in karst springs because of analytical costs.

The U.S. Geological Survey (USGS), in cooperation with the Tennessee Department of Environment and Conservation, Division of Superfund, is studying the occurrence, fate, and transport of chlorinated solvents in karst regions of Tennessee. One objective of this study is to evaluate several monitoring strategies for karst springs. To accomplish this objective, (1) monitoring techniques incorporating the use of continuous water-quality monitors, automatic VOC samplers, portable gas chromatographs (GCs), and passive adsorption samplers were evaluated; (2) VOC data were collected by using these monitoring techniques at three karst springs in Middle Tennessee; and (3) the effect of various sampling intervals on the characterization of VOC concentrations and loads were examined.

Purpose and Scope

This report presents VOC, water-quality, discharge, and rainfall data collected at three karst springs in Middle Tennessee from February 2000 to May 2001. Many of the VOC samples were collected by using automatic samplers and were analyzed by using a portable GC. Water-quality monitors were used to continuously measure temperature, dissolved oxygen, specific conductance, and pH. Detailed descriptions of the automatic sampler and portable GC methods and quality-control data also are presented.

Study Sites

Wilson Spring is located about 4 miles north-northeast of Lewisburg in the Central Basin karst region of Tennessee (fig. 1) as described by Wolfe and others (1997). The geology of the Central Basin is characterized by thick-bedded limestones that alternate with thin-bedded shaly limestones, both of Ordovician age (Farmer and Hollyday, 1999). Uplift of the Nashville Dome resulted in the development of extensive fracturing in this region. Dissolution of the limestone has enlarged these fractures, resulting in the development of karst features; and ground-water flow is predominantly in these solution openings. The thin-bedded shaly formations generally act as confining units. The thin-bedded Lebanon Limestone of Ordovician age caps the hills of this region and retards the downward movement of water. Surface streams that run off the Lebanon Limestone onto the Ridley Limestone can move into the upper Ridley 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 the Ridley Limestone (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 for one of these cave streams (Crawford and Ulmer, 1994) and

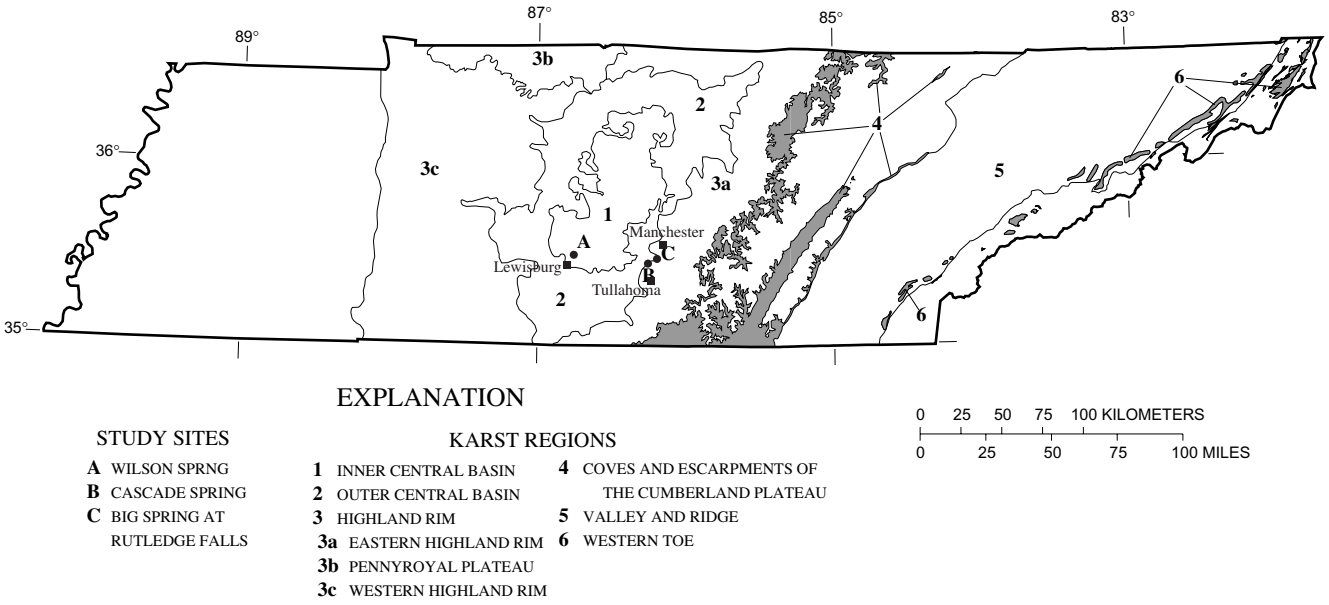

Figure 1. Location of study sites and karst regions of Tennessee. (Modified from Wolfe and others, 1997.)

discharges from about 0 to 10 ft^3/s (Thomas Hensel, AMEC, written commun., 2000).

In October 1990, a train derailment near Wilson Spring released more than 15,000 gallons of chloroform. Chloroform pooled on top of the thin-bedded unit of the Ridley Limestone, and then moved southwest downdip along weathered bedding planes until the chloroform was trapped by less weathered rock of low permeability (Crawford and Ulmer, 1994). Water containing chloroform was transported southeast, along the strike of the bedding planes, to Wilson Spring. Since 1992, a private consulting company has been collecting continuous discharge and rainfall data and monthly VOC data at Wilson Spring. Data from this monitoring indicate that chloroform concentrations range from 1 to 5 mg/L seasonally (Thomas Hensel, AMEC, written commun., 2000). Water from the spring is impounded and treated before being released into Big Rock Creek.

Big Spring at Rutledge Falls is located about 5 miles southwest of Manchester, Tenn., and 5 miles northeast of Tullahoma, Tenn., on the escarpment of the Highland Rim karst region (fig. 1). The spring discharges approximately 3.5 ft^3/s from the Manchester aquifer into Crumpton Creek (Keith Dobson, Aerospace Center Support, written commun., 2000). Spring discharge emerges near the contact between the Chattanooga Shale of late Devonian and early Mississippian age and the overlying Fort Payne Formation of Mississippian age. The Chattanooga Shale ranges from 20 to 30 feet thick and is considered to be a regional confining unit in Tennessee (Burchett, 1977). The Fort Payne Formation ranges from 20 to 230 feet thick and is predominantly cherty limestone. The Manchester aquifer is a regional aquifer composed 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 escarpment of the Highland Rim where the contact between the Fort Payne Formation and the Chattanooga Shale crops out. Tetrachloroethylene (PCE) and trichloroethylene (TCE) have been detected in water samples collected from the spring at concentrations of about 2 and 7 µg/L, respectively (Keith Dobson, Aerospace Center Support, written commun., 2000).

Left and right Cascade Springs are located 3.5 miles north of Tullahoma, Tenn. The springs are located on the escarpment of the Highland Rim karst region and discharge from the Manchester aquifer in a hydrogeologic setting similar to the setting described for Big Spring at Rutledge Falls. The combined flow of the Cascade Springs is approximately 5.5 ft^3/s (Johnson, 1995). Left Cascade Spring is the sole source of water for the Wartrace Water System, which supplied 0.52 million gallons of water per day in 1989 to the Town of Wartrace, 14 miles northwest of Tullahoma (Johnson, 1995). Johnson (1995) reported that approximately 1 µg/L of trans-1,2-dichloroethylene has been detected in water samples collected from left

Cascade Spring. Henceforth in this report, the name Cascade Spring refers to left Cascade Spring.

METHODS

Gaging stations were established during February 2000 at Wilson Spring, Big Spring at Rutledge Falls, and Cascade Spring (USGS station numbers 03599102, 03596485, and 03596110, respectively). Water-quality monitors were used to measure temperature, dissolved oxygen, specific conductance, and pH at 10- or 15-minute intervals in the springs. Automatic samplers were used to collect VOC samples during selected storms, and VOC samples were analyzed by using a portable GC.

Discharge and Rainfall Measurement

Spring discharge was measured using procedures described by Carter and Davidian (1968). Continuous stage recorders described by Buchanan and Somers (1968) were used to collect stage data in 0.01-foot increments. Stage data were collected at 15-minute intervals at Cascade Spring and Big Spring at Rutledge Falls, and at 10- or 15-minute intervals at Wilson Spring. Discharge was measured by using methods described by Buchanan and Somers (1969). Discharge ratings were developed by using methods described by Kennedy (1984) and were applied to the continuous stage data to produce discharge records (Kennedy, 1983). A tipping-bucket rain gage was used to collect rainfall data (15-minute intervals) at Cascade Spring. Rainfall data (10-minute intervals) at Wilson Spring were obtained from AMEC (formerly Ogden Environmental and Energy Services).

The USGS gage at Wilson Spring could not accurately measure gage heights below 0.08 foot because of the placement of the water-level sensor in the flume. Discharge data were obtained from AMEC for gage heights below 0.08 foot and for periods of missing record. Discharge data collected from February 10, 2000, to October 10, 2000, by the USGS were collected at 15-minute intervals, whereas, data obtained from AMEC were collected at 10-minute intervals. AMEC discharge data collected at 10 and 20 minutes after the hour were averaged and reported as 15 minutes after the hour. Likewise, discharge data collected at 40 and 50 minutes after the hour were averaged and reported as 45 minutes after the hour. AMEC rainfall data collected at 10 and 20 minutes after the hour were added together and reported as 15 minutes after the hour. Likewise, rainfall data collected at 40 and 50 minutes after the hour were added together and reported as 45 minutes after the hour.

Continuous Water-Quality Monitoring

General procedures described by Wood (1976), Wilde and Radtke (1998), and Wagner and others (2000) were used for field measurements of temperature, dissolved oxygen, specific conductance, and pH. Water-quality monitors were enclosed in perforated polyvinyl chloride (PVC) pipe and placed directly in Cascade Spring (fig. 2) and Big Spring at Rutledge Falls. At Wilson Spring, the monitor was placed in a tub just below the lip of the flume (fig. 3) because of the shallow water depth inside the flume; dissolved-oxygen data were not collected at this spring. During field visits, specific conductance and temperature were checked with a hand-held meter to compare the water-quality conditions in the tub and the spring.

Field measurements were made at 15-minute intervals at Cascade Spring and Big Spring at Rutledge Falls and at 10- or 15-minute intervals at Wilson Spring. The water-quality monitors were calibrated before deployment by using standard reference solutions following the manufacturer's instructions (Hydrolab Corporation, 1999). At approximately 3-week intervals, data were downloaded from the monitors, calibration of the monitors was checked, and monitors were recalibrated as needed.

Portable Gas Chromatograph Analyses

The portable GC method described in this report is suitable for the measurement of microgram per liter concentrations of selected VOCs in water samples. VOCs measured during this study are listed in table 1. The U.S. Environmental Protection Agency (EPA) Environmental Technology Verification Program has evaluated the portable GC used during this study. The EPA performance verification documented high linear relations between portable GC and laboratory results, with correlation coefficients greater than 0.96 for low concentrations (less than 100 µg/L) of 16 VOCs including PCE, TCE, and chloroform (Einfeld, 1998).

Figure 2. Stream gaging, water-quality monitoring, and volatile organic compound sampling equipment at Cascade Spring.

Figure 3. Water-quality monitoring and volatile organic compound sampling equipment at Wilson Spring.

Summary of Method

An internal pump in the purge unit and polytetrafluoroethylene (PTFE) tubing were used to transfer water samples from sample containers to the sample cell in the purge unit (cell fill). An inert gas was then vigorously passed through the water in the sample cell, transferring VOCs from the water phase into the gas phase. The gas flow was initially diverted to the vent (purge/cell exhaust) then passed through an adsorbent trap (located in the main GC unit) that retained and concentrated the VOCs (purge/sampling). The flow of gas was then diverted from the column through the trap to the vent to remove water vapor (dry purge). The flow of gas was then reverted back through the trap to the column and allowed to resume its normal flow (delay). The trap was then quickly heated, and VOCs released from the trap were carried into the stainless-steel capillary column (desportion). Between each water sample, the sample cell in the purge unit was automatically rinsed with volatile blank water (VBW).

Compounds eluting from the GC column were tentatively identified by comparing their retention times to retention times obtained by the measurement of control samples under the same conditions used for the water samples. The identification of compounds was verified by the analysis of selected duplicate samples by the USGS National Water Quality Laboratory (NWQL). The concentrations of identified compounds in water samples were measured by relating the detector response (peak area) to the detector response for known concentrations of control samples analyzed under the same conditions used for the water samples.

Apparatus and Instrumentation

- *Portable purge unit* – Sentex (Fairfield, N.J.) on-line portable model purge unit with a 30-milliliter sample cell, internal pump (150 milliliter per minute pumping rate), and electricity and purge gas provided by the portable GC.
- *Portable GC* – Sentex Sentograph Plus II with an internal carrier gas cylinder and rechargeable batteries; direct on-column, sampling loop, and carboxen trap injection systems; an oven with operating temperature up to 179 °C; and microargon ionization (MAID) and electron capture detectors (ECD).
- *Data system* – Laptop computer and Sentex software (version 1.56, Aquascan mode) were used to operate the portable purge unit and GC and to obtain retention time and peak area data.
- *Capillary column* – Restek Corporation (Bellefonte, Pa.) MXT-volatiles capillary column, treated stainless steel (30-meter length, 0.53-millimeter inside diameter), diphenyl/dimethyl polysiloxane stationary phase (3-micrometer film thickness).
- *GC conditions* – Oven, 70 °C (isothermal); column pressure, 10 pounds per square inch; cell fill, 60 seconds; purge/cell exhaust, 10 seconds; purge/sampling, 60 seconds; dry purge, 60 seconds; delay, 60 seconds; desportion, 4 seconds; detector, MAID; peak integration, constant baseline.
- *Syringes* – Gas-tight glass syringes (ranging in size from 10 to 500 µL) equipped with PTFE plungers.

Reagents and Consumable Materials

- *Carrier gas* – Ultra high purity (greater than 99.995 percent) argon.
- *Sample bottles* – Baked 40-, 125-, and 250-mL glass amber bottles; caps with PTFE-faced silicone septa.
- *2-mL vials* – Amber glass, screw-top vials.
- *Caps for 2-mL vials* – Solid caps with PTFE liner and caps with PTFE-faced silicone septa.
- *Volatile blank water (VBW)* – Generated by purification of tap water through activated charcoal filtration and de-ionization with a high-purity, mixed-bed resin (Nanopure, Barnstead, Dubuque, Iowa, D4802 Organic-free cartridge kit).
- *Analytical standards* – Single component standards containing 100 µg/mL of selected VOCs (table 1) dissolved in methanol (ULTRA Scientific, North Kingstown, R.I.). Custom standard containing 100 µg/mL each of PCE, TCE, 1,1-dichloroethylene (1,1-DCE), cis-1,2-DCE, and 1,1,1-trichloroethane (1,1,1-TCA) in methanol (ULTRA Scientific).
- *Pasteur pipettes*
- *Hydrochlorous acid (HCl)* – 1:1 solution of HCl and water in 30-mL PTFE squeeze bottles.

Sample Analysis

- *Sample preparation* – If chilled, a sample was allowed to warm to room temperature. If a compound was known to be present at a high concentration (greater than 20 µg/L), the sample was

diluted prior to analysis. During dilutions, a gas-tight syringe was used to remove the sample from the septum-capped sample vial and to transfer the sample to a septum-capped vial containing the appropriate amount of VBW. Syringes were rinsed with VBW between each dilution.

- *Sample injections* – A sample was quickly uncapped, the PTFE tubing from the purge unit was placed in the bottom of the sample container, and pumping of the sample to the internal cell of the purge unit was initiated using the GC software.

Preparation of Standards and Controls

- *Laboratory blanks* – Blanks were prepared using acidified VBW. One drop of HCl added to 40 mL of VBW was sufficient to achieve a pH of about 2. Laboratory blanks included test blanks, continuing set blanks, carryover blanks, and equipment blanks.
- *Stock standard solutions* – Analytical standards were opened, transferred to 2-mL vials using Pasteur pipettes, capped (with solid caps), and stored in a freezer. New stock standard solutions were prepared approximately every 2 months. Upon creation of a new stock solution, two sets of standards were prepared and analyzed (one from the new stock solution and one from the previously used stock solution) to verify the integrity of the previously used stock solution.
- *Working standard solutions* – Solid caps on stock solution containers were quickly removed and replaced with septum caps. Gas-tight syringes (10 or 25 µL) were used to transfer stock solution to capped sample bottles containing acidified VBW. One drop of HCl added to 40 mL of solution was sufficient to achieve a pH of about 2. Fresh working standard solutions were prepared daily and included detector conditioning, calibration, and continuing calibration verification standards.

Calculation and Reporting of Results

- *Qualitative identification* – Historical data from each of the study sites were obtained to identify the VOCs typically detected in each spring. Single component standards were then used to determine retention times for each of these compounds (table 2). Replicate samples were collected during storms and analyzed by the NWQL to verify the continued presence of previously identified VOCs at each spring.
- *Calibrations* – The calibration range for the method is equivalent to concentrations from 0.25 to 20 mg/L without dilution of samples. Initial calibration data were entered into a computer spreadsheet (Microsoft Excel, Microsoft, Inc., Seattle, Wash.). Graphs were made from the GC data by plotting peak areas on the x-axis and concentrations of the calibration standards on the y-axis. The spreadsheet was used to determine a trend line for the data points using a quadratic curve fit. The equation of the trend line and the correlation coefficient value (r^2) were included with the graph for each compound. Initial calibration data were accepted if the r^2 values for all curves were greater than or equal to 0.99 for all compounds.
- *Quantitation* – Concentrations were determined by entering peak area data in a computer spreadsheet (Microsoft Excel) containing equations for trend lines from the most recent calibration curves. For diluted samples, the dilution factor was incorporated into the calculation for determining final concentrations of samples.
- *Detection/reporting limits* – The GC software allowed signal fluctuations (noise) to be suppressed. The noise-threshold value was set at a level that filtered out all normal signal fluctuations, preventing false positives. Because false positives were not an issue, the smallest concentration of a compound that could be continuously detected was used as an estimated detection and reporting limit (table 2). For diluted samples, reporting limits were raised according to the dilution factor.

Quality-Control Procedures

- *Test blanks* – Test blanks were analyzed prior to beginning an analytical sequence to ensure that the GC system was free of contaminants.
- *Continuing set blanks (CSBs)* – CSBs were analyzed periodically during the analytical sequence to confirm the continued absence of contaminants in the GC system.
- *Carryover blanks (COBs)* – COBs were analyzed after samples or standards with concentrations (typically greater than 10 µg/L) known to produce detectable carryover. Multiple COBs were sometimes needed after analysis of samples or

standards containing high concentrations of VOCs (20 to 50 µg/L).

- *Laboratory equipment blanks* – Laboratory equipment blanks were used to verify that syringes used for sample dilutions were free of contaminants. Equipment blanks using VBW were processed by using the same procedures used to process samples.
- *Detector conditioning standards* – Several standards were analyzed at the beginning of each day to obtain a stable detector response. Detector response was considered stable when concentrations in two consecutive standards were within 20 percent of the concentrations in the previous standard. Typically, three or four standards (with concentrations of 5 µg/L) were needed.
- *Initial calibration standards* – Solutions containing concentrations ranging from 0.25 to 20 µg/L (0.25, 0.50, 1.0, 2.0, 5.0, 10, and 20 µg/L) were used as calibration standards.
- *Continuing calibration verification standards (CCVs)* – Surrogate solutions were not added to samples; therefore, frequent analysis (after approximately every six samples) of CCVs was performed. The CCV concentration was varied during the analysis to collect quality-control information at different concentrations. If the result for a CCV was not within 20 percent of the expected value, new calibrations were performed.
- *Matrix spike control* – Matrix spike samples were used to evaluate effects of sample-matrix interferences on analyte recovery. Matrix spike samples were prepared by spiking replicates of environmental samples with appropriate amounts of stock solution. Matrix spike samples were prepared using the same stock solution and procedures used to prepare working standards.
- *External laboratory replicates* – Selected concurrent field replicates were sent to the NWQL to confirm the identification and quantitation of VOCs detected using the portable GC. The NWQL used gas chromatography/mass spectrometry methods described by Connor and others (1998) during the determination of selected VOCs (table 3). Quality-assurance and quality-control practices used by the NWQL are described in Pritt and Raese (1995).
- *Laboratory split replicates* – For selected samples, multiple dilutions were prepared and analyzed to quantify the variability resulting from dilution process.
- *Analytical sequence* – Samples were analyzed in a consistent sequence. The sequence always began with a test blank to prove the system was free of contamination before analyzing samples. After the system was shown to be free of contaminants, several detector-conditions standards were analyzed until a stable detector response was obtained. Once a stable detector response was obtained, a CSB was analyzed to verify that the system was still free of contaminants. Then, a CCV or series of calibrants were analyzed. A CCV, a COB, and a CSB bracketed each group of samples (typically no more than six samples per group). Each analytical sequence also was ended with a CCV, a COB (if necessary), and a CSB. Equipment blanks and matrix spike controls were included with samples and were randomly analyzed during the analytical sequence.

Volatile Organic Compound Sample Collection

VOC samples were collected from springs by using dip-sampling methods (immersing hand-held 40-mL vials) and by using automatic samples. Dip samples were collected periodically, mostly during base-flow conditions and were processed by using methods described by Wilde and others (1999a; 1999b). During selected storms, automatic samplers collected samples at Cascade Spring and Wilson Spring. The following method was used to automatically collect VOC samples.

Summary of Method

A bladder pump and PTFE tubing were used to transfer water samples from springs to automatic samplers. The automatic samplers mechanically opened a valve in the sampler container cap, inserted a needle through the cap to the bottom of a vial, and rinsed the vial with three volumes of sample. The sample then was collected as the needle was slowly removed from the vial, and the valve was automatically closed creating an airtight seal with no headspace. The bladder and sampling lines were rinsed with water from the spring just before the collection of each sample. Samples were removed from the automatic sampler, acidified, and chilled until analysis.

Apparatus and Instrumentation

- *Automatic samplers* – ISCO, Inc. (Lincoln, Nebr.) model 6100 automatic VOC samplers were used. The samplers held 25 vials.
- *Automatic sampler pump* – The samplers were equipped with bladder pumps constructed of stainless steel and PTFE. An air compressor (built into the sampler) expanded and contracted the bladder, gently pushing water from the pump to the sampler without applying suction or vacuum to samples. At Cascade Spring, the pump was placed directly in the spring (fig. 2); at Wilson Spring, the pump was placed in a tub along with the continuous water-quality monitor (fig. 3).
- *Tubing* – Polyethylene tubing was used to transfer air from the air compressor in the sampler to the bladder pump. PTFE-lined polyethylene tubing was used to transfer samples from the pump to the sampler. At Wilson Spring, the tubing was enclosed in insulated PVC pipe (fig. 3)
- *Sample containers* – Standard 40-mL VOC vials.
- *Sample container caps* – Valve caps (ISCO, Inc.) were used during the collection of samples. These caps were replaced with standard septum caps for 40-mL VOC vials after collection and preservation of samples.
- *Power supply* – The sampler installed at Cascade Spring was powered by 12-volt batteries (ISCO, Inc.). The sampler at Wilson Spring was powered using an alternating current power converter.
- *Sampler houses* – The automatic samplers were placed in small, insulated houses at the springs to protect the samplers. The sampler house at Cascade Spring contained an open bottom and was placed directly in the spring pool (fig. 2) to moderate temperature changes inside the sampler house. The sampler house at Wilson Spring was placed on a bluff above the spring (fig. 3) and contained a heater to prevent samples from freezing during cooler periods.
- *Thermometers* – Temperature changes inside the sampler houses were monitored using maximum/minimum recording thermometers.
- *Sampler activators* – The automatic samplers were equipped with liquid-level actuators that are used to initiate sampling when a specific water level is reached.
- *Rain gages* – Liquid-level actuators were placed in simple rain gages constructed out of plastic funnels and PVC pipe. The rain gages were attached to the top of the sampler houses (fig. 3) and were used to initiate sample collection during the early stages of a storm before discharge increased significantly.

Sample Collection

- *Sampler activation* – The sampler activators were placed in the rain gages so that the samplers would be activated after about 0.25 inch and 0.5 inch of rainfall at Wilson and Cascade Springs, respectively.
- *Sample preservation* – The valve cap was removed from a sample vial, HCl was added to the sample, and the valve cap was replaced with a septum cap. Four drops of HCl added to 40 mL of sample was typically sufficient to achieve a pH of about 2. Samples were stored at about 2 ^{o}C.
- *Equipment cleaning* – Samplers were programmed to automatically rinse the bladder and sample tubing prior to collecting a sample to reduce carryover from previous samples.
- *Sampling intervals* – Samplers were programmed to collect samples at 15-minute intervals after automatic activation at the beginning of storms. During subsequent manual activations, sampling intervals were gradually increased depending on the intensity and the duration of a storm.

Quality-Control Procedures

- *Trip blanks* – Each set of automatically collected samples included a trip blank to verify that samples were not contaminated between the time of collection and the time of analysis. The trip blank consisted of VBW in a capped 40-mL VOC vial and occupied 1 of the 25 slots in each sampling carousel.
- *Equipment blanks* – Equipment blanks were used to quantify the amount of carryover between samples collected using the automatic samplers. Equipment blanks using VBW were processed using the same procedures used to process samples.
- *Replicates* – Concurrent replicates were collected from the springs by using dip-sampling methods to quantify the variability introduced from the collection, processing, shipping, and analysis of samples. Additional replicates were collected to determine the variability associated with specific aspects of sample collection and included

sampling location replicates and sampling method replicates.

- *Sampling location replicates* – Replicate samples were collected from different sampling locations (tub and flume) at Wilson Spring. These replicates were used to determine whether volatilization resulted in significant differences between chloroform concentrations in water from the flume and water from the tub where samples were collected by using the automatic sampler.
- *Sampling method replicates* – Replicate samples also were collected using different sampling methods (automatic samplers and dip) at Wilson Spring and Cascade Spring. Samples collected using the automatic samplers often remained in the field for several days before retrieval and preservation. When the automatic samplers were manually activated, replicate samples were collected by using dip methods and were immediately preserved. Results from these replicates were used to determine if volatilization, biodegradation, or other processes resulted in significant loss of VOCs from the automatically collected samples (between the time of collection and preservation).

QUALITY-CONTROL DATA

Quality-control samples associated with the use of the portable GC included external laboratory (NWQL) replicates, laboratory split replicates, and matrix spike samples. Quality-control data associated with the use of the portable GC are presented in tables 4 through 9 (at the end of the report). Field replicates were collected during 64 of the 600 sampling times at Wilson Spring, during 36 of the 199 sampling times at Cascade Spring, and during 28 of the 55 sampling times at Big Spring. Quality-control data for field replicates and trip blanks are presented for Wilson Spring (tables 10 through 13), Cascade Spring (tables 14 through 16), and Big Spring (tables 16 and 17) at the end of the report.

External Laboratory Replicates

Water samples analyzed by the NWQL included 25 replicates collected from Wilson Spring, 16 replicates collected from Cascade Spring, and 13 replicates collected from Big Spring. Concentrations of cis-1,2-DCE measured in replicates analyzed using the portable GC and in replicates analyzed by the NWQL were similar (fig. 4). Concentrations of cis-1,2-DCE in Cascade Spring replicate samples analyzed by using the portable GC ranged from –11.8 to 33.3 percent different from concentrations in replicates analyzed by the NWQL (table 6). Chloroform concentrations in Wilson Spring replicates analyzed by using the portable GC were typically less than concentrations in replicates analyzed by the NWQL (fig. 4). In 17 of the 25 sets of replicates, chloroform concentrations were less

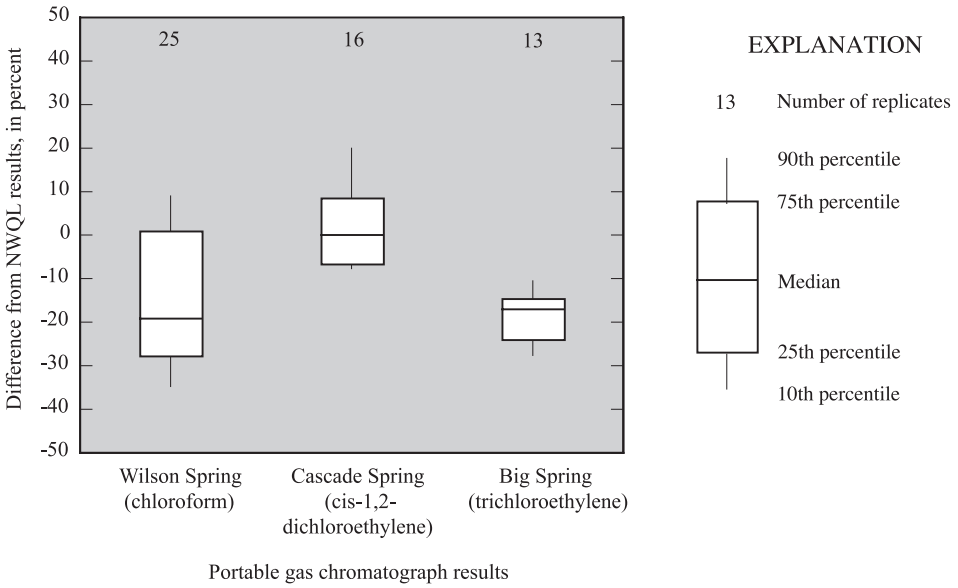

Figure 4. Volatile organic compound results for replicate samples analyzed using the portable gas chromatograph as compared to results for replicate samples analyzed by the USGS National Water Quality Laboratory (NWQL).

in samples analyzed by using the portable GC than in samples analyzed by the NWQL (table 4). The median difference for chloroform concentrations in Wilson Spring replicates analyzed by using the portable GC samples when compared to replicates analyzed by the NWQL was –19.2 percent (fig. 4). TCE concentrations in Big Spring replicates analyzed using the portable GC were consistently less than concentrations in replicates analyzed by the NWQL (fig. 4). TCE concentrations in Big Spring replicates analyzed using the portable GC ranged from –32.6 to 0.0 percent different from concentrations in replicates analyzed by the NWQL (table 8), with a median percentage difference of –17.4 (fig. 4). Although chloroform and TCE concentrations in portable GC replicates were typically less than concentrations detected in NWQL replicates, the concentrations detected by the different methods were highly correlated (Pearson's r>0.96) (figs. 5 and 6).

Laboratory Split Replicates

One concern during the analysis of samples from Wilson Spring was that the dilution of samples might affect the accuracy of the portable GC results. Split replicates were created during the dilution process for 33 samples collected from Wilson Spring and were analyzed using the portable GC (table 5).

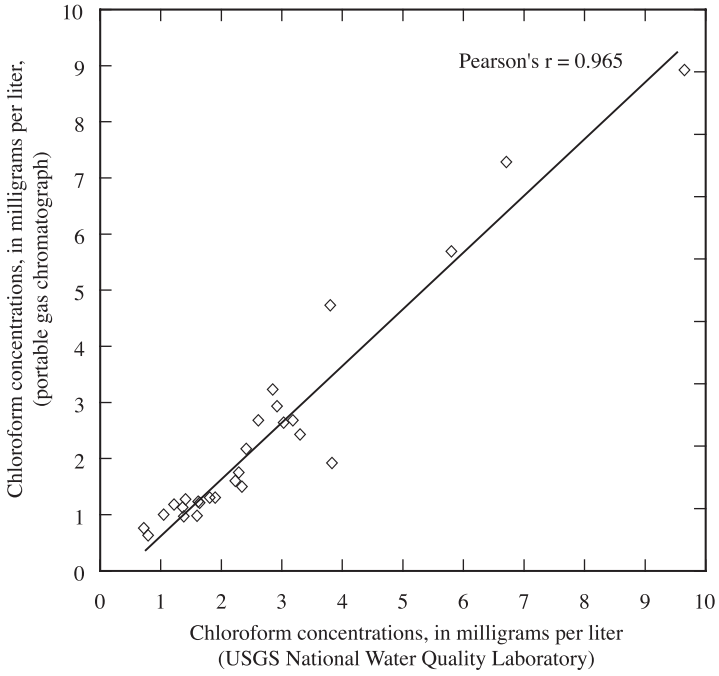

Figure 5. Chloroform results for replicate samples analyzed using different methods (includes results for volatile blank water spike samples from table 4).

Although the dilutions used during the analysis of these split replicates ranged from 1:100 to 1:1,000, chloroform concentrations in split replicates were similar (fig. 7); 82 percent of the relative differences between split replicates were within about 15 percent (table 5) of each other.

Field-Matrix Spikes

Field-matrix spikes were created using three samples collected from Cascade Spring and two samples collected from Big Spring. Field-matrix spikes were not created for samples collected from Wilson Spring because of the high concentrations (greater than 1 mg/L) of chloroform present in the samples. Recoveries for VOCs in the Cascade Spring field-matrix spikes ranged from 85.6 to 101.4 percent (table 7). Recoveries for VOCs in the Big Spring field-matrix spikes ranged from 80.0 to 134.0 percent (table 9). Most of the recoveries for VOCs were between 80 and 120 percent (fig. 8).

Concurrent Replicates

Concurrent replicates were collected using dip-sampling methods to provide a measure of the variability inherent in the entire process of sample collection, processing, and analysis. These concurrent replicates were collected during 24, 24, and 19 sampling times at Wilson, Cascade, and Big Springs, respectively. The relative difference between concentrations in concurrent replicate samples collected using dip-sampling methods was consistently (95 percent or more of the time) less than 15 percent and frequently (75 percent or more of the time) within 10 percent for the primary contaminant at each of the karst springs (fig. 9; tables 10, 14, and 17).

Sampling Location Replicates

One concern during the sampling at Wilson Spring was that chloroform might have been volatilized as water flowed out of the flume and into the tub. Sampling location replicates (replicates from tub and flume) were collected during 27 sampling times at Wilson Spring. If significant volatilization had occurred, chloroform concentrations in samples from the tub would have been consistently less than concentrations in replicate samples from the