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Geologic and Tributary Influences on the Chemistry of a Headwater Stream

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Abstract

Water samples were collected weekly from June 12 to August 14, 1995, from Big Spring Run (BSR) in West Virginia. BSR originates in Big Spring Cave, where three stream samples were collected. In addition, 18 BSR sites were sampled downstream from the cave, three from its tributaries, and one above and below the stream's confluence with Elklick Run. Along its length (653 m), the geology is Greenbrier limestone in the headwaters, Pocono sandstone in the midsection and Hampshire sandstone and shale in the downstream section. As a result, water chemistry was strongly influenced by biogeochemical and hydrologic processes.

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Introduction

The chemistry of forest streams is the result of many biogeochemical processes. As a result, streamwater chemistry can be highly variable, which, in turn, can greatly affect the populations, diversity, and habitat of aquatic organisms, in-stream nutrient cycling, and potential uses of the water resource.

Water quality at a particular location along a stream length can be influenced so greatly by one or more variables, that there is little change in chemistry for long distances—even if these variables are absent downstream. In this situation, the dominant influence may be diminished only by dilution, e.g., nonaffected soil water, groundwater, or tributaries entering the stream channel. In other systems, particularly those with low ionic strength, even small physical, chemical, or biological changes can affect water quality.

The objective of this study was to examine the influences of geology and tributary inputs on the chemistry of a headwater stream in the central Appalachians. Along its length, the bedrock geology changes three times and the mineralogy is much different in the headwaters than near the mouth. Because the stream originates within a cave, the physical environments differ between the uppermost and downstream reaches. Thus, this 653-m stream is ideal for examining the effects of biogeochemical extremes on water chemistry over a relatively short distance.

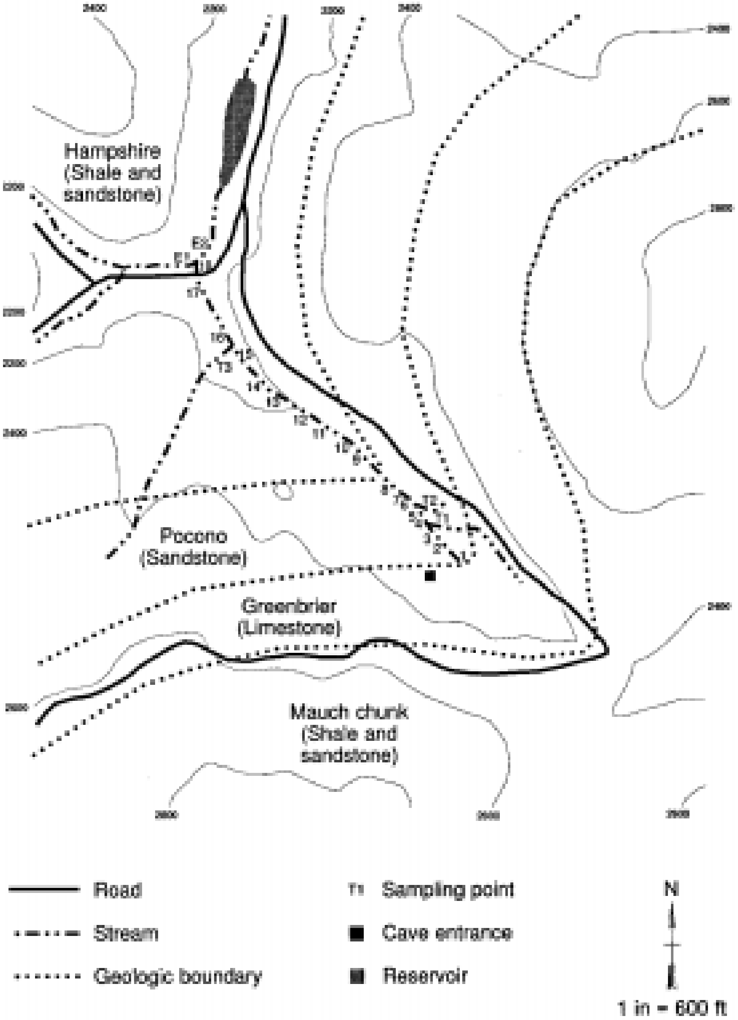

Figure 1.—Approximate locations of sampling sites in the 653-m Big Spring Run (1-18), tributaries (T1-T3), and Elklick Run (E1-E2). Contour line designations are in feet.

Methods

Study Site

The study stream, Big Spring Run (BSR), is located within the USDA Forest Service's Fernow Experimental Forest in Tucker County, West Virginia (latitude: 39°2¢30²N; longitude: 79°40¢00²W). BSR originates within Big Spring Cave and continues for 653 m to its confluence with Elklick Run (Fig. 1). Surficial streamwater is present within the limestone cave, but the stream runs below ground and resurfaces outside the cave at the base of a limestone outcrop.

The cave and point of resurgence are located within the Mississippian-age Greenbrier limestone formation (Fig.1). Eighty-seven percent (by weight) of Greenbrier limestone is composed of calcium carbonate ($CaCO_3$) (Reger 1923). Almost immediately downstream of BSR's resurgence to the surface, bedrock geology is Pocono sandstone (also Mississippian age) (Fig. 1). Finally, for approximately one-third of the stream's length, the geology is the Hampshire Series (Devonian age). This bedrock is a fine-ground micaceous sandstone and shale that is about 68 percent quartz (Reger 1923).

Three small unnamed tributaries (T1-T3) also feed into BSR (Fig. 1). Surface headwaters of tributary T1 originate in the Greenbrier formation and enter BSR in the Pocono formation. Surface waters of tributary T2 are entirely within the Pocono formation. Tributary T3 begins in the Pocono formation but is mostly within the Hampshire formation.

Sampling Sites and Procedures

From June 12 to August 14, 1995, one-liter grab samples were collected every Tuesday at 3 sites in Big Spring Cave (C1-C3), 18 sites in BSR downstream of the cave (1-18), 1 site in each tributary just upstream of their confluences (T1-T3), and in Elklick Run just upstream (E1) and downstream (E2) from the BSR confluence (Fig.1). Samples were collected from the thalweg and at middepth when possible. High-density polyethylene bottles were rinsed three times with streamwater prior to sample collection. The bottles were cleaned (Edwards and Wood 1993) but were not acid washed because samples were not analyzed for metals. Water samples were returned to the Northeastern Research Station's Timber and Watershed Laboratory at Parsons, West Virginia (about 16 km from BSR) for analyses of electrical conductivity, pH, alkalinity (as $CaCO_3$), calcium (Ca), sulfate (SO_4), and nitrate (NO_3). Protocols approved by the U.S. Environmental Protection Agency were used (Edwards and Wood 1993). Water temperature and dissolved oxygen (O_2) were measured in situ at each sampling point with a YSI model 57 meter[1].

Results and Discussion

Electrical conductivity was high along the entire length of BSR, averaging 144.8 mS cm^{-1} (Fig. 2). This result reflects limestone in the headwaters. In many nearby streams that flow through only sandstone and/or shale, average conductivity is less than 30 mS cm^{-1} (Kochenderfer and Edwards 1991; Helvey et al. 1982; Stephenson et al. 1995). The influence of limestone was not diluted as the stream flowed through less soluble materials and received tributary waters from these areas, i.e., average conductivity was about 150 mS cm^{-1}.

Alkalinity and Ca were the primary contributors to conductivity. This is not surprising because of the limestone in the headwaters. Equivalent conductivity calculations (see Edwards and Helvey 1991) showed that these two components accounted for 87.6 percent of the average conductivity along the length of BSR.

Calcium and alkalinity did not change significantly along the length of BSR (Figs. 3-4), that is, the regression slopes of concentration vs. distance were not significantly different from zero. Both Ca and alkalinity increased slightly downstream (for about 100 m) of the confluence with T2, which had significantly higher concentrations of both constituents than BSR. Tributary T1 had no effect on Ca or alkalinity in BSR. Presumably, the flow contributions from T1 were insufficient to alter the chemistry of BSR, even though T1 had higher concentrations than T2. Although streamflow was not measured in this study, T2 appeared to contribute more flow to BSR than T1.

If geology alone was responsible for the elevated Ca and alkalinity in T1 and T2, these concentrations would have been similar to those in BSR. We believe that dust-size particles of limestone on the limestone-graveled road uphill from and adjacent to T1 and T2 (Fig. 1) caused the elevated Ca and alkalinity (the road is only about 3.5 m from the streambanks in some locations) (Helvey and Kochenderfer 1987).

The buffering capacity of streamwater from the Greenbrier formation dominated the entire length of BSR. Both Ca and alkalinity were close to their headwater values over the 653-m stream length (Figs. 3-4). Even the contribution of waters from T3, which had negligible concentrations of alkalinity and Ca, did not significantly dilute or reduce headwater characteristics. The dominant chemical influence of the headwaters of Big Spring Run was apparent even after merging with the less alkaline Elklick Run; Ca and alkalinity were higher in E2 (downstream from the confluence) than in E1 (Figs. 3-4).

The high Ca concentrations were associated with streamwater pH from 7.17 to 7.53; pH was slightly lower within Big Spring Cave and for the first two sampling sites near the cave, averaging 7.21 (Fig. 5). Downstream, pH increased steadily, reaching 7.5 and remaining at approximately that value nearly to the stream's confluence with Elklick Run.

The pH values downstream may have been higher due to tributary inputs, and/or they may have been an artifact of pH depression within the cave and the initial resurgent samples. The elevated pH in T1 and T2 (Fig. 5) may have caused the pH of BSR to increase to pH 7.5 downstream from their confluence. Because an approximate increase of only 0.5 unit would have been needed, the tributaries might have influenced this change while not substantially influencing alkalinity and Ca for a long distance downstream. The pH within the cave could have been depressed if the partial pressure of carbon dioxide (CO_2) in cave water had been higher than in the resurgent stream (Hem 1970). In the confined cave atmosphere, CO_2 diffusion to the ambient atmosphere would be retarded. After exiting the cave, excess CO_2 would be liberated to the ambient atmosphere and pH would increase until an equilibrium was attained.

As with Ca and alkalinity, BSR influenced the pH of Elklick Run. The average value of the samples from Elklick Run upstream from the BSR confluence was 7.27; downstream from the confluence, the average pH was approximately 7.35.

Concentrations of SO_4 and NO_3 also were lower in the cave than immediately downstream from it (Figs. 6-7). These apparent decreases may have been due to lower oxidation rates within the cave relative to those present in water exposed to the ambient atmosphere. However, if oxidation was retarded, the controlling factor was not a lack of dissolved O_2 because the latter was highest within the cave water (Fig. 8).

Sulfur and nitrogen oxidation result from microbial reactions (Brady 1984), though auto-oxidation of sulfide can occur in alkaline waters (Stumm and Morgan 1981). Besides O_2, temperature and organic carbon are the primary physicochemical factors controlling these processes (Brady 1984; Janzen and Bettany 1987). Temperatures within the cave were relatively constant throughout the year and were neither extreme nor microbially inhibiting (Brady 1984; Fig. 8). It is more likely that differences in organic carbon availability were responsible for the differences in SO_4 and NO_3 concentrations inside and immediately outside the cave.

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[1] The use of trade, firm, or corporation names in this paper is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture or the Forest Service of any product or service to the exclusion of others that may be suitable.

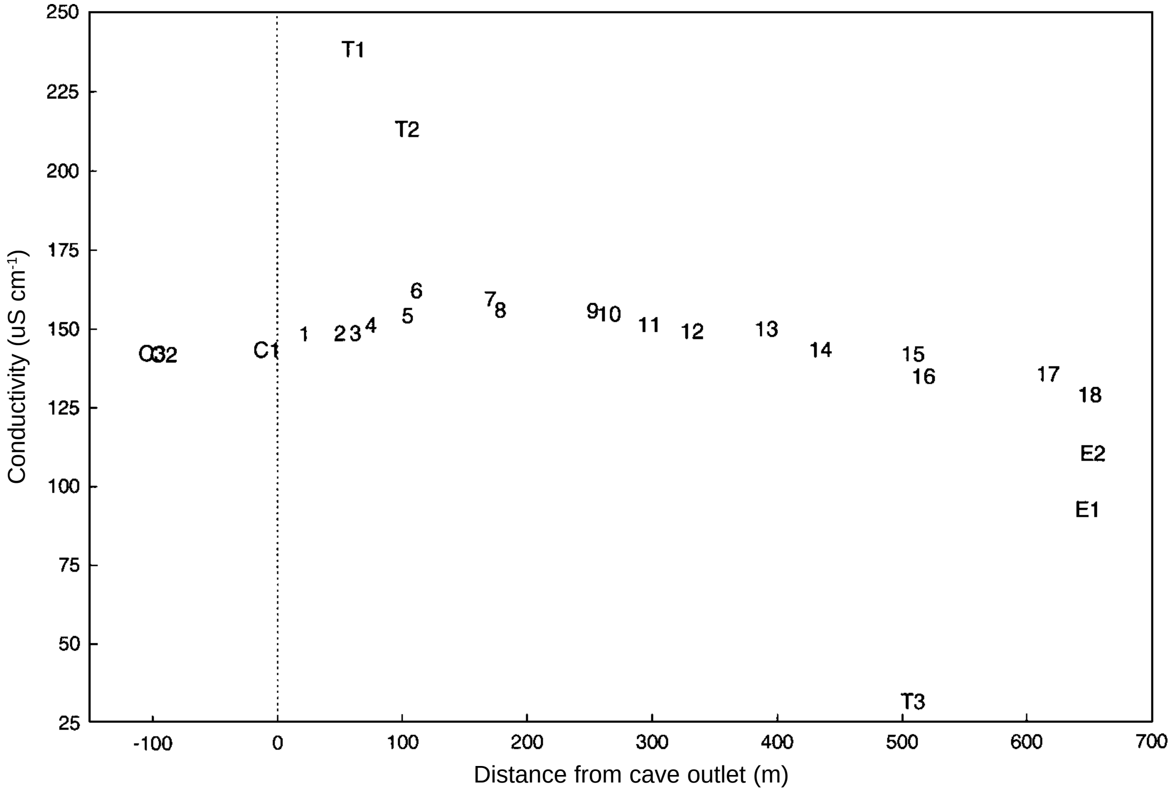

Figure 2.—Average electrical conductivity at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

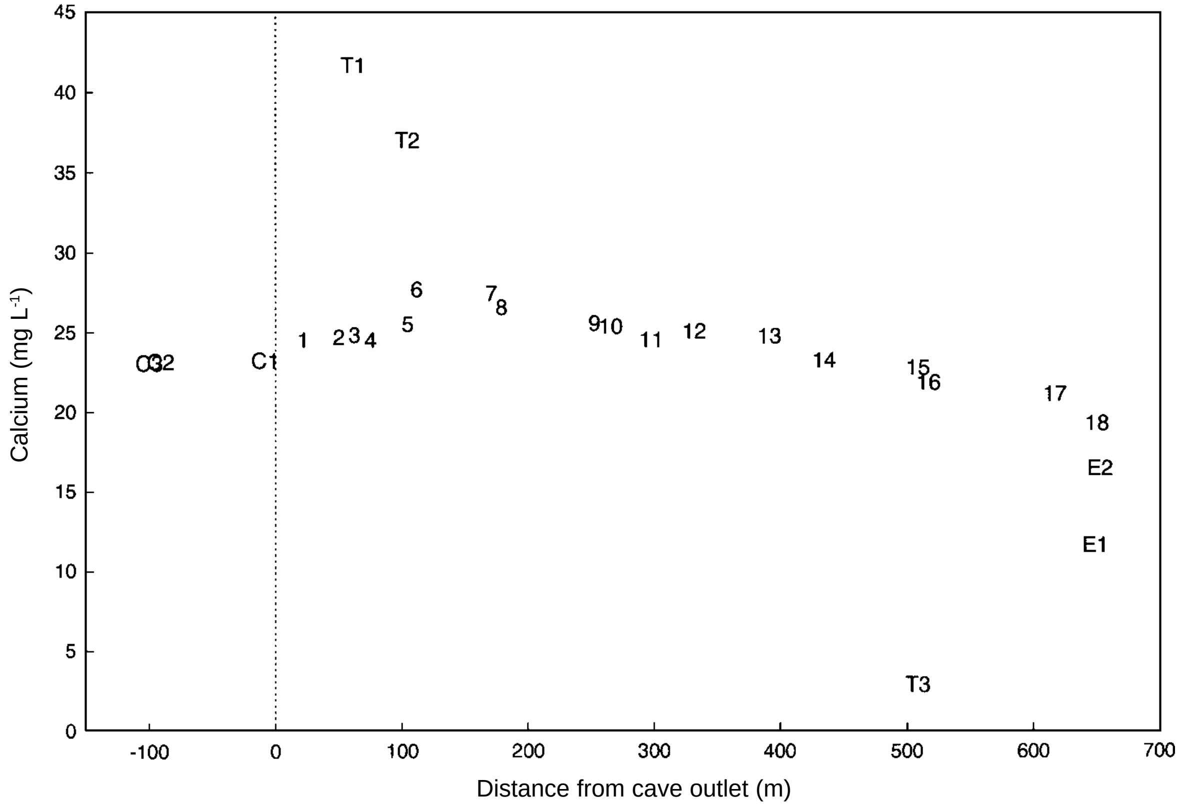

Figure 3.—Average calcium concentrations at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

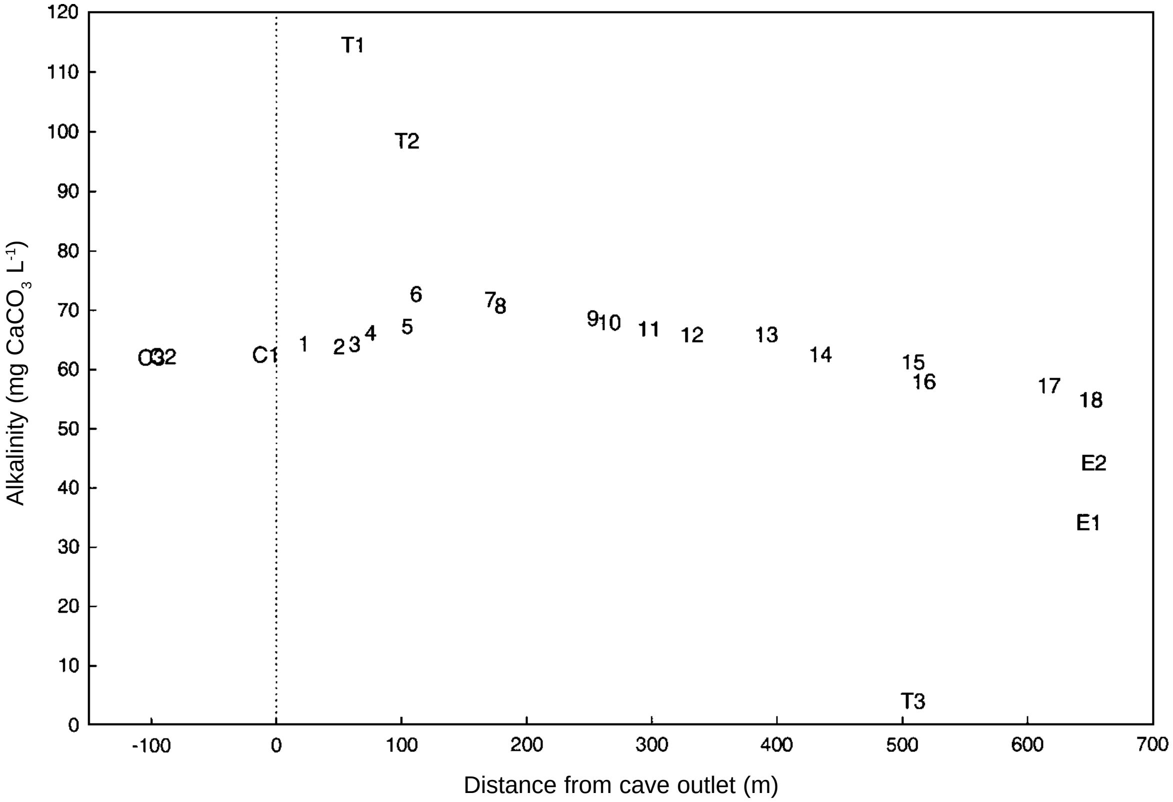

Figure 4.—Average alkalinity concentrations at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

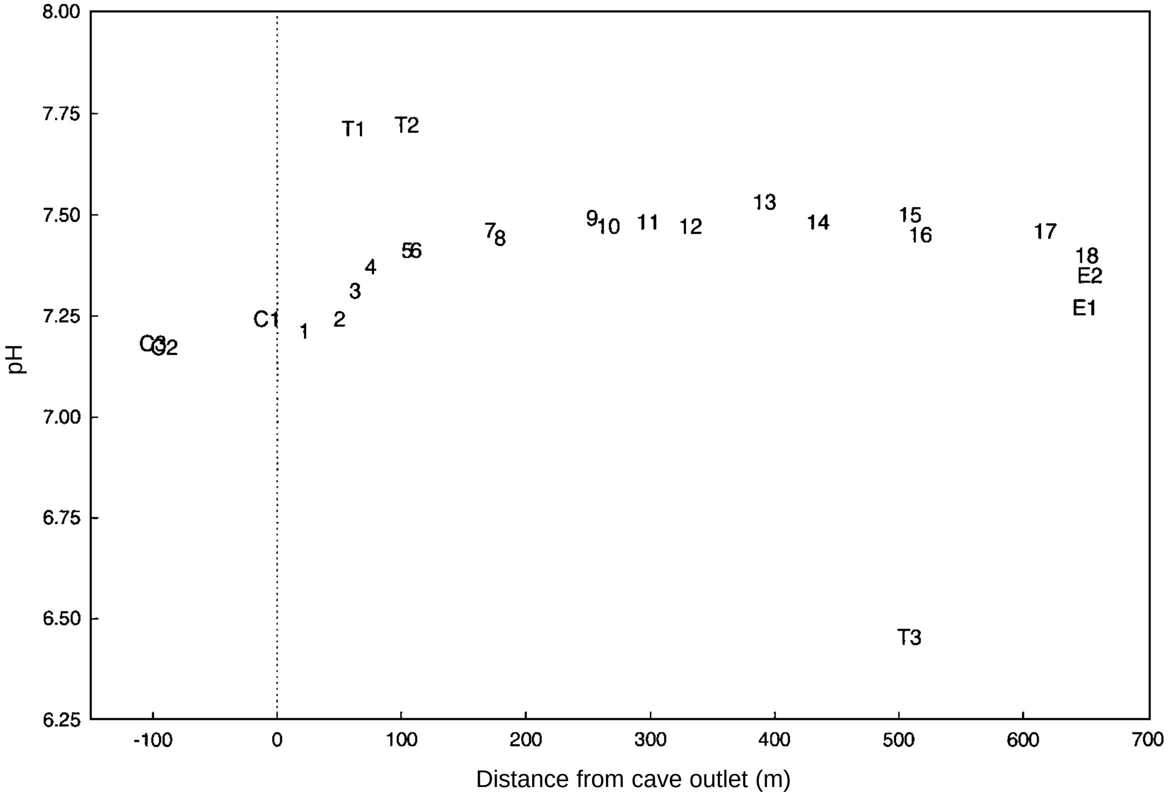

Figure 5.—Average pH at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

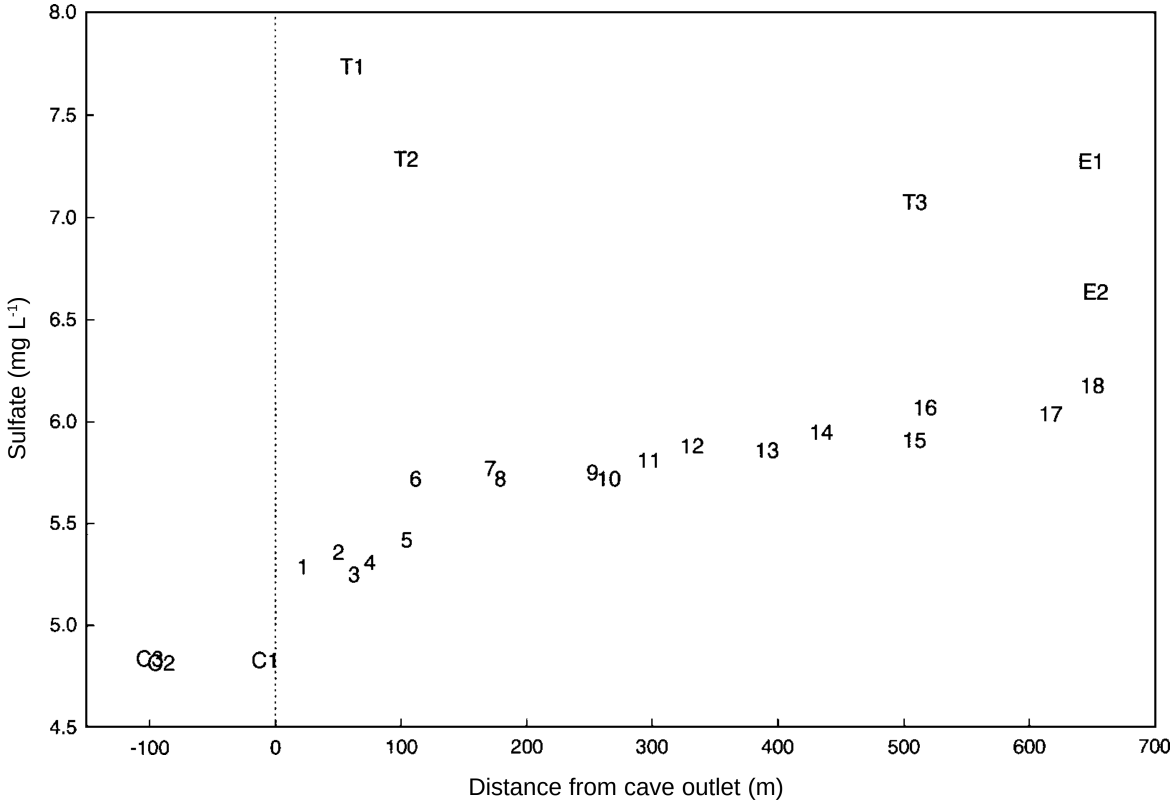

Figure 6.—Average sulfate concentrations at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

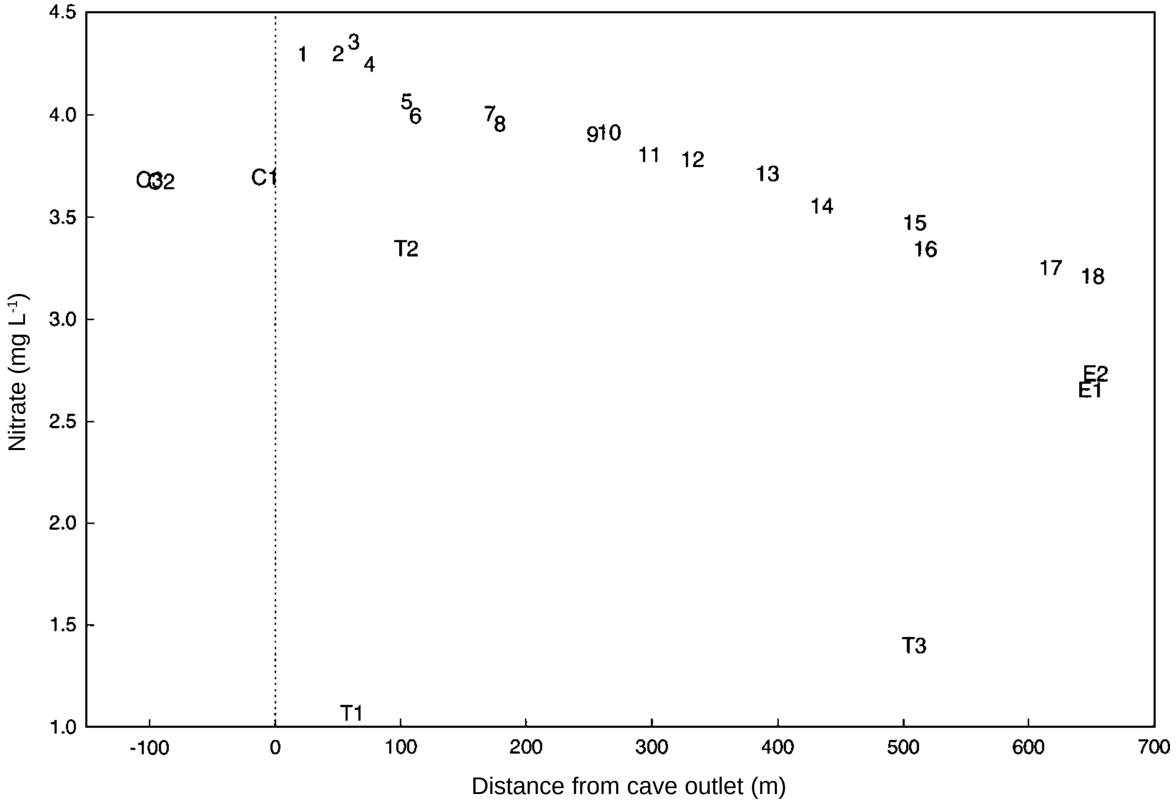

Figure 7.—Average nitrate concentrations at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

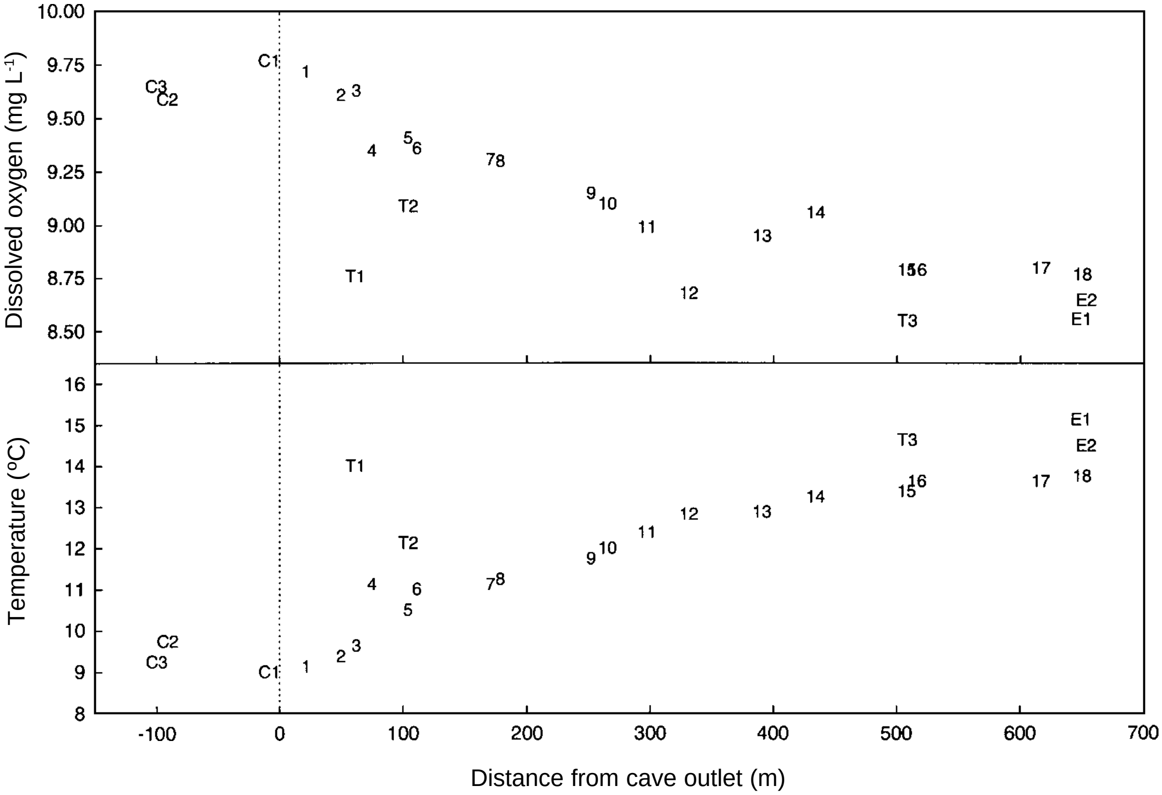

Figure 8.—Average dissolved oxygen concentrations and water temperature at each sampling site. Negative distances on the x-axis indicate sampling sites within Big Spring Cave.

We believe that organic carbon was not limiting in the cave but rather was more abundant outside the cave. Bat guano is believed to be a source of organic carbon inside and outside (i.e., transported from inside to outside), while inputs of organic matter from the surrounding forest vegetation and litter layer contributed additional organic carbon outside the cave. Five species of bats are known to inhabit Big Spring Cave during at least part of the year (unpublished data), and some bats use the cave year round.

In this region, inputs of SO_4 and NO_3 from the atmosphere are among the highest of those measured in the United States (NADP/NTN 1987). Consequently, we hypothesized that concentrations of these two ions might change with distance from the cave. SO_4 in BSR increased significantly (a=0.05), at an average rate of 0.0016 mg L^{-1} m^{-1}, along its length outside the cave (Fig. 6), while NO_3 decreased at an average rate of 0.0013 mg L^{-1} m^{-1} in the resurgent portion of BSR (Fig. 7).

The higher SO_4 concentrations in T1 and T2 (Fig. 6) were similar to those in many nearby streams located in sandstone and shale (Stephenson et al. 1995; Kochenderfer et al. 1991). Thus, the Pocono formation appears to substantially influence SO_4 concentrations in these two tributaries. Also, the influence of the more acidic geology downstream is evident in higher SO_4 concentrations in T3 and Elklick Run (Fig. 6).

The decreases in NO_3 were surprising (Fig. 7) given the high NO_3 deposition and additional organic-matter load available outside the cave. The decrease in NO_3 in the resurgent waters of BSR probably was due to progressive downstream dilution.

Concentrations of NO_3 are much higher within Big Spring Cave and throughout BSR than in most streams in this area. Generally, only streams also within the Greenbrier formation have similar concentrations (Stephenson et al. 1995; Griffith and Perry 1993). In fact, these concentrations are much higher than what would be expected from inputs of atmospheric deposition. Nor can they be explained by geologic inputs since nitrogen compounds are negligible in minerals. The primary source of NO_3 in these limestone streams is believed to be bat guano, which has produced high NO_3 concentrations in other cave-derived streams (Hem 1970). While not all of the watersheds holding these high NO_3 streams have caves, the groundwater chemistry in many of these watersheds is similar because of the continuity of the limestone formations.

Although high, NO_3 concentrations do not exceed the EPA limit for safe drinking water (45 mg NO_3 L^{-1}) (U.S. Environ. Prot. Agency 1976). The NO_3 dilution that occurs downstream further reduces potential effects of these high concentrations on downstream water quality and water usage.

The low NO_3 concentrations in T1 and T3 (Fig. 7) were more typical of those in most of the other streams in this area. Interestingly, although T2 surficially flows only through the Pocono formation, its average NO_3 concentration suggests that it is derived from a groundwater component influenced by the upslope Greenbrier formation. Likewise, the relatively high average NO_3 concentration in Elklick Run above the confluence with BSR suggests that Elklick Run is similarly influenced by the Greenbrier formation in its headwaters.

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Keywords: Biogeochemistry, cavewater, cations, anions, pH

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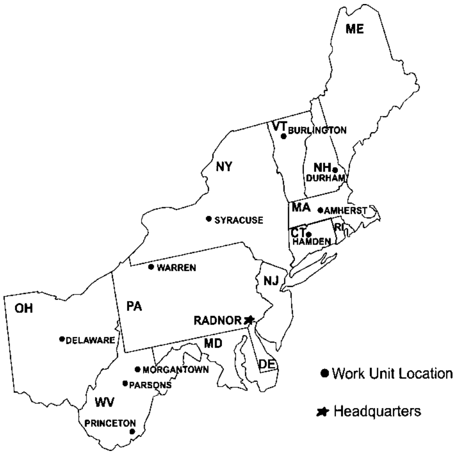

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