

**Figure 6.** Chlorinated-ethylene results for replicate samples analyzed using different methods (includes results for volatile blank water spike samples from tables 6 and 8).

flume. Chloroform concentrations in samples collected from the tub at Wilson Spring using dip-sampling methods were similar to concentrations in replicates collected from the flume using dip-sampling methods (fig. 10). Chloroform concentrations in dip samples collected from the tub ranged from -23.3 to 13.3 percent different from concentrations in dip samples collected from the flume (table 11). About 80 percent of the chloroform concentrations in dip samples from the tub were within 6.2 percent of chloroform concentrations in dip samples from the flume (fig. 10, table 11).

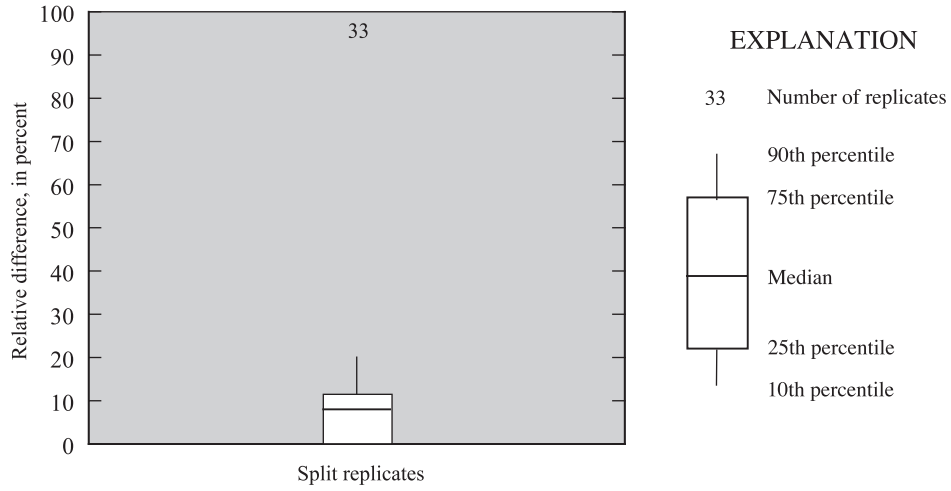
### Sampling Method Replicates

Another concern during the sampling at Wilson and Cascade Springs was that volatilization and biodegradation could result in losses of VOCs from automatically collected samples. Many of the automatically collected samples remained in the field for several days before retrieval and preservation (tables 12 and 15). Maximum temperatures inside the sampler houses were as high as 40 °C at Wilson Spring (table 12). Sampling method replicates (automatic sampler and dip) were collected during 32 sampling times at Wilson Spring and during 9 sampling times at Cascade Spring. If volatilization or biodegradation

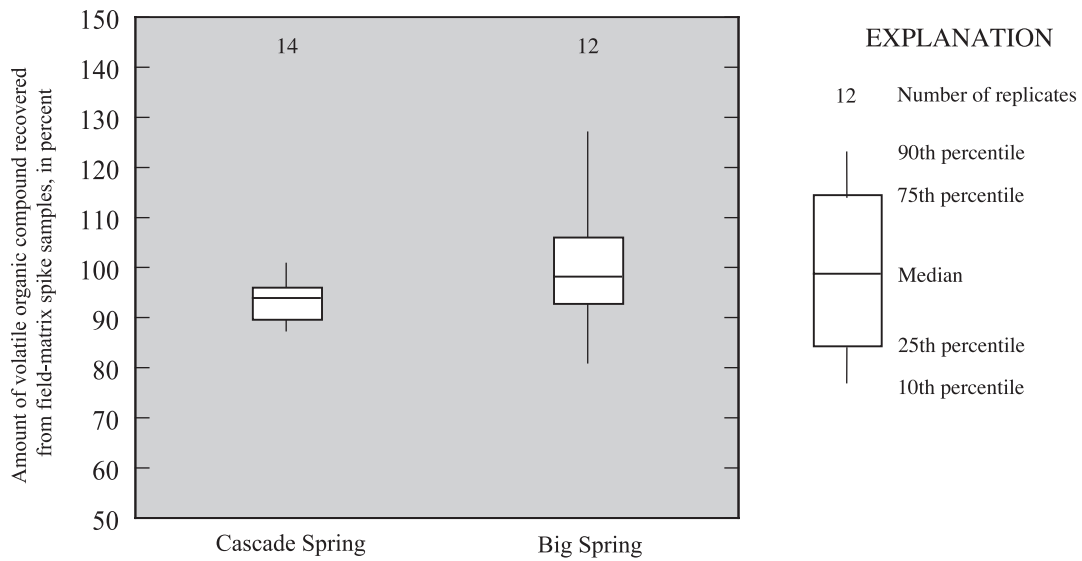
was occurring, VOC concentrations detected in automatically collected samples would have been consistently less than concentrations detected in replicate dip samples that were immediately preserved upon collection from the flume at Wilson Spring. VOC concentrations in automatically collected samples were similar to concentrations in replicates collected using dip-sampling methods (fig. 11). Chloroform concentrations in automatically collected samples ranged from -21.4 to 26.8 percent different from concentrations in dip samples collected from the tub at Wilson Spring (table 12). Concentrations of cis-1,2-DCE in automatically collected samples from Cascade Spring ranged from -4.7 to 34.1 percent different from concentrations in dip samples (table 15). More than 80 percent of the chloroform concentrations detected in automatically collected samples at Wilson Spring were within 12 percent of concentrations in dip samples, and more than 80 percent of the cis-1,2-DCE concentrations in automatically collected samples at Cascade Spring were within 10 percent of concentrations in dip samples (fig. 11, tables 12 and 15).

### Field Equipment and Trip Blanks

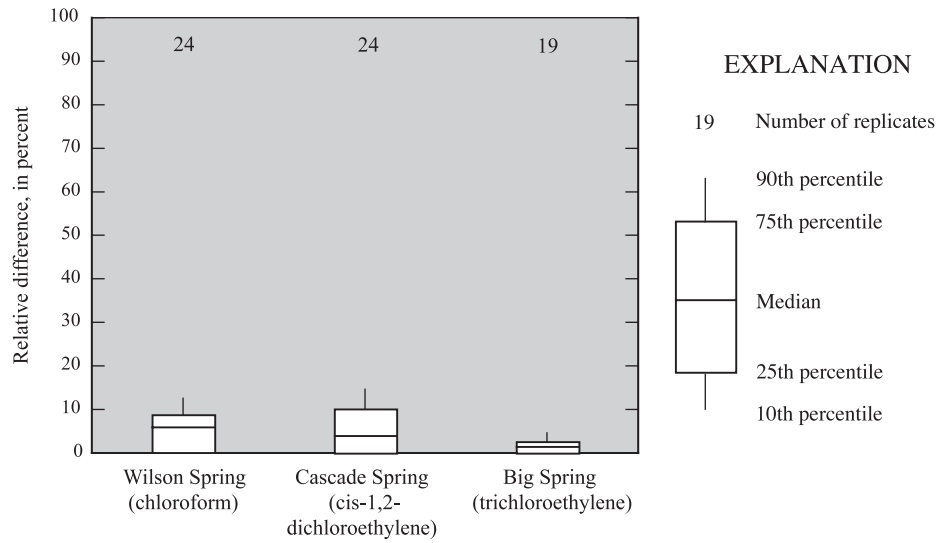
Before the collection of equipment blanks at Wilson Spring, samples were collected from the flume and the tub using dip methods and from the tub using the automatic samplers. The chloroform concentration in these replicates was about 2,700 µg/L (table 18). The automatic sampler pump then was removed from the tub, rinsed with VBW, and placed in a 5-gallon container of VBW. Sequential equipment blanks then were collected using the automatic sampler. A chloroform concentration of 25.0 µg/L was detected in the first equipment blank (table 18), representing a carry-over of less than 1 percent from the previous samples. About 7 and 6 µg/L of chloroform were detected in additional blanks collected using the automatic sampler. Much of the chloroform detected in the additional equipment blanks was probably from contamination of the VBW by the pump during the collection of the equipment blanks. Chloroform was not detected in a dip sample collected from the VBW container before the pump was placed in the container; however, about 4 µg/L of chloroform was detected in a dip sample from the 5-gallon VBW container after the equipment blanks were collected (table 18). Equipment blanks collected at Cascade Spring using similar procedures



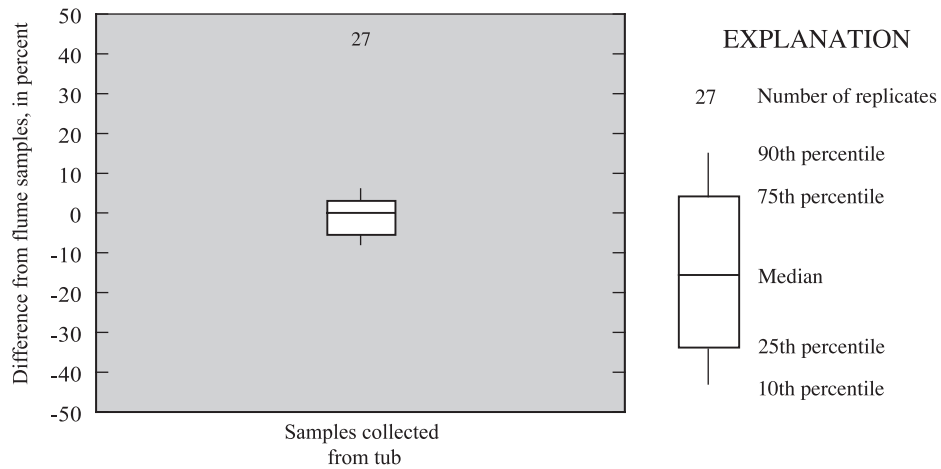
**Figure 7.** Chloroform results for split replicate samples collected at Wilson Spring.



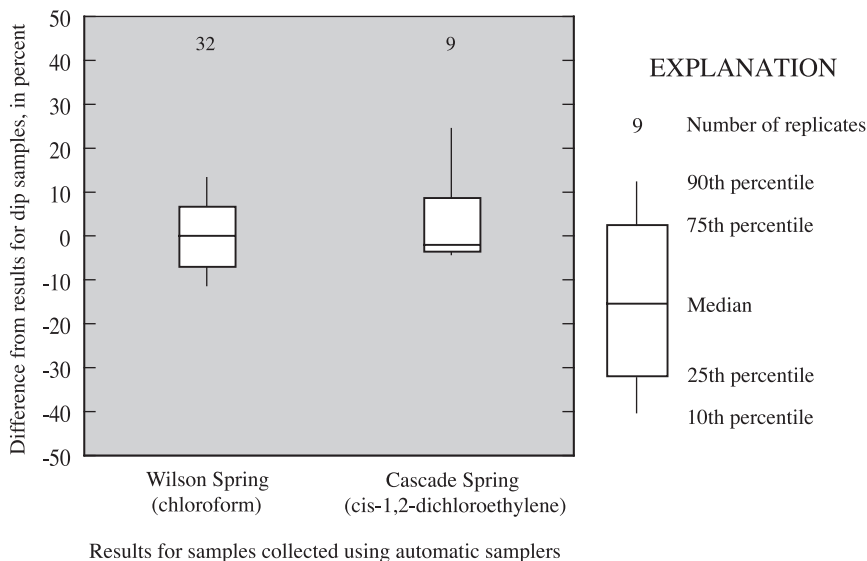
**Figure 8.** Volatile organic compound results for field-matrix spike samples collected at Cascade and Big Springs.



**Figure 9.** Volatile organic compound results for concurrent replicate samples collected at Wilson, Cascade, and Big Springs.



**Figure 10.** Chloroform results for replicate samples collected from the tub as compared to results for replicate samples collected from the flume at Wilson Spring (all samples were collected using dip methods).



**Figure 11.** Volatile organic compound results for replicate samples collected using automatic samplers as compared to results for dip samples at Wilson and Cascade Springs.

did not detect any carryover between samples (table 19). VOCs were not detected in any trip blanks during this study (tables 13 and 16). Trip blanks collected for Cascade Spring also served as trip blanks for Big Spring.

## RESULTS AND DISCUSSION

Continuous monitoring data collected from February 2000 through October 2000 were examined to determine the water-quality responses of the three springs to rainfall events. During this period, VOC samples were collected periodically at each site by using dip-sampling methods and were analyzed by using the portable GC or by the NWQL. The primary objectives of this initial phase of VOC sampling were to evaluate analytical methods and to obtain background information on VOC concentrations in the springs.

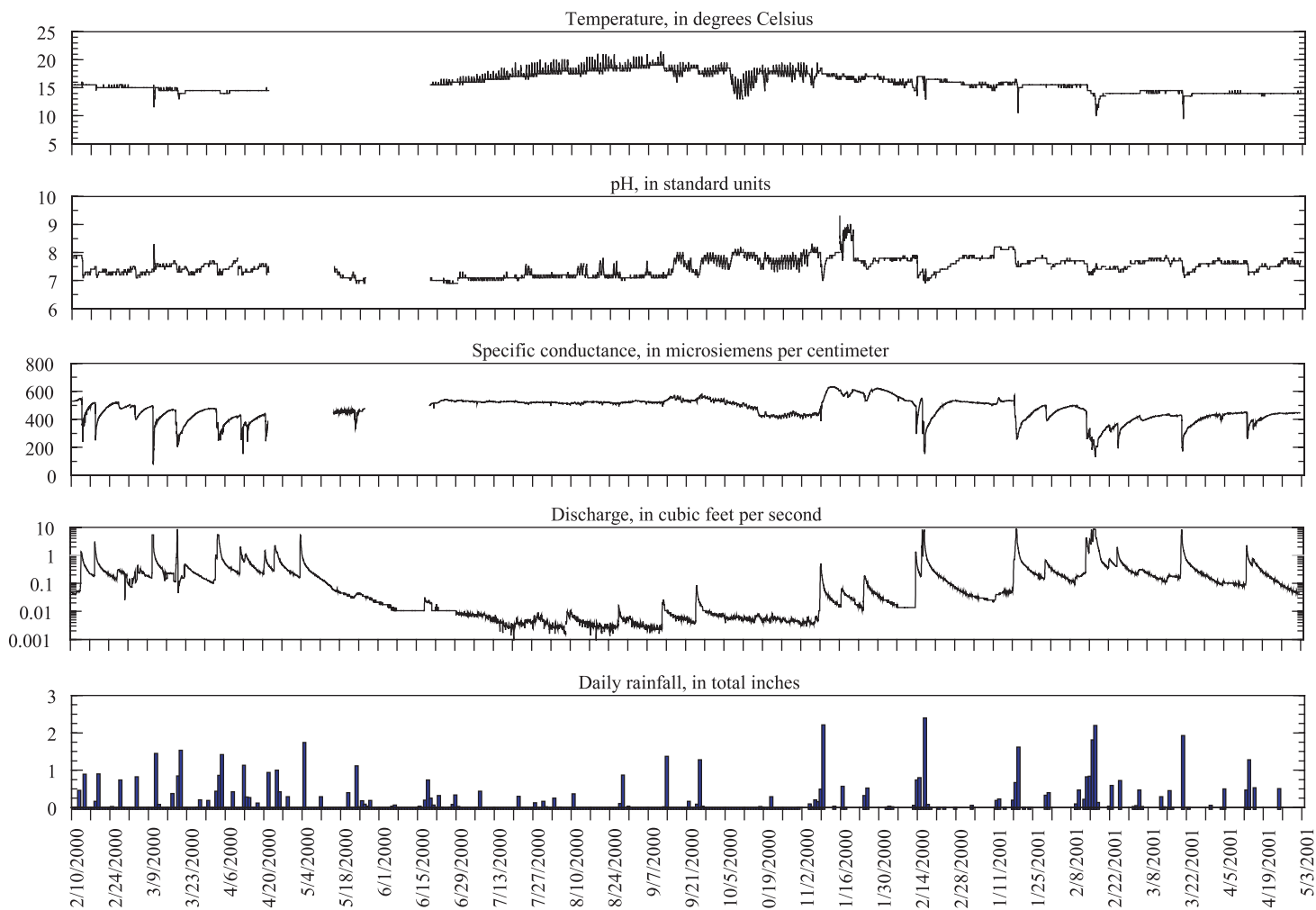
In November 2000, a more intensive phase of VOC sampling began in which the primary objectives were to evaluate sample collection methods and to document changes in VOC concentrations in the springs. During this more intensive sampling, VOC samples were collected weekly during base-flow conditions by using dip-sampling methods and as frequently as every 15 minutes during selected storms at

Wilson and Cascade Springs by using automatic samplers.

### Continuous Water-Quality Monitoring

Continuous monitoring data indicated that the three springs respond differently to rainfall. At Wilson Spring, water quality and discharge changed rapidly after rainfall. Discharge ranged from less than 0.001 ft<sup>3</sup>/s to greater than 8.7 ft<sup>3</sup>/s (fig. 12). Specific conductance ranged from 81 to 663 μS/cm, and pH ranged from 6.9 to 9.3. Rapid changes were recorded during many storms; for example, on March 11, 2000, specific conductance decreased from 492 to 81 μS/cm, and pH increased from 7.3 to 8.4 within a 3-hour period (fig. 12).

Significant water-quality changes were detected during most of the storms between November 2000 and May 2001 at Wilson Spring. During the first large storm of fall 2000, about 3 inches of rain fell, and discharge increased from about 0.005 ft<sup>3</sup>/s to a peak flow of about 0.5 ft<sup>3</sup>/s on November 9. As discharge increased, specific conductance increased from about 430 μS/cm on November 8 to a maximum value of 633 μS/cm on November 13, 2000 (fig. 12). The characteristics of the water-quality responses during storms at Wilson Spring varied. About 2 inches of rain fell on January 18 and January 19, 2001 at Wilson



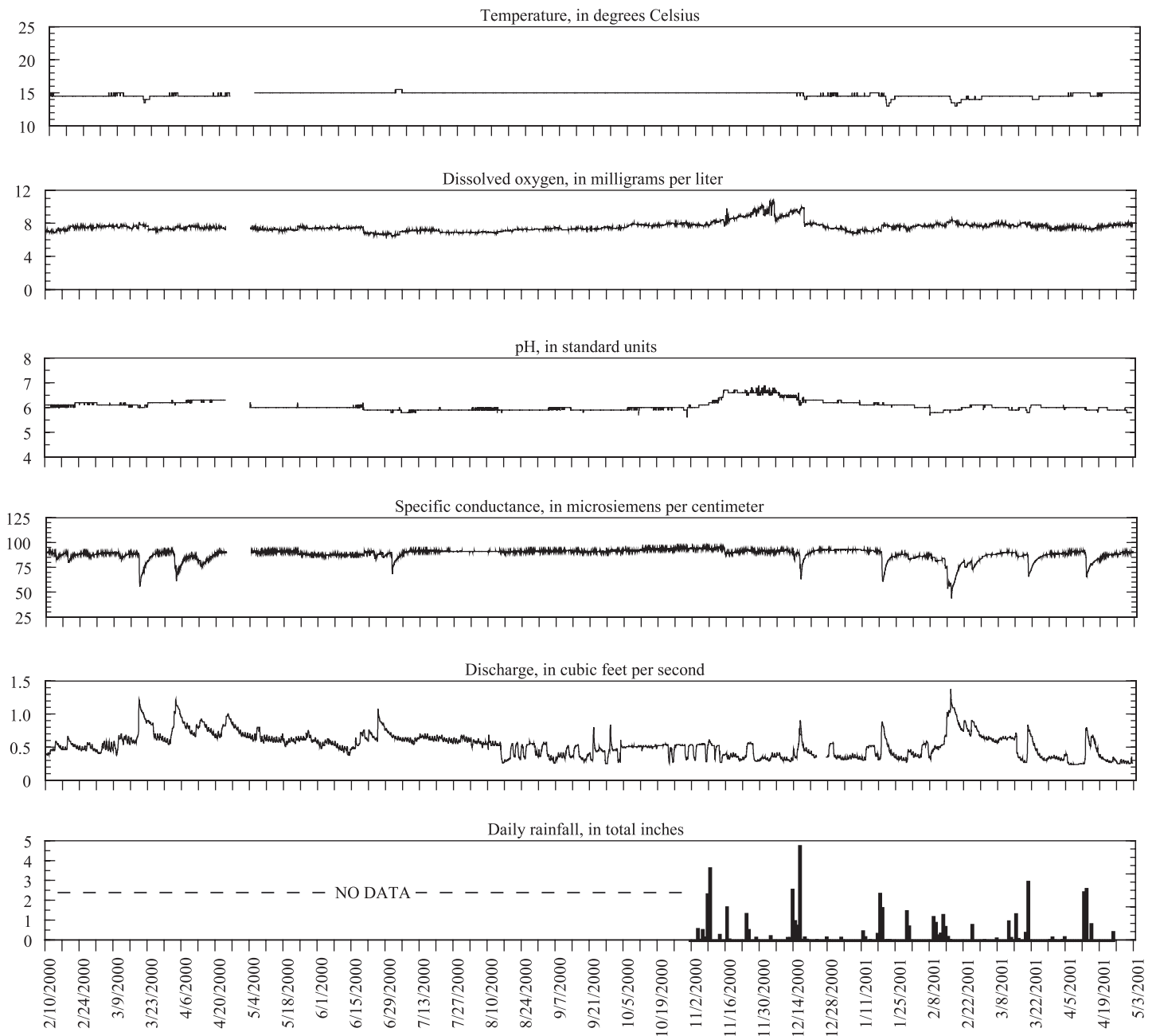
**Figure 12.** Continuous monitoring data collected at Wilson Spring from February 2000 to May 2001. (Line gaps indicate missing data.)

Spring. During this storm, specific conductance briefly increased from approximately 530 to 574  $\mu\text{S}/\text{cm}$  on January 18; however, specific conductance quickly decreased to less than 260  $\mu\text{S}/\text{cm}$ . Specific conductance eventually increased to 503  $\mu\text{S}/\text{cm}$  on January 30, 2001 at which time another storm began. Between February 1, 2001 and May 2001, the specific conductance typically decreased shortly after storms with no initial increase in response to rainfall (fig. 12).

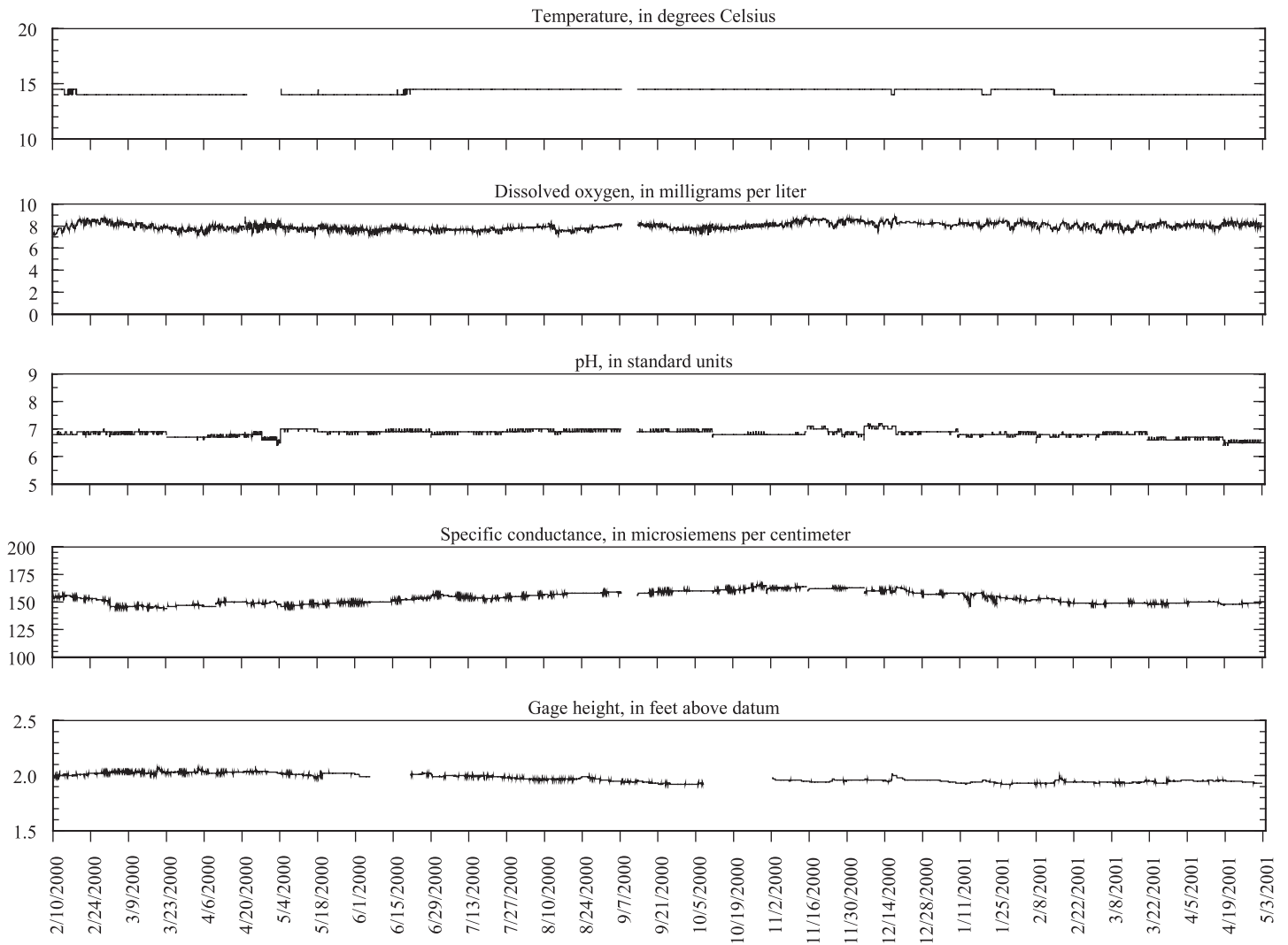
At Cascade Spring, some variation in water quality and discharge also was detected. Specific conductance ranged from 43 to 96  $\mu\text{S}/\text{cm}$ , and pH ranged from 5.6 to 6.9 (fig. 13). These changes were not as frequent and did not occur as quickly after rainfall as the changes at Wilson Spring. For example, about 7 inches of rain fell between November 4 and November 9, 2000; about 1.5 inches fell on November 16,

2000; and about 2 inches fell between November 24 and November 25, 2000, without any significant changes in specific conductance being recorded (fig. 13). The first change in specific conductance because of a storm was after approximately 9 inches of rain fell between December 13 and December 16, 2000. During this storm, specific conductance decreased from about 90  $\mu\text{S}/\text{cm}$  on December 13, 2000, to about 60  $\mu\text{S}/\text{cm}$  on December 17, 2000 (fig. 13). During other storms between January 1, 2001 and May 2001, similar decreases in specific conductance were observed (fig. 13).

At Big Spring, water quality and discharge varied little. Specific conductance ranged from 144 to 166  $\mu\text{S}/\text{cm}$ , and pH ranged from 6.4 to 7.2 (fig. 14). Gage height ranged from 1.91 to 2.08 feet above datum, and no significant changes in gage height were observed during storms (fig. 14). Even during a large



**Figure 13.** Continuous monitoring data collected at Cascade Spring from February 2000 to May 2001. (Line gaps indicate missing data. Discharge data do not include water captured by Wartrace Water System.)



**Figure 14.** Continuous monitoring data collected at Big Spring at Rutledge Falls from February 2000 to May 2001. (Line gaps indicate missing data.)

storm between December 13 and December 16, 2000, in which approximately 9 inches of rain fell at nearby Cascade Spring, no significant changes in water quality were detected at Big Spring. Gage height increased slightly from 1.95 to 2.02 feet above datum between December 13 and December 17, 2000, and specific conductance decreased slightly from 162 to 158  $\mu\text{S}/\text{cm}$  on December 17, before increasing to 164  $\mu\text{S}/\text{cm}$  on December 18.

Three discharge measurements were made at Big Spring during the study. The measured discharges were 3.37, 3.52, and 3.12  $\text{ft}^3/\text{s}$  at gage heights of 2.00, 2.00, and 2.04 feet above datum, respectively. These discharge measurements were comparable to five measurements made from May 1999 through October 1999 during which the discharge ranged from 3.33 to 3.70  $\text{ft}^3/\text{s}$  (Keith Dobson, Aerospace Center Support, written commun., 2000). Continuous monitoring results from the initial phase of sampling were used to assist with the design of the second phase of monitoring which focused on more intensive VOC sampling at the springs.

## Volatile Organic Compounds

From February 2000 through October 2000, dip samples were collected at 34, 26, and 27 different times from Wilson, Cascade, and Big Springs, respectively. The continuous monitoring data collected during this period indicated that water quality at Wilson and Cascade Springs was affected by storms. Automatic VOC samplers were installed at these two springs for more intensive sampling during the second phase of monitoring (November 2000 to May 2001). During the second phase of monitoring, VOC samples were collected during 566, 172, and 28 sampling times at Wilson, Cascade, and Big Springs, respectively, with most of the VOC samples (495 from Wilson Spring and 131 from Cascade Spring) collected using automatic samplers.

The continuous monitoring data indicated that water quality at Big Spring at Rutledge Falls did not change significantly during storms. VOC dip samples were collected at approximately 1-week intervals at Big Spring during the second phase of monitoring. VOC data for the entire study period (March 2000 to May 2001) are presented in tables 20 through 22 (at the end of the report). Samples were collected during a total of 600, 198, and 55 sampling times at Wilson, Cascade, and Big Springs, respectively.

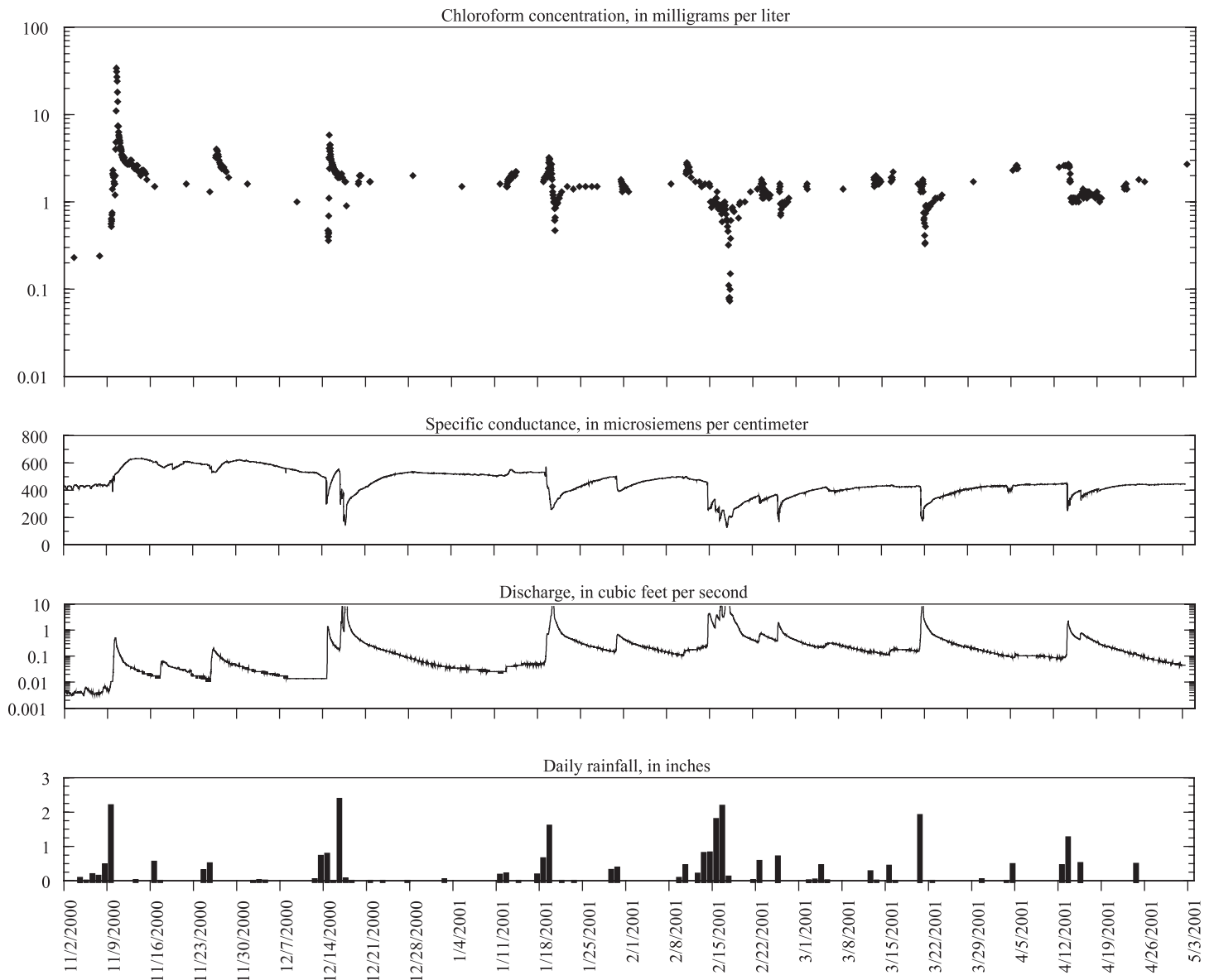
At Wilson Spring, chloroform concentrations ranging from 0.76 to 4.7  $\text{mg}/\text{L}$  were detected during the VOC sampling conducted from March 2000 through September 2000 (table 20). During the more intensive sampling from November 2000 to May 2001, chloroform concentrations ranged from 0.073  $\text{mg}/\text{L}$  to approximately 34  $\text{mg}/\text{L}$  (fig. 15 and table 20). The greatest change in chloroform concentrations was detected during the first storm of fall 2000. During this storm, chloroform concentrations quickly (within 6 hours) increased from about 0.5 to 34  $\text{mg}/\text{L}$  before quickly decreasing (within 6 hours) to about 5  $\text{mg}/\text{L}$  (fig. 16). Chloroform concentrations eventually decreased to about 3  $\text{mg}/\text{L}$  within a day.

The characteristics of the responses during storms at Wilson Spring varied (figs. 16-18). During a storm beginning on January 18, 2001, chloroform concentrations increased from 1.8 to 3.2  $\text{mg}/\text{L}$  during about a 10-hour period, then decreased to a low of 0.5  $\text{mg}/\text{L}$  within the next 24 hours before returning to about 1.5  $\text{mg}/\text{L}$  within a few days (fig. 17). The lowest chloroform concentration detected (0.07  $\text{mg}/\text{L}$ ) was on February 16, 2001, after approximately 6 inches of rain fell during the previous 4 days (fig. 18).

At Cascade Spring, cis-1,2-DCE concentrations ranging from 0.48 to 1.8  $\mu\text{g}/\text{L}$  were detected from March 2000 through October 2000 (table 21). From November 2000 to May 2001, cis-1,2-DCE concentrations ranged from 0.30  $\mu\text{g}/\text{L}$  to 1.4  $\mu\text{g}/\text{L}$ , as concentrations appeared to be gradually decreasing (fig. 19). During November 2000, the average cis-1,2-DCE concentration detected was approximately 1.4  $\mu\text{g}/\text{L}$ ; however, by April 2001, concentrations were consistently less than 1.0  $\mu\text{g}/\text{L}$ . In addition to the gradual decrease in cis-1,2-DCE concentrations, some short-term decreases in concentration were recorded during storms. For example, cis-1,2-DCE concentrations decreased from 1  $\mu\text{g}/\text{L}$  on February 8, 2001, to 0.30  $\mu\text{g}/\text{L}$  on February 16, 2001, after approximately 3 inches of rain fell during this period (fig. 20).

At Big Spring at Rutledge Falls, TCE concentrations ranging from 7.0 to 11  $\mu\text{g}/\text{L}$  were detected during periodic sampling from March 2000 through October 2000 (table 22). VOC samples collected at approximately 1-week intervals from November 2000 to May 2001 indicated a gradual decrease in TCE concentrations (fig. 21). During this period, TCE concentrations ranged from 5.6 to 11  $\mu\text{g}/\text{L}$ . Monthly averages for TCE concentrations detected by using the portable GC





**Figure 15.** Chloroform concentrations and selected continuous monitoring data at Wilson Spring, November 2000 to May 2001.