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Surface-Water Hydrology and Quality at the Pike Hill Superfund Site, Corinth, Vermont, October 2004 to December 2005

Scientific Investigations Report 2007–5003

U.S. Department of the Interior
U.S. Geological Survey

SDMS Doc ID 529096

Cover. *Top right*, photograph of mine workings at the Pike Hill Superfund site, Corinth, Vermont. *Middle*, photograph of mine waste at the Pike Hill Superfund site, Corinth, Vermont. *Lower left*, photograph of Pike Hill Brook above Richardson Road near Corinth, Vermont.

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By Richard G. Kiah, Jeffrey R. Deacon, Nadine M. Piatak, Robert R. Seal II, James F. Coles, and Jane M. Hammarstrom

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U.S. Geological Survey

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Suggested citation:
Kiah, R.G., Deacon, J.R., Piatak, N.M., Seal II, R.R., Coles, J.F., and Hammarstrom, J.M., 2007, Surface-water hydrology and quality at the Pike Hill Superfund Site, Corinth, Vermont, October 2004 to December 2005: U.S. Geological Survey Scientific Investigations Report 2007–5003, 61 p.

Acknowledgments

The authors acknowledge the effort provided by Thor Smith and Ann Chalmers, U.S. Geological Survey, for their assistance in the collection of data. Thanks also are extended to Edward Hathaway, U.S. Environmental Protection Agency, and Karen Rice, U.S. Geological Survey, for their technical reviews of this report.

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Conversion Factors, Abbreviated Water-Quality Units, and Datums

Multiply	By	To obtain
	Length	
inch (in)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
acre	0.004047	square kilometer (km^2)

pH: pH is given in standard units and may be converted to hydrogen-ion (H^+) concentration as follows:

$$H^+=10^{(-pH)}$$

Temperature: Temperature is given in degrees Celsius (°C) and may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Abbreviated water-quality units used in this report: Chemical concentrations in water are reported in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents as weight (milligrams) of chemical per unit volume (liter) of water. Micrograms per liter is a unit expressing the concentration of chemical constituents as weight (micrograms) of chemical per unit volume (liter) of water. Chemical loads in water are reported in kilograms per day (kg/d).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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Abstract

The hydrology and quality of surface water in and around the Pike Hill Brook watershed, in Corinth, Vermont, was studied from October 2004 to December 2005 by the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency (USEPA). Pike Hill was mined intermittently for copper from 1847 to 1919 and the site is known to be contributing trace elements and acidity to Pike Hill Brook and an unnamed tributary to Cookville Brook. The site has been listed as a Superfund site since 2004. Streamflow, specific conductance, pH, and water temperature were measured continuously and monthly at three sites on Pike Hill Brook to determine the variation in these parameters over an annual cycle. Synoptic water-quality sampling was done at 10 stream sites in October 2004, April 2005, and June 2005 and at 13 stream sites in August 2005 to characterize the quality of surface water in the watershed on a seasonal and spatial basis, as well as to assess the effects of wetlands on water quality. Samples for analysis of benthic macroinvertebrate populations were collected at 11 stream sites in August 2005.

Water samples were analyzed for 5 major ions and 32 trace elements. Concentrations of trace elements at sites in the Pike Hill Brook watershed exceeded USEPA National Recommended Water Quality Criteria acute and chronic toxicity standards for aluminum, iron, cadmium, copper, and zinc. Concentrations of copper exceeded the chronic criteria in an unnamed tributary to Cookville Brook in one sample. Concentrations of sulfate, calcium, aluminum, iron, cadmium, copper, and zinc decreased with distance from a site directly downstream from the mine (site 1), as a result of dilution and through sorption and precipitation of the trace elements. Maximum concentrations of aluminum, iron, cadmium, copper, and zinc were observed during spring snowmelt. Concentrations of sulfate, calcium, cadmium, copper, and zinc, and instantaneous loads of calcium and aluminum were statistically different (p<0.05) among the three continuously monitored sites (sites 1, 4, and 5). Instantaneous loads of aluminum, iron, and copper decreased by one to three orders of magnitude from site 1 to a site 1.1 mi downstream (site 4). Instantaneous loads of sulfate were similar between sites 1, 4, and at a site 3 mi downstream (site 5). Instantaneous loads of cadmium and zinc were similar between sites 1 and 4, and loads of iron and copper were similar between sites 4 and 5.

Loads of chemical constituents were compared at site 1 (closest to the mine waste piles) and site 5 (near the mouth of Pike Hill Brook and below a majority of the wetlands). Annually, the loads of dissolved cadmium and zinc at site 1 were about five times greater than loads at site 5, and the load of dissolved copper at site 1 was about 17 times greater than at site 5. The ratio of loads for dissolved cadmium, copper, and zinc to total cadmium, copper, and zinc at site 1 was about 1.

Samples collected in Pike Hill Brook upstream and downstream from the wetlands during low flows in August 2005 showed that oxidation of ferrous iron and precipitation of iron-hydroxides were probably not affecting trace metals in the wetlands through sorption; however, a significant portion of the iron entering the wetlands was in particulate form and may have transported sorbed copper and other trace metals. Thus, aerobic activity in the wetlands was probably not affecting metal cycling in the watershed. Concentrations and loads of sulfate may be unlikely to define unequivocally the role of the wetlands with regard to anaerobic bacterial sulfate reduction; however, bacterial sulfate removal may have affected loads of sulfate. Loads of copper increased downstream from the wetlands and may reflect the reductive dissolution of ferric hydroxide particulates in anaerobic parts of the wetlands. Concentrations of dissolved iron increased downstream from the wetlands.

The most apparent effects on the macroinvertebrate assemblages caused by high levels of acid rock drainage were seen in the abundance of organisms and richness of taxa. A decrease in the macroinvertebrate abundance was strongly correlated to increasing values of the Hazard Index (rho = -0.929); this response was most apparent in the Pike Hill Brook sites farther from the mine waste piles. At sites most affected by acid rock drainage, stoneflies were not quite as sensitive as mayflies and caddisflies.

Introduction

The Pike Hill Brook watershed is in the town of Corinth in eastern Vermont (fig. 1). Pike Hill was mined intermittently for copper from 1847 to 1919, and the site is known to be contributing trace elements and acidity to Pike Hill Brook and an unnamed tributary to Cookville Brook (U.S. Environmental Protection Agency, 2004). The Pike Hill Superfund Site was placed on the U.S. Environmental Protection Agency (USEPA) National Priorities List in 2004 and consists of three abandoned mines.

The Pike Hill mines are primarily on the top and northeastern exposures of Pike Hill, in an area referred to as the Vermont copper belt (fig. 1). This area contains the Eureka and Union mines. A smaller mine, the Smith mine, is on the southern exposure of Pike Hill. The Pike Hill site includes open mine cuts, trenches, adits, shafts, waste rock, and several small piles of flotation tailings.

Copper was discovered on Pike Hill sometime before 1847 (U.S. Environmental Protection Agency, 2004). Mining at Pike Hill exploited Besshi-type massive sulfide deposits in the Waits River Formation (Silurian), which consists of calcareous pelite, pelite, minor quartzose metalimestone and metadolostone, and sparse calcite marble (Piatak and others, 2006a). The bedrock at Pike Hill contains large amounts of carbonate minerals that may contribute alkalinity and hardness to local surface waters.

Trace elements released into local streams and rivers may be toxic to aquatic life and possibly to human health. The weathering of mine wastes further releases trace elements and sulfate into waterways, affecting the local water quality. Trace elements may be transported downstream as dissolved material or sorbed to particulate matter. Dissolved trace elements are mainly removed from waters by precipitation and sorption, especially with hydroxides formed from iron and aluminum (Kelly, 1988). Sorbed trace elements can settle out of the water column or be transported downstream depending on water velocity.

To understand the fate and transport of contamination associated with acid rock drainage (ARD) at the Pike Hill Superfund Site, the U.S. Geological Survey (USGS), in cooperation with USEPA, used an integrated (physical, chemical, and biological) approach to assess the hydrology and quality of waters in and around the Pike Hill Brook watershed. A streamflow- and surface-water-quality monitoring network was operated from October 2004 to September 2006. Water-quality samples were collected monthly from November 2004 to September 2006. Biological samples were collected in August 2005. This report presents data collected from October 2004 to December 2005, complements a companion study focused on the geochemistry of the solid mine wastes and drainage environments of the abandoned mine sites (Piatak and others, 2006a), and will be used by water-resources managers to help determine the nature and extent of contamination and what additional studies may be necessary to perform as part of a remedial investigation and feasibility study for cleanup of the Pike Hill Superfund Site.

Purpose and Scope

This report (1) characterizes the surface-water hydrology and water quality of Pike Hill Brook over an annual cycle; (2) provides estimates of annual and seasonal constituent loads in Pike Hill Brook; (3) describes the effects of natural wetlands on the water quality of Pike Hill Brook; and (4) explains the correlation of the benthic macroinvertebrate assemblage data with the water-quality data. The data presented in this report were collected at 14 stream sites from October 2004 to December 2005 (fig. 1, table 1) and include streamflow; specific conductance; pH; water temperature; concentrations of sulfate (SO_4), calcium (Ca), aluminum (Al), iron (Fe), cadmium (Cd), copper (Cu), zinc (Zn); and benthic macroinvertebrate assemblages. Concentrations of Ca, Al, Cd, Cu, Fe, and Zn are presented in this report as dissolved unless noted as total. A dissolved sample is derived from a filtered (less than 0.45 micron) water sample. Cd, Cu, and Zn are recognized as priority pollutants by the USEPA, whereas Al and Fe are considered non-priority pollutants.

Streamflow and water-quality data collected for the study are stored in the USGS National Water Information System (*http://nwis.waterdata.usgs.gov/nwis*). The taxonomic identification and count for benthic macroinvertebrates are listed in appendix 1. The State of Vermont Department of Environmental Conservation (VT-DEC) biocriteria metrics are listed in appendix 2.

Description of the Study Area

The study area, in the town of Corinth in east-central Vermont, is in the Connecticut River Basin (fig. 1). The area is mountainous with elevations ranging from about 1,190 ft at the mouth of Pike Hill Brook to 1,965 ft at the summit of Pike Hill (fig. 1). Mean annual precipitation varies with elevation and ranges from 39 to 42 in/yr (accessed at *http://water.usgs.gov/osw/streamstats/Vermont.html* on June 5, 2005). The local mean annual temperature from 1971 to 2000 was 5.1°C with a range of –2.2 to 12.3°C (National Oceanic and Atmospheric Administration, 2002). Surface water from the northeastern exposure of Pike Hill discharges primarily to Pike Hill Brook. Pike Hill Brook originates near the mines and waste piles, has a total stream length of about 4.2 mi, and a contributing drainage area of 4.67 mi^2 at the mouth (accessed at *http://water.usgs.gov/osw/streamstats/Vermont.html* on June 5, 2005). Pike Hill Brook flows approximately 2.2 mi from its source before entering a series of natural wetlands and then flows approximately 2 mi before entering the Waits River (fig. 1). The wetlands constitute about 0.2 percent of the total drainage area or 0.83 mi^2 (accessed at *http://water.usgs.gov/osw/streamstats/Vermont.html* on June 5, 2005). A stream also drains the southern exposure of Pike Hill. This unnamed tributary flows approximately 1 mi to the confluence with Cookville Brook, which flows into the Waits River.

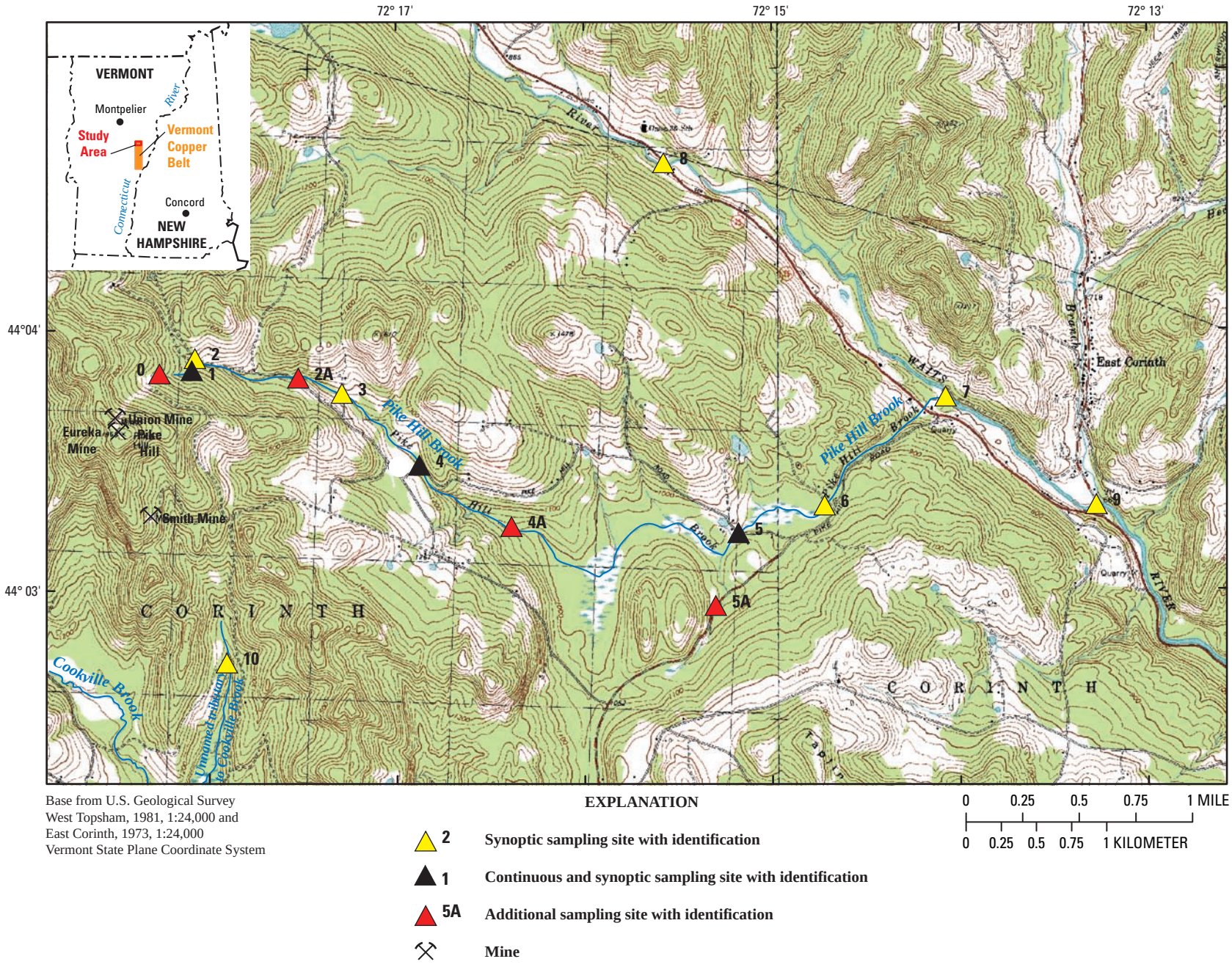

Figure 1. Sampling site locations and site-identification numbers in the Pike Hill, VT, study area.

Table 1. Selected characteristics of sampling sites for the Pike Hill, VT, study area.

[USGS, U.S. Geological Survey; Latitude and longitude are given in degrees°, minutes', and seconds"; mi², square miles; L, August 2005 low-flow sampling site; B, benthic invertebrate sampling site; C, continuously monitored site; S, synoptic sampling site; ft, feet; mi, mile]

Site number (fig. 1)	Site name	USGS station number	Latitude	Longitude	Drainage area (mi²)	Monitoring status	Purpose of monitoring site
0	Pike Hill Brook below Eureka and Union mines near Bradford, VT	011398299	44°03'50"	72°18'18"	0.05	L	Represented water-quality conditions directly downstream from the Eureka and Union mines and waste rock piles.
1	Pike Hill Brook above Richardson Road near Bradford, VT	01139830	44°03'50"	72°18'07"	.11	B,C,S,L	Represented water-quality conditions 800 ft downstream from site 0.
2	Tributary to Pike Hill Brook at Richardson Road near Bradford, VT	011398302	44°03'53"	72°18'06"	.06	B,S,L	Represented background water-quality conditions. Flows into Pike Hill Brook 100 ft downstream from site 1.
2A	Pike Hill Brook at Richardson Road near Bradford, VT	01139831	44°03'49"	72°17'36"	.36	L	Represented water-quality conditions 0.5 mi downstream from site 1.
3	Pike Hill Brook at Carpenter Place near Bradford, VT	01139832	44°03'45"	72°17'19"	.45	B,S,L	Represented water-quality conditions 0.7 mi downstream from site 1 after initial opportunity for precipitation and sorption of metals.
4	Pike Hill Brook at Pike Hill Road, west crossing, near Bradford, VT	01139833	44°03'28"	72°16'54"	1.10	B,C,S,L	Represented water-quality conditions above the wetlands, 1.1 mi downstream from site 1.
4A	Pike Hill Brook above wetlands near Bradford, VT	01139834	44°03'14"	72°16'26"	1.6	B	Represented benthic invertebrate assemblages directly above the wetlands, 1.6 mi downstream from site 1.
5	Pike Hill Brook at Pike Hill Road near Bradford, VT	01139838	44°03'12"	72°15'12"	3.64	B,C,S,L	Represented water-quality conditions after a majority of the wetlands, 3 mi downstream from site 1.
5A	Tributary to Pike Hill Brook at Brook Road near Bradford, VT	011398378	44°02'54"	72°15'20"	.26	L	Represented background water-quality conditions. Flows into Pike Hill Brook 900 ft upstream from site 5.
6	Pike Hill Brook at Miller Road near Bradford, VT	01139839	44°03'19"	72°14'45"	4.39	B,S,L	Represented water-quality conditions below the wetlands, 3.8 mi downstream from site 1.
7	Pike Hill Brook at mouth near Bradford, VT	01139840	44°03'44"	72°14'06"	4.67	B,S,L	Represented water-quality conditions at the mouth of Pike Hill Brook.
8	Waits River at VT 25 near Bradford, VT	01139826	44°04'38"	72°15'36"	42.7	B,S,L	Represented background water-quality conditions, 1.8 mi upstream from confluence with Pike Hill Brook.
9	Waits River at Village Road near Bradford, VT	01139841	44°03'19"	72°13'18"	50.6	B,S,L	Represented water-quality conditions 0.8 mi downstream from confluence with Pike Hill Brook.
10	Unnamed tributary to Cookville Brook near Bradford, VT	01139940	44°02'43"	72°17'56"	.41	B,S,L	Represented water-quality conditions down-gradient of Smith mine and in headwaters of unnamed tributary to Cookville Brook that drains the southern exposure of Pike Hill.

Methods of Data Collection and Analysis

The sampling program for the study integrated physical, chemical, and biological data to assess water quality at 14 stream sites: 9 sites on Pike Hill Brook, 2 sites on the Waits River, 2 sites on tributaries to Pike Hill Brook, and 1 site on a tributary to Cookville Brook (fig. 1, table 1). Three sites (sites 2, 5A, and 8) were selected to represent background water-quality conditions. Continuous monitoring of streamflow, specific conductance, pH, and water temperature was conducted at three sites (sites 1, 4, and 5) in Pike Hill Brook to characterize the variations in these parameters during an annual cycle. Water samples representing the different weather conditions that can affect constituent concentrations in samples, such as those observed from an increase in runoff during rain or snowmelt events, were collected monthly at the three continuously monitored sites. Synoptic water samples, representing a range in streamflows, were collected at 10 sites to assess the water quality of streams in and around the Pike Hill Brook watershed spatially and seasonally. Water samples were collected during summer low-flow conditions at 13 sites to evaluate the effects of the wetlands on the water quality of Pike Hill Brook (fig. 1, table 1). Benthic macroinvertebrate samples were collected during summer low-flow conditions at 11 sites (table 1).

Hydrologic Data

Continuous record streamflow-gaging stations were established using protocols described in Rantz and others (1982). Records of stage were obtained using electronic data loggers and stage sensors. Stage readings were related to measurements of streamflow to obtain a stage-streamflow relation used in computing continuous streamflow. Continuous streamflow-gaging stations were at Pike Hill Brook above Richardson Road near Bradford, VT (USGS station 01139830, site 1), Pike Hill Brook at Pike Hill Road, west crossing, near Bradford, VT (USGS station 01139833, site 4), and Pike Hill Brook at Pike Hill Road near Bradford, VT (USGS station 01139838, site 5) (fig. 1, table 1). Stage values were recorded every 5 minutes at site 1 and every 15 minutes at site 5 from October 2004 to December 2005. Stage values were recorded every 15 minutes at site 4 from June 2005 to December 2005. Instantaneous streamflow measurements were made at all water-quality synoptic sites. Streamflow was measured by the conventional current meter method, by use of a portable Parshall flume, volumetrically, or with an acoustic Doppler current profiler using published USGS protocols (Rantz and others, 1982; Buchanan and Somers, 1969; Kilpatrick and Schneider, 1983; and Oberg and others, 2005).

Water-Quality Data

Specific conductance, pH, and water temperature data were collected continuously at sites 1, 4, and 5 using published USGS protocols (Wagner and others, 2000). Values were recorded every 5 minutes at site 1 and every 15 minutes at site 5 from November 2004 to December 2005, and every 15 minutes at site 4 from June 2005 to December 2005. Water samples were collected using standard USGS protocols (Wilde and Radtke, 1998; Wilde and others, 1999) at sites 1 and 5 from November 2004 to December 2005 and at site 4 from June 2005 to December 2005. Additional samples were collected at sites 1 and 5 during spring rains and snowmelt. Four synoptic water samples were collected at sites 1 through 9 during a range in streamflow conditions in November 2004, April 2005, June 2005, and August 2005. Three synoptic water samples were collected at site 10 in November 2004, June 2005, and August 2005. The synoptic samples were collected to represent low, normal, and high streamflow conditions. Based on recorded streamflow at site 5, November samples represented the 75th percentile flow-duration, April samples represented the 5th percentile flow duration, June samples represented the 30th percentile flow duration, and August samples represented the 95th percentile flow duration. Flow-duration percentiles, in this usage, are the percentage of time a streamflow is expected to be equaled or exceeded at a given location. The April samples were used to describe high-flow conditions and are referred to in this report as the high streamflow samples. The August samples were used to describe low-flow conditions and are referred to in this report as the low streamflow samples. The median constituent concentration and mean instantaneous load of the four synoptic samples was used to describe normal streamflow samples.

Specific conductance, pH, and water temperature were determined by use of a combination of continuous monitors and discrete measurements at the time of water sample collection. Water samples were collected for the analysis of 5 major ions and 32 trace elements. All water samples were analyzed by the USGS Geologic Discipline Analytical Chemistry Services Group in Denver, CO. Major-ion and trace-element concentrations were analyzed using inductively coupled plasma-mass spectrometry unless otherwise noted. Sulfate concentrations were analyzed using ion chromatography.

Benthic Macroinvertebrate Data

Benthic macroinvertebrate samples were collected in August 2005 during low streamflows using a Slack sampler with a 500-micron mesh designed to cover 2.69 ft^2 (0.25 m^2) of substrate area (Cuffney and others, 1993). At each site, macroinvertebrates were collected at four locations in a swift-flowing area of a sampling reach (typically riffles), and these four samples were composited to characterize the macroinvertebrate assemblage in a 10.76-ft^2 (1-m^2) area of substrate. Under typical sampling situations, the USGS method

recommends collections at five locations for a composite, thereby covering a substrate area of 13.45 ft^2 (1.25 m^2). The change to sampling 10.76 ft^2, however, was based on the method used by VT-DEC for high-gradient streams. The composited samples were preserved in 70-percent isopropyl alcohol and shipped to EcoAnalysts Inc., Moscow, ID, for a 300-individual organism count for taxonomic identifications and metric calculations (abundance, dominance, richness, composition, functional feeding groups, diversity/evenness, and biotic indices).

Quality-Control Procedures

Daily mean streamflow computations were based upon records of stage and discrete measurements of streamflow in addition to observations of other factors, such as weather conditions, as described in Rantz and others (1982). The accuracies of the continuous streamflow and water-quality records listed in the appendixes are based on a scale of four classifications ranging from excellent to poor (Novak, 1985; Wagner and others, 2000).

Field quality-control procedures included the collection of blanks and replicates. Field blanks provide information on bias or the potential for contamination of analytical results by sample collection, processing, and analysis. Analytical results from the field-blank samples showed that concentrations for constituents presented in this report were less than the laboratory reporting level. Replicate samples provide information on the variability of analytical results caused by sample collection, processing, and analysis. Differences in concentrations in environmental and replicate samples for SO_4, Ca, Al, Fe, Cd, Cu, and Zn were less than 5 percent, so sample processing and analysis did not introduce enough variation in the environmental data to affect interpretation of results. Analytical laboratory quality-control procedures are summarized in Taggart (2002).

Data Analysis and Statistical Methods

Selected results from the three continuously monitored sites and the synoptic sampling sites are presented in the following sections and are shown as a series of graphs and plots used to analyze the data. Mean pH values for samples in this report were determined by converting instantaneous pH values to hydrogen-ion (H^+) concentrations, calculating the mean of the instantaneous H^+ concentrations, and converting the mean H^+ concentration back into pH units (Wagner and others, 2000). Statview statistical software was used for all statistical analyses (SAS Institute, Inc., 1998).

A statistical analysis of the physical and water-quality parameters was conducted to investigate the fate and transport of constituents in Pike Hill Brook. The Kruskal-Wallis statistical test, a non-parametric analysis of variance (ANOVA) test that uses ranked data, was performed on physical and water-quality parameters to determine if there were statistical differences among the three continuously monitored sites. The level of significance for ANOVA was set at alpha equal to 0.05. If a significant difference was found, the Tukey's multiple-comparison test was used to determine which groups differed significantly (Helsel and Hirsch, 1992). Specific conductance and pH values along with measured concentrations and instantaneous loads for SO_4, Ca, Al, Fe, Cd, Cu, and Zn were examined among sites by use of boxplots. A Spearman rho correlation test, which calculates a correlation coefficient based on the ranks of data, was used to determine the relation among concentrations of SO_4, Ca, Al, Fe, Cd, Cu, and Zn. Spearman rho tests whether two constituent concentrations are independent of each other and ranges from values of -1 to +1. A value of -1 indicates that high ranks of one constituent are correlated to low ranks of the other constituent, whereas a value of +1 indicates that high ranks of one constituent are correlated to high ranks of the other constituent.

Standards outlined in the USEPA National Recommended Water Quality Criteria (NRWQC) and adopted by the State of Vermont were used to compare trace-element concentrations from this study to water-quality guidelines (U.S. Environmental Protection Agency, 2006). The Criteria Maximum Concentration (CMC) standards were used to assess acute toxicity to the aquatic community and are referred to in this report as acute toxicity standards. The Criterion Continuous Concentration (CCC) standards were used to assess chronic toxicity to the aquatic community and are referred to in this report as chronic toxicity standards. The acute and chronic toxicity standards for Cd, Cu, and Zn were adjusted based on hardness according to the NRWQC (U.S. Environmental Protection Agency, 2006).

The LOAD ESTimator (LOADEST) computer program (Runkel and others, 2004) was used to estimate loads of dissolved and total SO_4, Al, Fe, Cd, Cu, and Zn at sites 4 and 5. LOADEST is based on a regression equation in which time series of streamflow and constituent concentration are used as calibration data for the estimation of constituent loads. Explanatory variables within the regression model include various functions of streamflow and time (seasonality). Regression equations were developed for each constituent (SO_4, Ca, Al, Fe, Cd, Cu, and Zn) at each site, models were fit using all possible combinations of these variables, and the best model was selected on the basis of the Akaike Information Criteria (Akaike, 1981). The specific method used for model calibration and load estimation is described by Runkel and others (2004).

The small drainage area of 0.11 mi^2 at site 1 precludes it from being modeled using LOADEST. Concentrations of chemical constituents, however, may be correlated to physical factors of surface waters such as streamflow, water temperature, specific conductance, and pH (Christensen and others, 2000). Multiple regression analysis was used to evaluate variables that can affect concentrations of SO_4, Al, Fe, Cd, Cu, and Zn at site 1, and concentrations of Ca at sites 1, 4, and 5. A stepwise regression procedure was used to select variables that were significant in predicting concentrations of dissolved and total SO_4, Ca, Al, Fe, Cd, Cu, and Zn. A vari-

able was considered significant if the difference between the mean and hypothesized standard error (*t* value) was greater than the absolute value of 2 (Helsel and Hirsch, 1992), and if the probability (*p* value) of the dependent variable was less than 0.01. The relation of significant variables with respect to concentrations was assessed graphically. If the graph showed curvature to the relationship, the log of the variable was used to transform it to a more linear relation. Multiple regression equations to estimate constituent concentrations were developed with the significant predictor variables for concentrations of SO_4, Ca, Al, Fe, Cd, Cu, and Zn. The strength of the regression equations was evaluated by use of the coefficient of determination (R^2) and the mean square error (MSE). The R^2 is a dimensionless measure of the fraction of the variance explained by regression and ranges from 0 to 1. The greater the explained variability is compared to the unexplained variability, the stronger the equation. The MSE is a measure of the variance between the measured and estimated concentrations and represents the portion of the data that is not explained by the regression equation. For the purposes of this study, a regression equation was acceptable if the R^2 was greater than 0.75 and the MSE was less than 0.50.

The regression equations were applied to the continuous water-quality data to estimate instantaneous concentrations for SO_4, Ca, Al, Fe, Cd, Cu, and Zn at site 1. Estimated daily mean concentrations and the recorded daily mean streamflow were used to estimate annual and seasonal loads of SO_4, Ca, Al, Fe, Cd, Cu, and Zn (in kilograms per day) at site 1 and estimated annual and seasonal loads of Ca (in kilograms per day) at sites 4 and 5.

Surface-Water Hydrology

Based on 48 years of streamflow record (1958–2005) at the USGS streamflow-gaging station East Orange Branch at East Orange, VT (USGS station 01139800), local streamflow conditions during the study were normal. Normal streamflow is defined as annual mean streamflow that falls within the 25th to 75th percentile streamflow-duration. Mean streamflow for water year 2005 at East Orange Branch at East Orange, VT was 15.1 ft^3/s, and was similar to the annual mean streamflow of 15.7 ft^3/s for the period of record (Kiah and others, 2005).

Base-flow conditions, where streamflow is sustained by ground-water discharge, were present in Pike Hill Brook for much of the fall of 2004. Streamflow increased during November and December 2004 as a result of seasonal rains and reduced evapotranspiration. Streamflow decreased to base flow for the remainder of the winter. Spring snowmelt and rains increased streamflow above normal during April and May 2005. Streamflow decreased seasonally to base flow, again, for the summer and fall of 2005. Seasonal rains in mid- to late-October and November 2005 resulted in streamflows above normal through December 2005.

Surface-Water Quality

Sites 1, 4, and 5 have small drainage areas and are subject to rapid changes in streamflow and water chemistry during periods of intense rainfall. Specific conductance generally increased with an increase in streamflow at site 1 and decreased with an increase in streamflow at sites 4 and 5 (fig. 2). During summer base flow at sites 1 and 5, however, there was an increase in specific conductance as streamflow decreased (fig. 2). pH generally decreased with an increase in streamflow at site 1 and remained stable or decreased slightly with an increase in streamflow at sites 4 and 5 (fig. 3). Minimum water temperatures were observed periodically during the winter; maximum temperatures were recorded in July 2005. Summary statistics for the three continuously monitored sites on Pike Hill Brook are listed in table 2.

Specific Conductance and pH

The distribution of specific conductance and pH values in Pike Hill Brook with respect to distance from site 1 over a range in streamflows is shown in figure 4. The observed specific conductance and pH values at background sites and site 10 also are presented on this graph. Specific conductance values at background sites generally were lower than those observed at other synoptic sites (fig. 4A, table 3). The specific conductance in Pike Hill Brook decreased in a downstream direction from site 1 to site 5 and was similar among sites 5, 6, and 7 before the confluence with the Waits River. The specific conductance at site 10 was greater than values at background sites and similar to the specific conductance values at site 4. The specific conductance increased with increased streamflow at sites 1 and 3 and decreased when streamflow increased at site 2 and sites 4 through 10 (fig. 4A).

The pH values at background sites were greater than pH values at site 1 and were similar to pH values at sites 3, 4, 5, 6, 7, 9, and 10 during low and normal streamflows (fig. 4B, table 3). The pH in Pike Hill Brook generally increased from site 1 to site 7. The pH generally was greater than 7 standard units at site 5. The pH at site 10 was 7.9 standard units for the three samples.

Specific conductance and pH values among the three continuously monitored sites were tested to determine if there were statistically significant differences in the data. Specific conductance and pH values were significantly different among the three continuously monitored sites ($p<0.05$) (fig. 5). Changes in specific conductance and pH values at sites 1, 4, and 5 are likely the result of rapid dilution from rain and inflows (ground- and surface water). Specific conductance and pH can be affected by a flushing of efflorescent sulfate salts, which form on waste sulfide materials (Alpers and others, 1992). Efflorescent sulfate salts were found during a geochemical characterization of the Pike Hill mine waste (Piatak and others, 2006a). During a typical rain event, there is an initial dilution of waters in Pike Hill

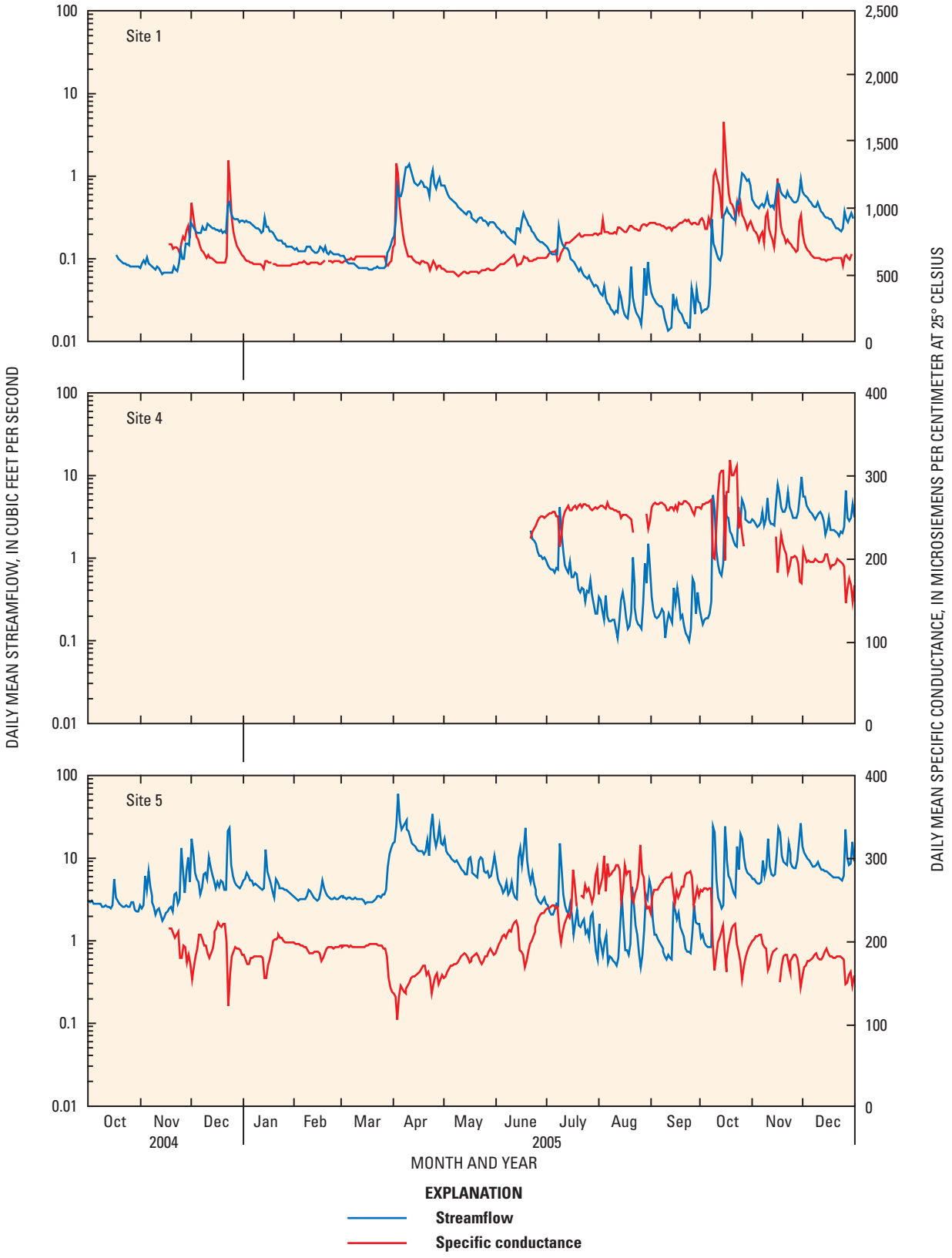

Figure 2. The relation of daily mean streamflow to daily mean specific conductance at the three continuously monitored sites in the Pike Hill, VT, study area.

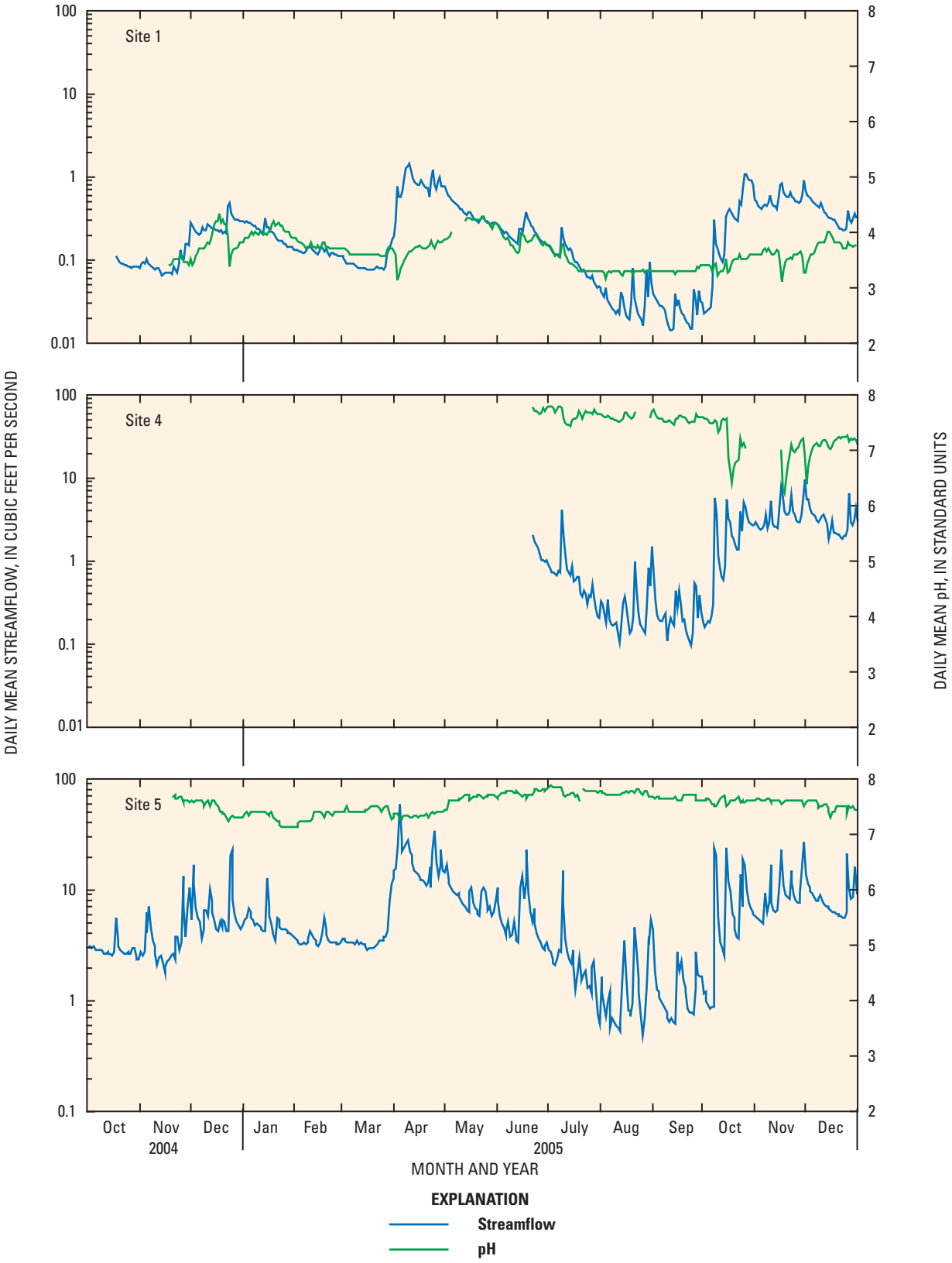

Figure 3. The relation of daily mean streamflow to daily mean pH at the three continuously monitored sites in the Pike Hill, VT, study area.

Table 2. Summary statistics of physical parameters from the three continuously monitored sites in the Pike Hill, VT, study area.

[ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; min, minimum; max, maximum. Refer to figure 1 and table 1 for site names, station numbers, and locations]

Site number (table 1; fig. 1)	Streamflow (ft^3/s)				Specific conductance (µS/cm)				pH (standard units)				Water temperature (°C)			
	Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max
[1]1	0.01	0.26	0.17	2.5	134	705	628	2,210	2.7	3.6	3.6	4.4	0.0	7.2	5.4	22.7
[2]4	.06	1.75	.89	16.0	130	240	253	327	6.1	7.2	7.6	7.8	.0	10.6	13.2	20.6
[1]5	.21	6.20	4.32	108	100	204	194	364	7.1	7.5	7.6	7.9	.0	7.8	4.7	26.9

[1] Statistics based on data collected from November 2004 to December 2005.

[2] Statistics based on data collected from June 2005 to December 2005.

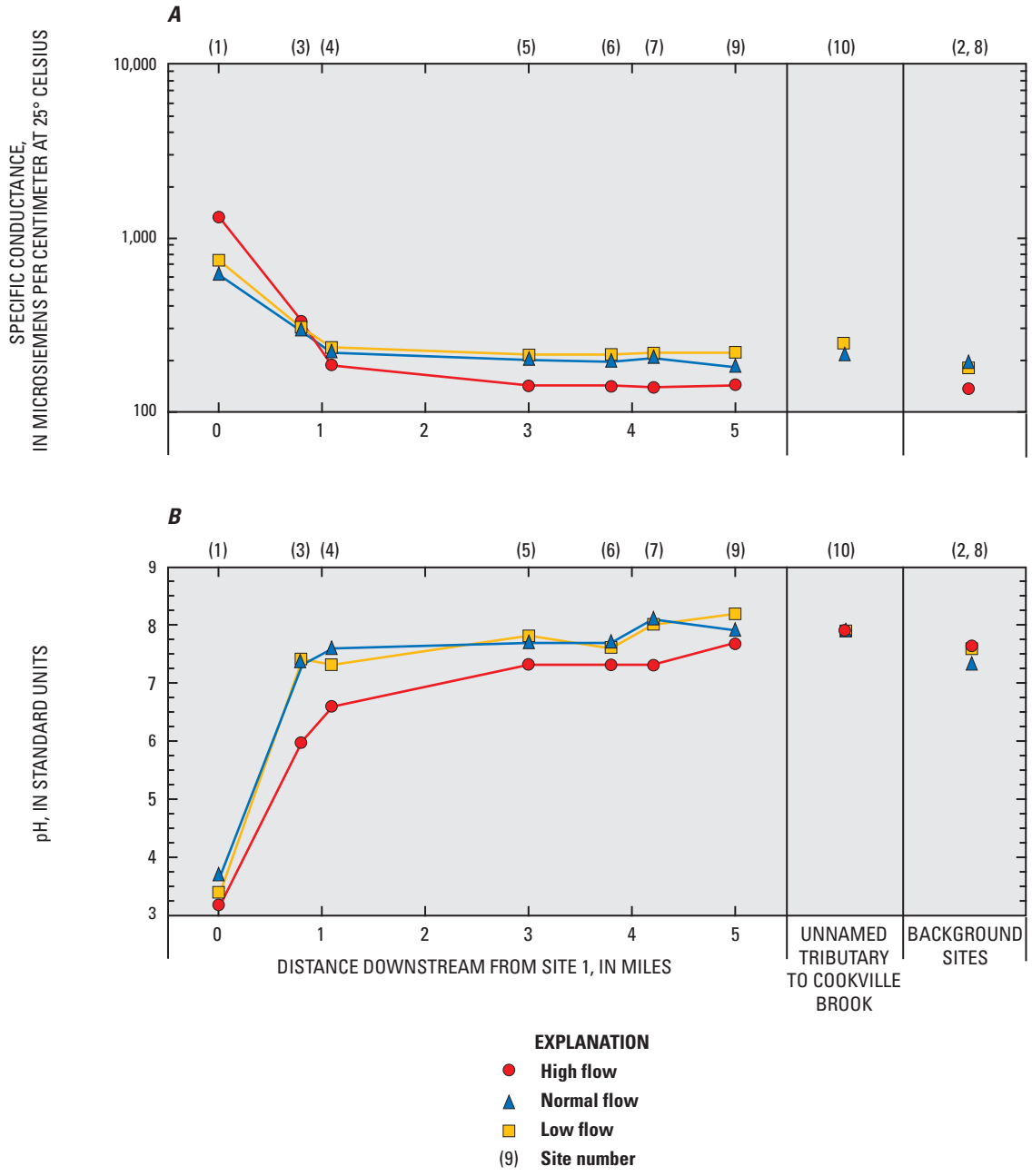

Figure 4. Distribution of (*A*) specific conductance, and (*B*) pH at the synoptic monitoring sites in the Pike Hill, VT, study area.

Table 3. Summary statistics of physical parameters for synoptic sampling sites in the Pike Hill, VT, study area.

[ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; min, minimum; max, maximum. Refer to figure 1 and table 1 for site name, station number, and location]

Site number (table 1; figure 1)	Streamflow (ft^3/s)				Specific conductance (µS/cm)				pH (standard units)				Water temperature (°C)			
	Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max
1	0.04	0.22	0.16	0.50	623	864	745	1,340	3.2	3.3	3.3	3.7	2.6	9.3	6.5	18.8
[1]2	.01	.15	.03	.41	133	175	180	208	6.8	7.2	7.5	7.7	1.7	9.0	6.5	18.8
3	.14	.90	.55	2.4	247	298	302	341	6.0	6.5	7.0	7.4	1.8	9.4	6.7	19.8
4	.24	2.5	1.2	7.4	187	214	216	237	6.6	6.9	7.1	7.6	1.5	7.9	6.8	15.3
5	.92	9.3	4.0	28	143	200	210	236	7.2	7.4	7.5	7.8	1.0	7.6	7.0	14.8
6	1.1	10	4.6	31	144	199	206	240	7.3	7.5	7.5	7.7	1.2	9.8	7.2	21.0
7	1.2	10	4.6	31	139	202	214	238	7.3	7.7	8.0	8.3	1.0	9.6	6.9	21.0
[1]8	27	118	89	238	143	184	189	217	7.2	7.6	8.0	8.4	1.7	7.5	5.6	15.3
[1]9	31	138	111	271	145	193	202	223	7.7	8.0	8.0	8.5	1.8	8.1	6.5	15.9
[2]10	.19	.41	.41	.63	214	226	214	251	7.9	7.9	7.9	7.9	7.1	13.5	14.9	18.6

[1] Streamflow statistics based on three observations.

[2] Streamflow statistics based on two observations; specific conductance, pH, and water temperature statistics based on three observations.

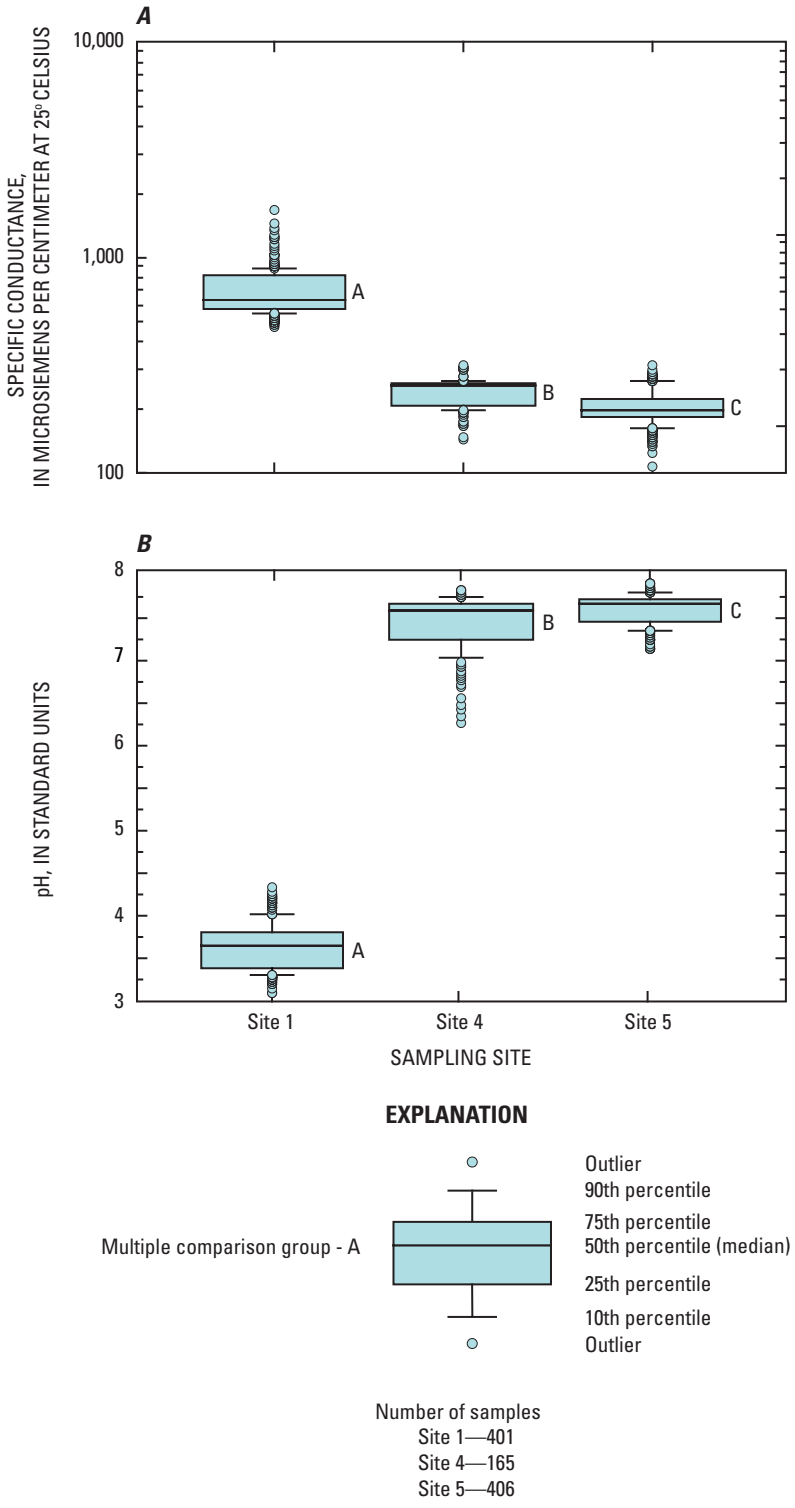

Figure 5. A comparison of daily mean (*A*) specific conductance, and (*B*) pH among the three continuously monitored sites in the Pike Hill, VT, study area.

Brook at site 1, which results in an initial decrease in specific conductance and an increase in pH (fig. 6). Overland flow and rapid infiltration through the waste rocks and tailings piles may dissolve and flush the highly soluble efflorescent sulfate salts, resulting in an increase in specific conductance and a decrease in pH (fig. 6).

Pike Hill Brook mixes with waters from tributaries as it flows downstream to site 4. Specific conductance decreases and pH increases with the dilution of constituents from an increase in streamflow in Pike Hill Brook (fig. 6). The mixing of ARD with waters of high pH may also cause the precipitation of Al and Fe hydroxides and sorption of trace metals (Lee, 2001). This may result in an initial decrease in specific conductance and an increase in pH. During the streamflow recession, the specific conductance increases to values greater than those measured prior to the event and pH decreases (fig. 6). Increases in specific conductance are likely the result of the associated increases in sulfate related to the acid generated by sulfide oxidation. Decreases in pH may result from a breakdown of the bicarbonate buffering system downstream of ARD as waters with more total acidity flow downstream following rain events, lessening the capacity of the water to buffer changes in pH (Kelly, 1988). Furthermore, oxidation of ferrous iron consumes acid, and hydrolysis of the ferric iron produces acid. Although hydrolysis of ferric iron at a pH greater than or equal to 7 standard units can take only minutes, the process may require hours as pH levels drop below 7 standard units (Haddad and Jenkins, 1984).

As streamflow increases at site 5 during rain events, the specific conductance decreases and the pH remains stable or slightly decreases (fig. 6). Over the streamflow recession following a rainfall event, the specific conductance and pH increase to levels similar to those observed prior to the event, suggesting that there is no or limited breakdown of the carbonate buffering system during rainfall events (fig. 6).

Major Ions and Trace Elements

Acute and chronic toxicity standards used in this report and the percentage of samples found exceeding the standards at eight sites and two background sites (sites 2 and 8) are listed in table 4. The acute and chronic toxicity standards for Cd, Cu, and Zn were calculated using a median hardness value from the 10 water-quality sampling sites of 98 mg/L (as $CaCO_3$). Concentrations of Al, Fe, Cd, Cu, and Zn were above acute and chronic toxicity standards at some sites, whereas no concentrations of Al, Fe, Cd, Cu, and Zn were above acute and chronic toxicity standards at background sites (table 4). Summary statistics for water-quality concentrations and instantaneous loading data are listed in tables 5 and 6, respectively. Concentrations of Al, Fe, Cd, Cu, and Zn in the stream sediments also are listed in table 5 (Piatak and others, 2006b).

Median concentrations and mean instantaneous loads are presented in the following sections. Median concentrations are presented to characterize typical concentrations and the repeated daily exposure to trace elements that may be observed at each site. Mean instantaneous loads are presented to characterize the average quantity of a trace element observed at each site and to describe the fate and transport of trace elements between sites.

A daily mean streamflow hydrograph for the data-collection period, the dates and instantaneous streamflow for the water-quality samples, and the distribution of water samples with respect to time for the three continuously monitored sites are shown in figures 7, 8, and 9. The variability in streamflow chemistry was represented by the collection of 24 water samples at site 1 (fig. 7A), 9 water samples at site 4 (fig. 8A), and 19 water samples at site 5 (fig. 9A). Because the instantaneous streamflow is used to represent the water samples, occasionally these data points do not fall on the line representing the daily mean streamflow. A cumulative frequency-duration curve showing the percentage of time that a given daily mean streamflow is expected to be equaled or exceeded, the streamflow at which water samples were collected, and the distribution of water samples across the various streamflows observed at sites 1, 4, and 5 are shown in figures 7B, 8B, and 9B, respectively. Ninety percent of the streamflows expected at sites 1 and 5 were represented by a water sample and represent the range in flow duration, except for extreme low streamflows (streamflows greater than 90^{th} percentile flow duration) (figs. 7B and 9B). Eighty percent of the streamflows expected at site 4 were represented by a water sample and represent the range in flow duration, except for extreme low streamflows (streamflows greater than 80^{th} percentile flow duration) (fig. 8B).

Sulfate and Calcium

SO_4 is derived from the oxidation of sulfide minerals and may be used to indicate the presence of ARD. Ca is derived from the weathering of carbonate minerals and can indicate additions of alkalinity and hardness to local surface waters.

The spatial distributions of median concentrations and mean instantaneous loads for SO_4 and Ca are shown in figures 10 and 11, respectively. Median concentrations of SO_4 and Ca at sites in Pike Hill Brook generally decreased with distance downstream from site 1, 3, and 4, and were similar at sites 5, 6, and 7 (figs. 10A and 11A, table 5). SO_4 concentrations at sites in Pike Hill Brook and site 10 were greater than concentrations at background sites. Ca concentrations at sites 1, 3, and 10 were greater than concentrations at background sites, whereas concentrations at sites 4, 5, 6, and 7 were similar to concentrations at background sites (table 5). The median concentrations of SO_4 and Ca at sites in the Waits River above and below the confluence with Pike Hill Brook (sites 8 and 9, respectively) were similar (table 5).

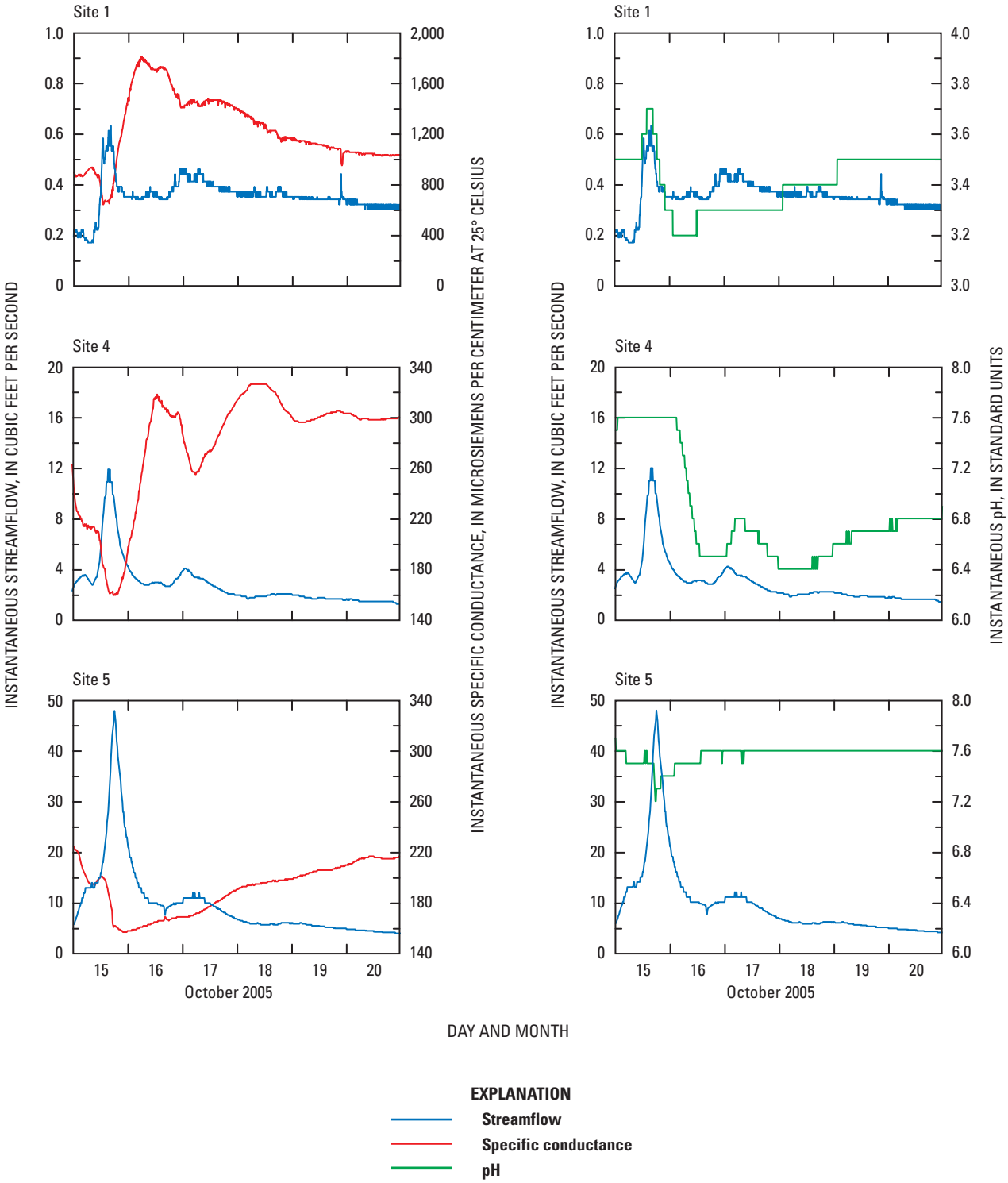

Figure 6. The typical response of instantaneous specific conductance and pH to streamflow events at the three continuously monitored sites in the Pike Hill, VT, study area.

Table 4. Summary of the U.S. Environmental Protection Agency National Recommended Water Quality Criteria for priority and non-priority pollutants and the percentage of exceedance at the Pike Hill, VT, study area.

[µg/L, micrograms per liter; acute standard, Criteria Maximum Concentration; chronic standard, Criteria Continuous Concentration. Refer to table 1 and figure 1 for site names, station numbers, and locations]

Pollutants	Acute standard (µg/L)	Percentage of samples exceeding acute toxicity standards								
		Site 1	Site 3	Site 4	Site 5	Site 6	Site 7	Site 9	Site 10	Background[1]
Priority pollutant										
Cadmium[2]	2.0	100	50	44	0	0	0	0	0	0
Copper[2]	13	100	100	78	32	25	25	0	0	0
Zinc[2]	120	100	100	56	0	0	0	0	0	0
Non-priority pollutant										
Aluminum[3]	750	100	0	0	0	0	0	0	0	0

Pollutants	Chronic standard (µg/L)	Percentage of samples exceeding chronic toxicity standards								
		Site 1	Site 3	Site 4	Site 5	Site 6	Site 7	Site 9	Site 10	Background[1]
Priority pollutant										
Cadmium[2]	0.24	100	100	100	26	25	25	0	0	0
Copper[2]	8.8	100	100	89	58	50	50	0	33	0
Zinc[2]	120	100	100	56	0	0	0	0	0	0
Non-priority pollutant										
Aluminum[3]	87	100	0	0	0	0	0	0	0	0
Iron	1,000	100	25	11	0	0	0	0	0	0

[1] Sites 2 and 8 (refer to table 1).

[2] Acute and chronic toxicity standards adjusted for hardness of 98 milligrams per liter (mg/L).

[3] Acute and chronic toxicity standards for waters with pH 6.5–9.0 and for total recoverable concentrations.

Table 5. Summary statistics for concentrations of sulfate, calcium, aluminum, iron, cadmium, copper, and zinc in water samples and a stream-sediment sample collected at sites in the Pike Hill, VT, study area.

[QW, water quality; mg/L, milligrams per liter; µg/L, micrograms per liter; min, minimum; max, maximum; <, less than; --, not calculated; %, percent; mg/kg, milligrams per kilogram. Refer to figure 1 and table 1 for site name, station number, and location]

Site number (table 1; figure 1)	Number of QW samples	Dissolved concentration															
		Sulfate (mg/L)				Calcium (mg/L)				Aluminum (Al) (µg/L)				Iron (Fe) (µg/L)			
		Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max
1	24	242	373	324	691	54.1	64.7	62.2	96.8	5,680	8,630	7,860	15,200	8,440	37,500	25,000	150,000
2	4	7.6	8.1	8.0	8.9	21.9	32.8	34.3	40.9	2	3	2	4	<50	--	<50	<50
3	4	95.0	118	106	162	36.7	44.8	45.0	52.6	10	14	14	20	<50	--	<50	18,700
4	9	31.7	56.8	51.0	97.0	26.1	36.8	37.4	45.1	<2	--	8	22	<50	--	--	2,680
5	19	7.1	16.2	14.1	32.2	14.7	27.8	29.5	39.8	2	9	8	18	<50	--	--	230
6	4	5.7	12.6	14.3	16.3	20.3	31.0	32.3	39.0	4	7	6	12	70	120	120	160
7	4	6.7	12.5	13.6	16.1	19.1	30.5	31.8	39.4	3	7	7	13	<50	--	--	110
8	4	6.0	6.8	6.5	8.0	21.9	31.5	32.3	39.5	5	11	12	16	<50	--	<50	<50
9	4	6.9	10.4	8.2	18.1	22.3	32.0	33.8	37.9	6	11	11	17	<50	--	<50	240
10	3	11.6	14.2	15.0	16.0	41.6	46.8	45.1	53.8	15	36	30	64	<50	--	<50	<50

Site number	Number of QW samples	Dissolved concentration												Stream sediment concentration[1]				
		Cadmium (Cd) (µg/L)				Copper (Cu) (µg/L)				Zinc (Zn) (µg/L)				Al	Fe	Cd	Cu	Zn
		Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max	(%)	(%)	(mg/kg)	(mg/kg)	(mg/kg)
1	24	8.11	25.6	18.8	92.8	1,940	6,900	3,720	30,800	1,870	3,230	2,670	7,340	3.03	21.5	5.8	8,070	1,070
2	4	<0.02	--	<0.02	<0.02	0.5	0.8	0.7	1.5	<0.5	--	1	2	5.76	3.36	0.5	262	134
3	4	1.61	6.40	2.54	18.9	24.0	848	38.0	3,290	247	674	380	1,690	5.08	7.64	3.2	3,530	675
4	9	.45	2.29	1.05	5.84	7.9	85.5	25.5	299	42	295	124	631	4.96	6.67	4.8	3,540	834
5	19	.08	.19	.16	.49	3.9	12.2	9.6	37.1	9	27	22	65	5.36	2.72	1.6	298	283
6	4	.09	.18	.15	.32	4.9	14.0	9.6	33.0	10	21	14	46	4.62	1.84	.9	119	191
7	4	.04	.12	.07	.28	4.3	13.0	8.0	30.0	5	16	9	40	4.29	1.4	1.4	98.1	224
8	4	<.02	--	<.02	<.02	<.5	--	<.5	0.5	<.5	--	--	3	3.8	2.04	.1	7.7	44
9	4	<.02	--	<.02	.02	.6	1.1	1.1	1.7	1	2	2	4	4.06	1.35	.1	8.0	43
10	3	.10	.13	.11	.18	3.6	6.3	4.0	11.0	13	18	15	25	4.74	2.43	1.5	539	685

[1] From Piatak and others, 2006b.

Table 6. Summary statistics of instantaneous loads of sulfate, calcium, aluminum, iron, cadmium, copper, and zinc in water samples collected at sites in the Pike Hill, VT, study area.

[min, minimum; max, maximum; <, less than. Refer to figure 1 and table 1 for site name, station number, and location]

Site number (table 1; figure 1)	Number of samples	Instantaneous load, in kilograms per day															
		Sulfate				Calcium				Aluminum				Iron			
		Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max
1	24	33.5	415	209	1,540	6.9	64.4	42.6	217	0.59	9.81	5.49	31.3	1.02	52.5	21.4	333
2	4	0.2	2.8	0.6	7.7	0.8	8.5	2.7	22.0	<.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.02
3	4	33.0	313	144	932	15.0	89.0	64.0	211	<.01	.03	.02	.06	.01	27.0	.03	108
4	9	26.9	325	137	935	24.3	174	89.2	469	.01	.03	.02	.06	.01	6.72	.05	48.2
5	19	18.0	411	271	1,570	89.6	682	464	2,560	.02	.42	.11	3.14	.06	1.60	.82	9.42
6	4	15.0	384	156	1,210	105	594	369	1,530	.01	.27	.08	.93	.29	3.05	1.08	9.75
7	4	20.0	366	152	1,140	116	569	358	1,440	.02	.28	.07	.97	.07	2.39	.51	8.47
8	3	525	1,800	1,370	3,490	2,220	7,230	6,710	12,760	.31	3.27	2.75	6.76	1.64	7.22	5.45	15.0
9	3	714	4,860	1,870	12,000	2,720	8,680	8,530	14,790	.44	3.62	3.26	7.16	1.88	28.0	17.0	66.0
10	2	7.4	15.0	15.0	23.0	21.0	43.0	43.0	64.0	.01	.05	.05	.10	.01	.02	.02	.04

Site number	Number of samples	Instantaneous load, in kilograms per day											
		Cadmium				Copper				Zinc			
		Min	Mean	Median	Max	Min	Mean	Median	Max	Min	Mean	Median	Max
1	24	0.001	0.035	0.014	0.182	0.19	10.5	2.38	68.4	0.22	3.84	1.78	15.4
2	4	<.001	<.001	<.001	<.001	<.01	<0.01	<0.01	<0.01	<.01	<0.01	<0.01	<0.01
3	4	.001	.029	.004	.109	.01	4.76	.06	19.0	.08	2.72	.54	9.72
4	9	<.001	.022	.004	.105	.01	1.10	.05	5.32	.05	2.58	.49	9.75
5	19	<.001	.006	.002	.032	.02	.49	.16	2.46	.02	.85	.46	4.28
6	4	<.001	.007	.002	.024	.02	.67	.11	2.46	.03	.95	.17	3.45
7	4	<.001	.006	.001	.021	.02	.62	.09	2.27	.01	.81	.11	3.01
8	3	<.001	.003	.002	.006	.02	.07	.05	.15	.02	.15	.13	.29
9	3	<.001	.006	.005	.013	.04	.51	.35	1.13	.08	1.12	.90	2.39
10	2	<.001	<.001	<.001	<.001	<.01	.01	.01	.02	.01	.02	.02	.04

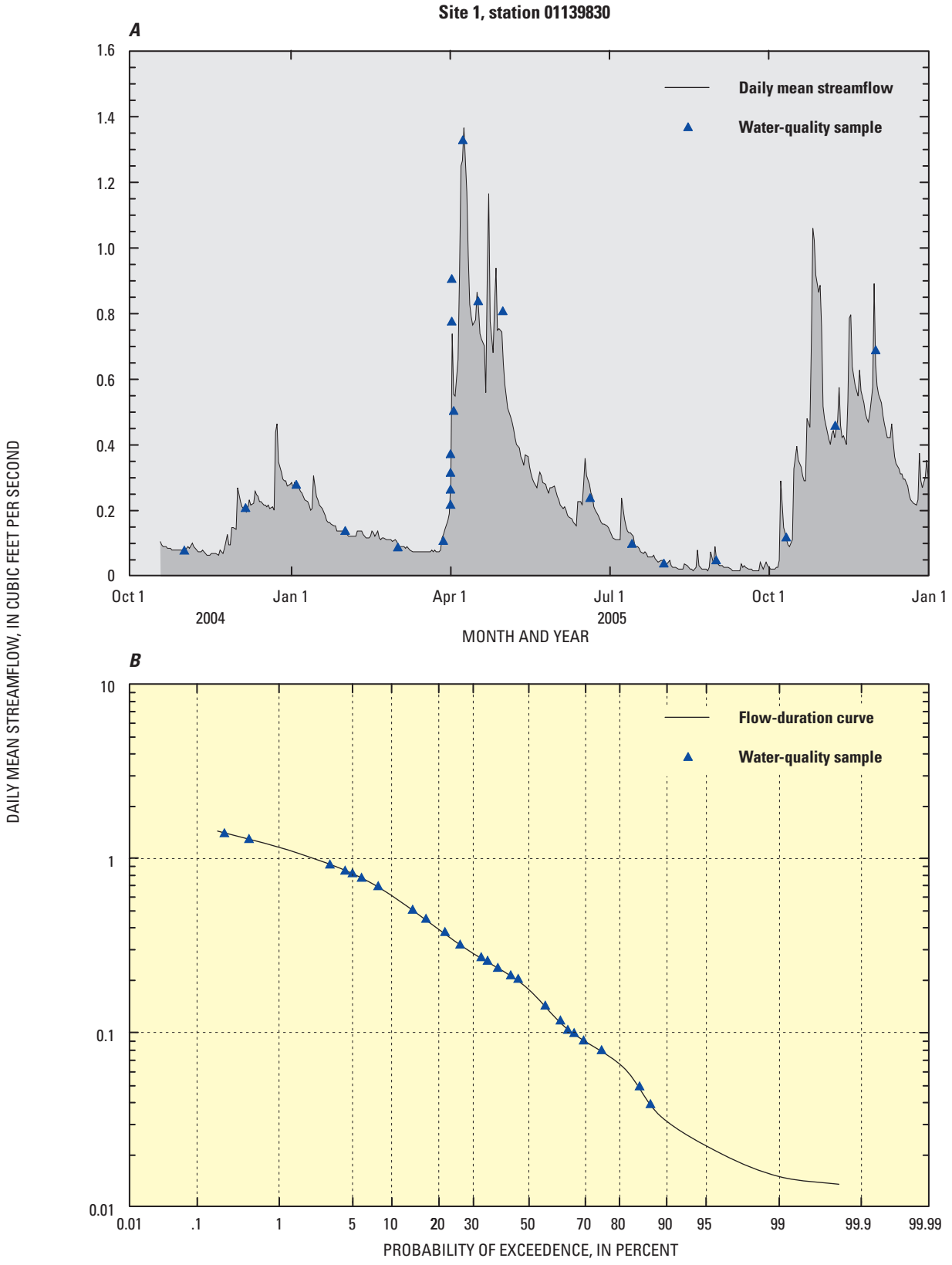

Figure 7. (*A*) Daily mean streamflow and time distribution of water-quality samples, and (*B*) flow-duration curve with streamflow distribution of water-quality samples for Pike Hill Brook above Richardson Road near Bradford, VT, station 01139830, site 1.

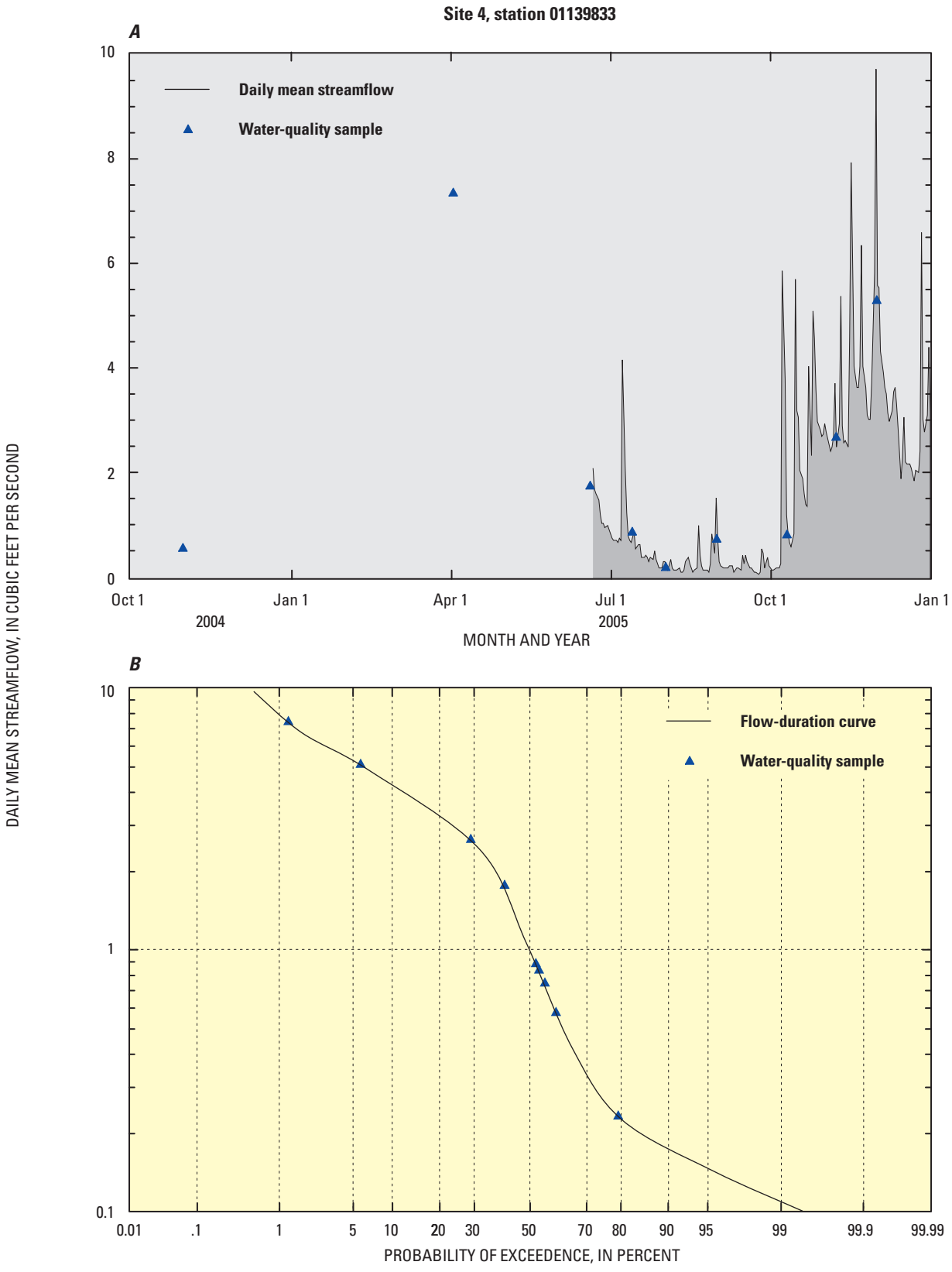

Figure 8. (*A*) Daily mean streamflow and time distribution of water-quality samples, and (*B*) flow-duration curve with streamflow distribution of water-quality samples for Pike Hill Brook at Pike Hill Road, west crossing, near Bradford, VT, station 01139833, site 4.

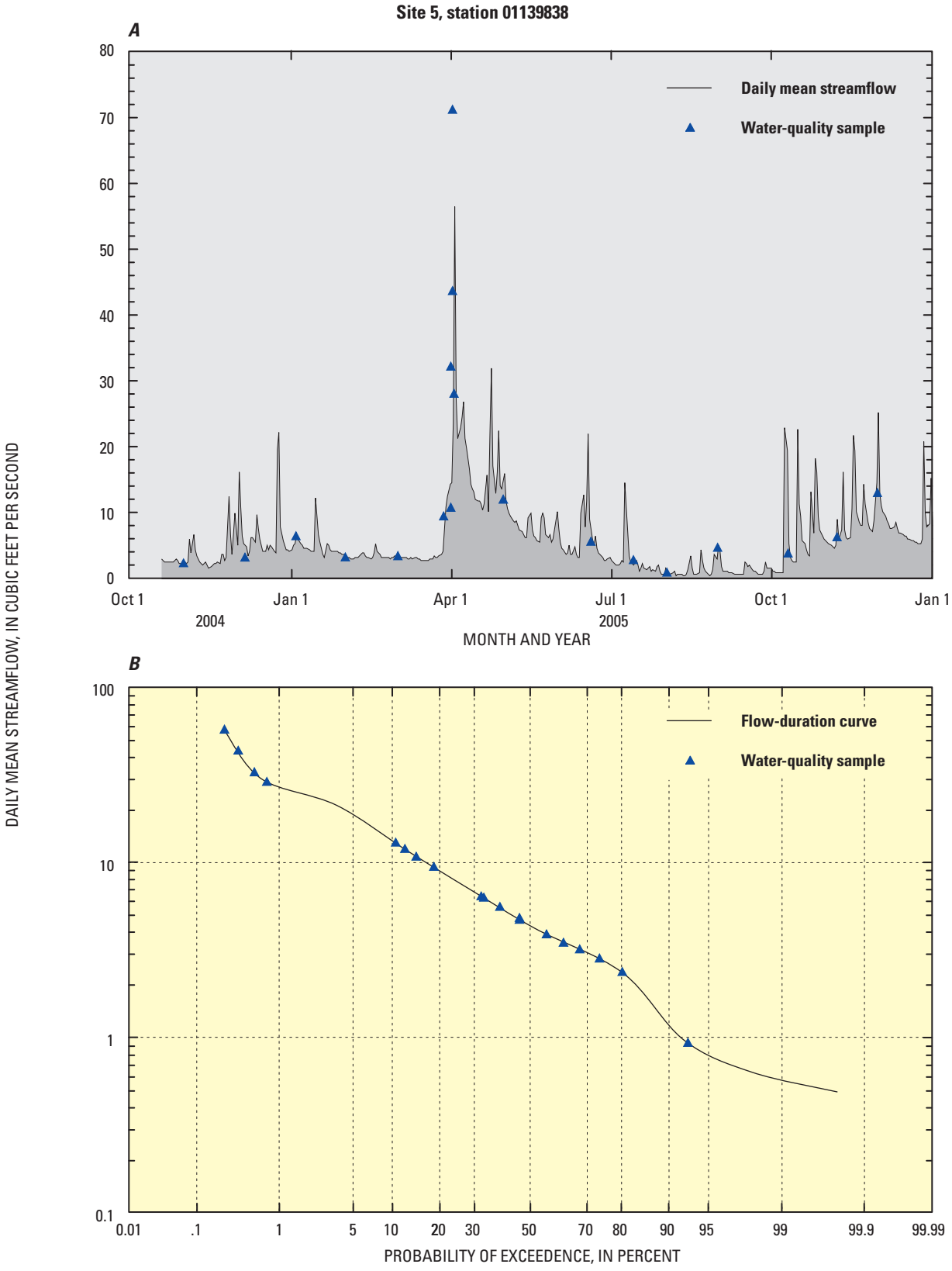

Figure 9. (*A*) Daily mean streamflow and time distribution of water-quality samples, and (*B*) flow-duration curve with streamflow distribution of water-quality samples for Pike Hill Brook at Pike Hill Road near Bradford, VT, station 01139838, site 5.

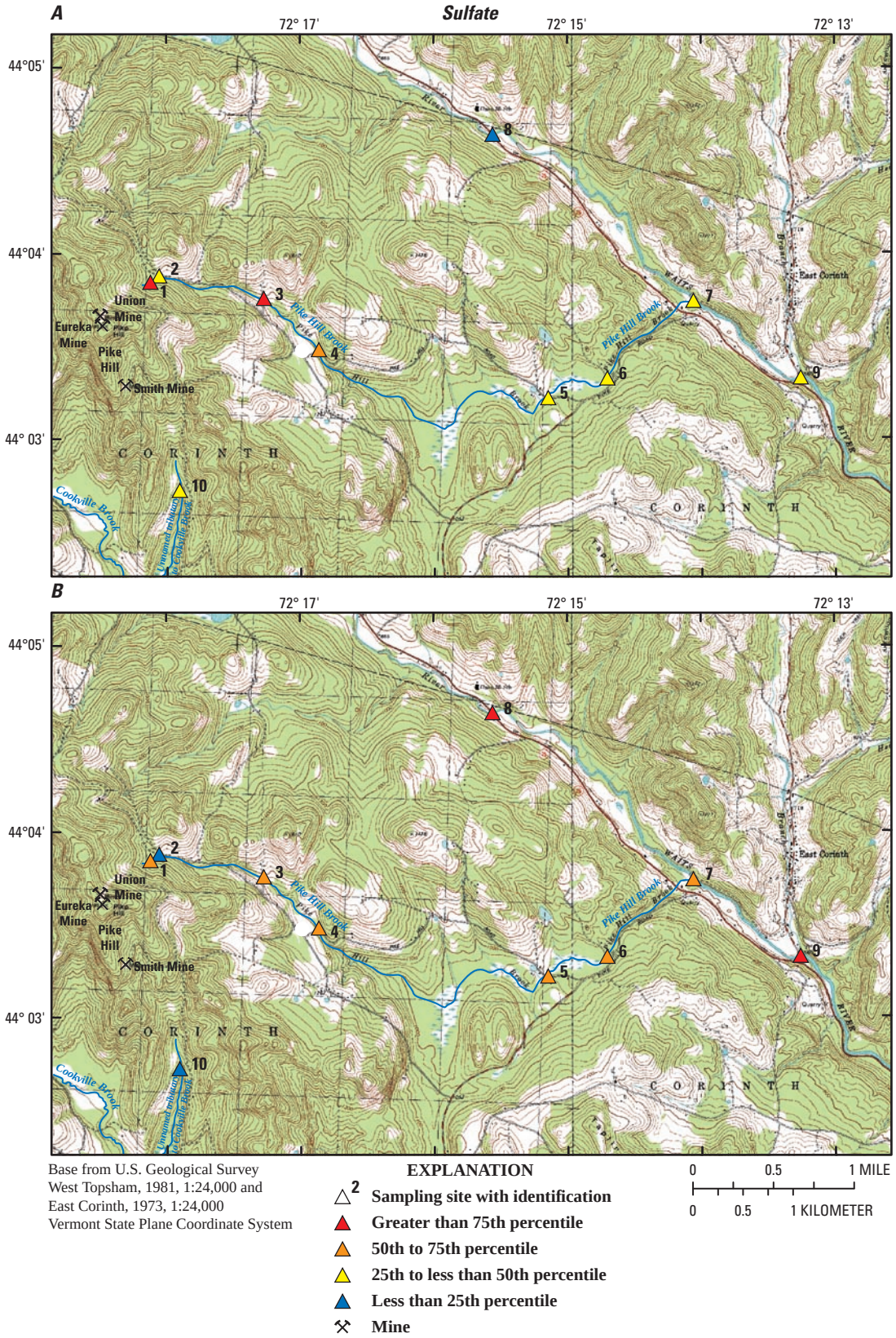

Figure 10. (*A*) Median concentrations of sulfate, and (*B*) mean instantaneous loads of sulfate in relation to percentiles of the data at synoptic sampling sites in the Pike Hill, VT, study area.

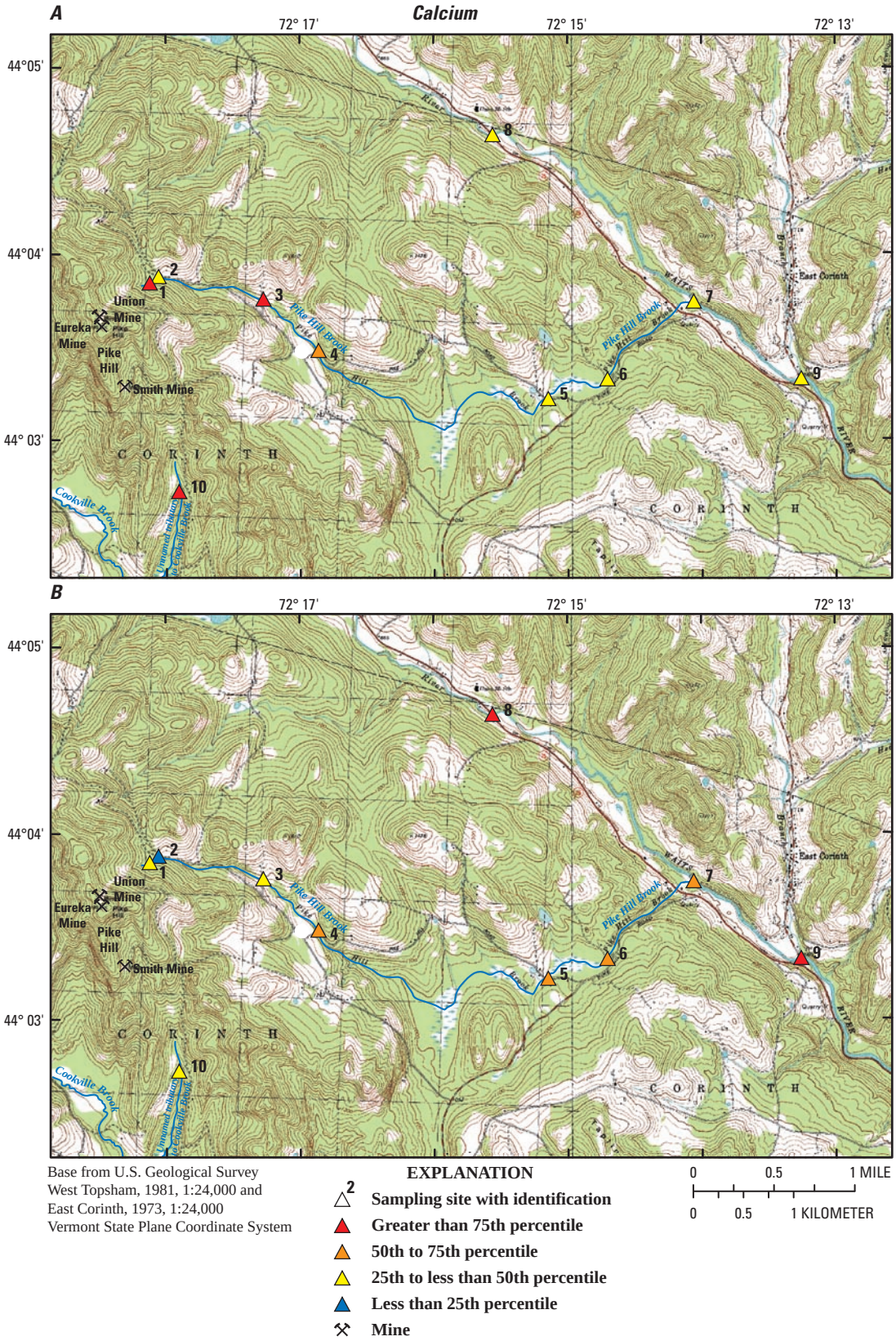

Figure 11. (*A*) Median concentrations of calcium, and (*B*) mean instantaneous loads of calcium in relation to percentiles of the data at synoptic sampling sites in the Pike Hill, VT, study area.

Instantaneous SO_4 loads at sites in Pike Hill Brook were similar with distance downstream from site 1 (fig. 10B, table 6), whereas instantaneous Ca loads at sites in Pike Hill Brook generally increased with distance downstream from site 1 (fig. 11B, table 6). The mean instantaneous load of SO_4 at site 10 generally was less than those at sites in Pike Hill Brook, whereas the mean instantaneous Ca load at site 10 was similar to those at sites 1 and 3 and less than at sites 4, 5, 6, and 7 (fig. 10B, table 6). The mean instantaneous SO_4 and Ca loads at site 9 were greater than those at site 8 (table 6).

A statistical analysis of SO_4 and Ca concentrations among the three continuously monitored sites showed significant differences in the data ($p<0.05$) (fig. 12A and 12C). Mean instantaneous loads of SO_4, however, decreased from site 1 (415 kg/d) to site 4 (325 kg/d) and increased from site 4 to site 5 (411 kg/d) (table 6) but were not significantly different among the three sites ($p>0.05$) (fig. 12B). This similarity indicated that dilution was affecting the change in concentrations of SO_4 in Pike Hill Brook. Instantaneous loads of Ca were significantly different among the three sites ($p<0.05$) (fig. 12D). The considerable increase in Ca loads between sites, in a downstream direction (table 6), probably resulted from an influx of Ca with the increase in streamflow.

Aluminum and Iron

Al and Fe are considered non-priority pollutants by the USEPA. Al and Fe sorb to particulates and precipitate out of the water column as Al and Fe hydroxides, as the pH of ARD increases. The critical pH for Al precipitation is about 5.2 standard units, whereas the critical pH for Fe precipitation is about 4.3 standard units (Kelly, 1988).

Concentrations of Al and Fe for 24 water-quality samples (100 percent) at site 1 were greater than the NRWQC standards for acute and chronic toxicity (table 4). The NRWQC standards for Al are based on the total concentration and on a pH range of 6.5 to 9.0, which is a higher pH range than that observed at site 1. Chronic toxicity standards were exceeded in one high streamflow sample for Fe at sites 3 and 4 (table 4). No sample concentrations of Al or Fe exceeded toxicity standards at background sites or sites 5, 6, 7, 9, and 10. Sample concentrations of Al and Fe at background sites generally were lower than those observed at other synoptic sites (table 5).

The spatial distribution of median concentrations and mean instantaneous loads for Al is shown in figure 13. The median concentration of Al at each site is shown relative to the NRWQC. The mean instantaneous loads at each site are shown in relation to percentiles of the observed loads for all synoptic samples. Percentiles, in this usage, are the percentage of the observed constituent loads that were equal to or smaller than the mean constituent load at each site.

Concentrations of Al and Fe differed in magnitude but were positively correlated (rho = 0.92, $p<0.0001$) and showed similar patterns in relation to streamflow. Concentrations of Al and Fe varied considerably among sites in Pike Hill Brook (table 5). Median concentrations of Al and Fe were greatest at site 1 and generally decreased with distance downstream from site 1. Median Fe concentrations, however, were greater at sites below the wetlands (sites 5, 6, and 7) than at sites 3 and 4 (table 5). Median Al concentrations at site 10 were greater than those in Pike Hill Brook downstream from site 1 (table 5). Concentrations of Fe at site 10 were below the detection limit of 50 µg/L for all streamflows sampled. Median Al concentrations at sites in the Waits River (sites 8 and 9) were similar to those in Pike Hill Brook downstream from site 1 (table 5).

The mean instantaneous Al and Fe loads generally decreased with distance between site 1 and site 4 and increased with distance between site 4 and site 6. Instantaneous Al loads increased in Pike Hill Brook downstream from site 4 during high flow, whereas instantaneous Fe loads increased in Pike Hill Brook downstream from site 4 during normal and low flows. The mean instantaneous Al loads at site 10 were similar to those at site 3 in Pike Hill Brook (table 6). The mean instantaneous Al and Fe loads in the Waits River below the confluence with Pike Hill Brook (site 9) were greater than those above the confluence with Pike Hill Brook (site 8) (table 6).

Concentrations and instantaneous loads of Al and Fe among the three continuously monitored sites were tested to determine if there were statistically significant differences in the data. Concentrations of Al and Fe were significantly greater at site 1 than at sites 4 and 5 ($p<0.05$) but were not significantly different between sites 4 and 5 ($p>0.05$) (figs. 14A and 14C, table 5). Concentrations of Fe, however, ranged from less than 50 to 2,680 µg/L at site 4 and ranged from less than 50 to 230 µg/L at site 5 (table 5). Instantaneous loads of Al were significantly different among the three continuously monitored sites ($p<0.05$) (fig. 14B) as mean instantaneous loads of Al decreased from site 1 (9.81 kg/d) to site 4 (0.03 kg/d) and increased from site 4 to site 5 (0.42 kg/d) (table 6). Instantaneous loads of Fe were significantly different between sites 1 and 4 and between sites 1 and 5 ($p<0.05$) but did not differ between sites 4 and 5 ($p>0.05$) (fig. 14D).

Concentrations of Al and Fe decreased with distance from site 1 as the result of dilution and through sorption and precipitation of the trace elements. These constituents were sorbed and precipitated as ARD became diluted with waters of high pH between sites 1 and 4. This dilution resulted in the sorption of trace elements to hydroxides formed from Al and Fe (Kelly, 1988). Instantaneous loads for dissolved Al and Fe decreased by 1 to 3 orders of magnitude between sites 1 and 4, most likely the result of sorption and precipitation with an increase in pH. Instantaneous Al loads increased between sites 4 and 5 during high streamflows, whereas instantaneous Fe loads increased between sites 4 and 5 during low and normal streamflows. The increase in Al loads probably resulted from an influx of Al from tributaries entering Pike Hill Brook. The increased Fe loads probably resulted from the dissolution of Fe hydroxides in the anaerobic areas of the wetlands.

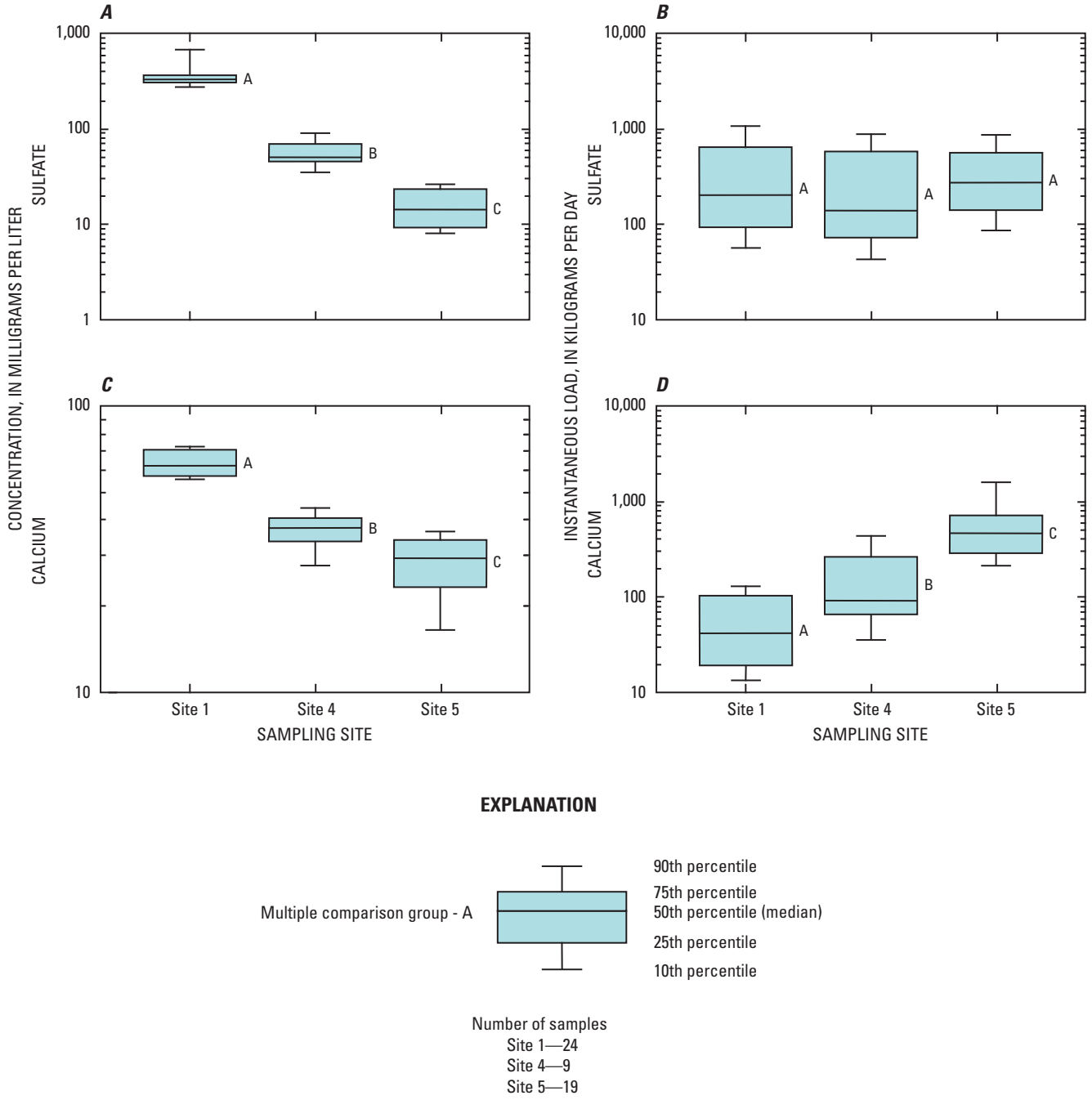

Figure 12. A comparison of (*A*) concentrations of sulfate, (*B*) instantaneous loads of sulfate, (*C*) concentrations of calcium, and (*D*) instantaneous loads of calcium among the three continuously monitored sites in the Pike Hill, VT, study area.

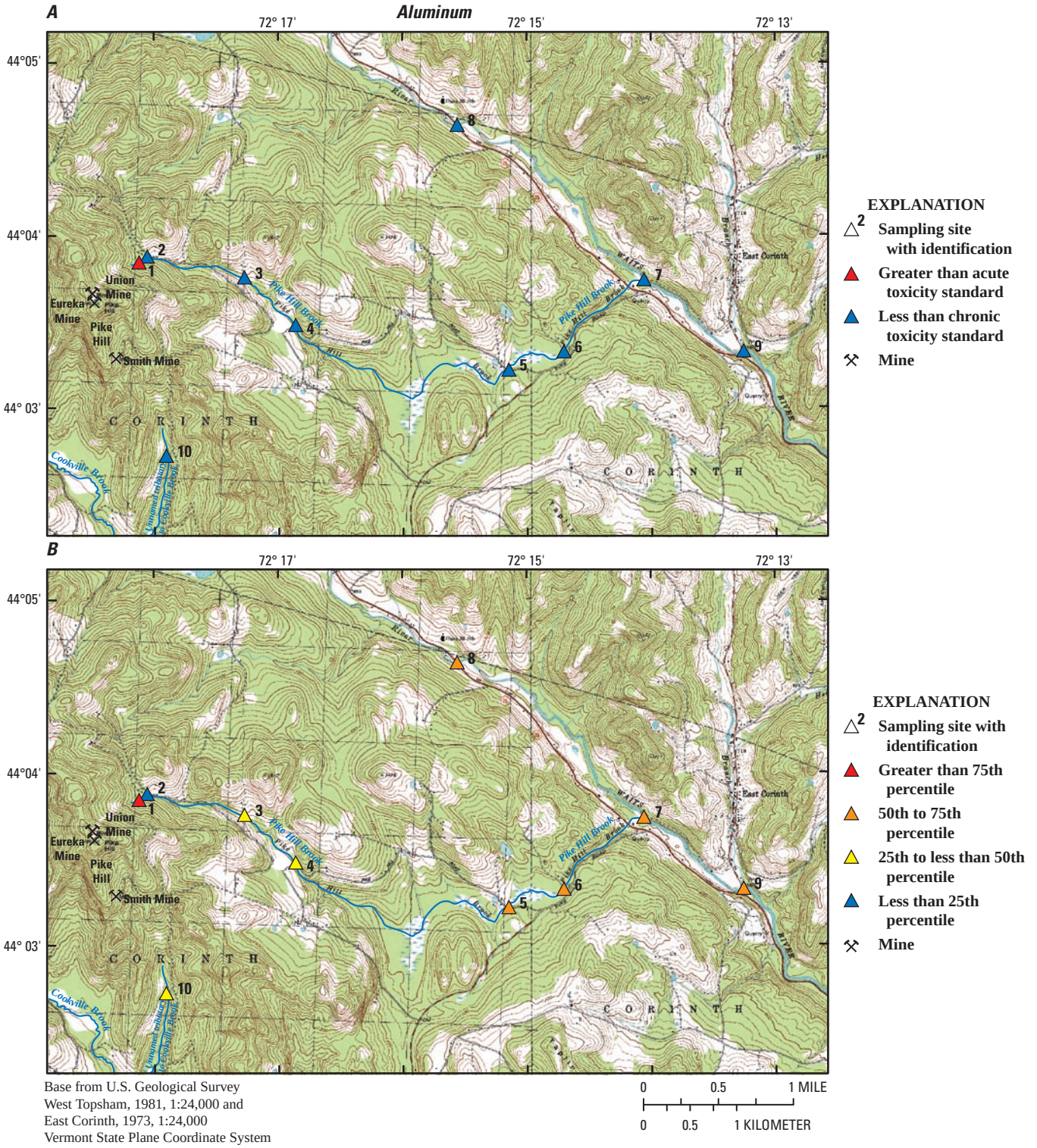

Figure 13. (*A*) Median concentrations of aluminum in relation to U.S. Environmental Protection Agency National Recommended Water Quality Criteria, and (*B*) mean instantaneous loads of aluminum in relation to percentiles of the data at synoptic sampling sites in the Pike Hill, VT, study area.

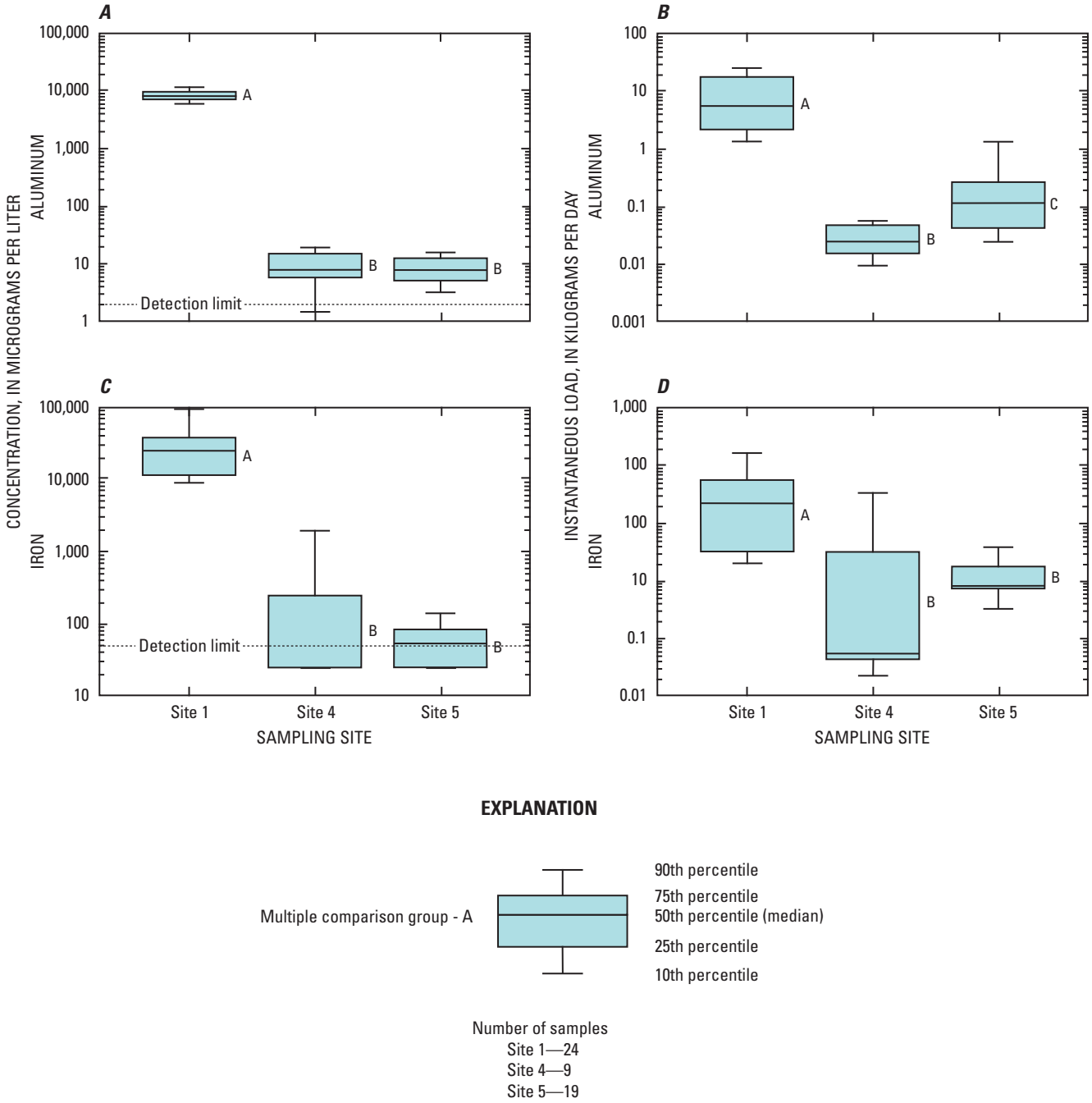

Figure 14. A comparison of (*A*) concentrations of aluminum, (*B*) instantaneous loads of aluminum, (*C*) concentrations of iron, and (*D*) instantaneous loads of iron among the three continuously monitored sites in the Pike Hill, VT, study area.

Kelly (1988) showed that the deep mixing of oxygen in water bodies caused adsorption of trace elements to the sediments. These trace elements may be desorbed during periods of anaerobic activity, which was expected during low streamflows.

Cadmium, Copper, and Zinc

Cd, Cu, and Zn are toxic to aquatic life and are considered priority pollutants by the USEPA. Cd, Cu, and Zn are removed from waters by precipitation and sorption, especially with hydroxides formed from Al and Fe (Kelly, 1988), can then settle out of the water column, or be transported downstream depending upon water velocity.

Concentrations of Cd, Cu, and Zn for all water samples at site 1 were greater than the NRWQC standards for acute and chronic toxicity (table 4). Concentrations of Cd exceeded acute toxicity criteria at sites 1, 3, and 4 during high flow, at sites 1 and 3 during normal flow, and at site 1 during low flow. Concentrations of Cd exceeded chronic toxicity criteria at all sites on Pike Hill Brook during high flow and at sites 1, 3, and 4 during normal and low flows. Concentrations of Cu exceeded acute toxicity criteria at all sites on Pike Hill Brook during high flow, at sites 1, 3, 4, and 5 during normal flow, and at sites 1 and 3 during low flow. Concentrations of Cu exceeded chronic toxicity criteria at all sites on Pike Hill Brook during high and normal flows, at site 10 during normal flows, and at sites 1, 3, and 4 during low flows. Concentrations of Zn exceeded acute and chronic toxicity criteria at sites 1, 3, and 4 during high flow conditions and at sites 1 and 3 during normal and low flow conditions. No concentrations of Cd, Cu, or Zn exceeded toxicity standards at background sites or site 9.

The spatial distribution of median concentrations and mean instantaneous loads for Cd and Cu is shown in figures 15 and 16. The median concentrations of Cd and Cu at each site are shown relative to the NRWQC. The mean instantaneous loads at each site are shown in relation to percentiles of the observed loads for all synoptic samples. Percentiles, in this usage, are the percentage of the observed constituent loads that were equal to or smaller than the mean constituent load at each site.

Concentrations of Cd and Zn differed in magnitude but were positively correlated (rho = 0.99, $p<0.0001$) and showed similar patterns in relation to streamflow. Cd, Cu, and Zn concentrations and instantaneous loads at sites in Pike Hill Brook (sites 1, 3, 4, 5, 6, and 7) generally decreased with distance downstream from site 1 (table 5). The median Cd and Zn concentrations at site 10 were similar to those in Pike Hill Brook at sites 5, 6, and 7, whereas the median Cu concentration at site 10 was less than those at sites in Pike Hill Brook (table 5). Concentrations of Cd in the Waits River (sites 8 and 9) were equal to or below the detection limit of 0.2 µg/L for all streamflows sampled (table 5). The median Cu and Zn concentrations in the Waits River below the confluence with Pike Hill Brook (site 9) were greater than those above the confluence with Pike Hill Brook (site 8) (table 5).

Mean instantaneous loads of Cd, Cu, and Zn at sites in Pike Hill Brook (sites 1, 3, 4, 5, 6, and 7) generally decreased with distance downstream from site 1 (figs. 15B and 16B, table 6). Median Cu loads in Pike Hill Brook, however, increased with distance from site 4 to site 5 (table 6). Instantaneous Cd, Cu, and Zn loads at site 10 were lower than those observed at sites in Pike Hill Brook for all streamflows sampled (table 6). Mean instantaneous Cd, Cu, and Zn loads in the Waits River below the confluence with Pike Hill Brook (site 9) were greater than those above the confluence with Pike Hill Brook (site 8) (table 6).

A statistical analysis of concentrations of Cd, Cu, and Zn among the three continuously monitored sites showed significant differences among the three sites ($p<0.05$) (fig. 17). Instantaneous loads of Cd and Zn, however, were significantly different between sites 1 and 5 ($p<0.05$) but not significantly different between sites 1 and 4 or between sites 4 and 5 ($p>0.05$) (fig. 17). Instantaneous loads of Cu were significantly different between sites 1 and 4 and between sites 1 and 5 ($p<0.05$) but did not differ between sites 4 and 5 ($p>0.05$) (fig. 17).

Concentrations of Cd, Cu, and Zn decreased with distance from site 1 as the result of dilution and through sorption and precipitation of the trace elements. These constituents were sorbed and precipitated as ARD became diluted with waters of high pH between sites 1 and 4. Sorbed trace elements settled out of the water column or were transported downstream as the result of a decrease in water velocity between sites 4 and 5. Instantaneous loads for dissolved Cu decreased by two orders of magnitude between sites 1 and 4, most likely the result of sorption and precipitation with an increase in pH. Instantaneous loads of Cd and Zn, however, were similar between sites 1 and 4. This similarity indicated that dilution is affecting the change in concentrations of Cd and Zn between sites 1 and 4 and that Cu was sorbed to Al and Fe hydroxides. Similarly to instantaneous loads of Fe, instantaneous loads of Cu increased between sites 4 and 5 during low and normal streamflows, probably resulting from the dissolution of Fe hydroxides in anaerobic areas of the wetlands.

Effects of Spring Rains and Snowmelt on Constituent Concentrations and Loads

Samples collected at sites 1 and 5 in late March and early- to mid-April were used to describe the effects of spring rains and snowmelt on constituent concentrations and loads. The distribution of Cu and Zn concentrations over time at sites 1 and 5 is shown in figure 18. Although the magnitude of concentrations was different, the changes in Cu concentration relative to changes in streamflow were similar to those of SO_4 and Fe concentrations, whereas changes in Zn concentrations relative to changes in streamflow were similar to those of Al and Cd concentrations. Therefore, concentrations of Cu and Zn were used to describe the patterns for the constituents during spring rains and snowmelt in the following sections.

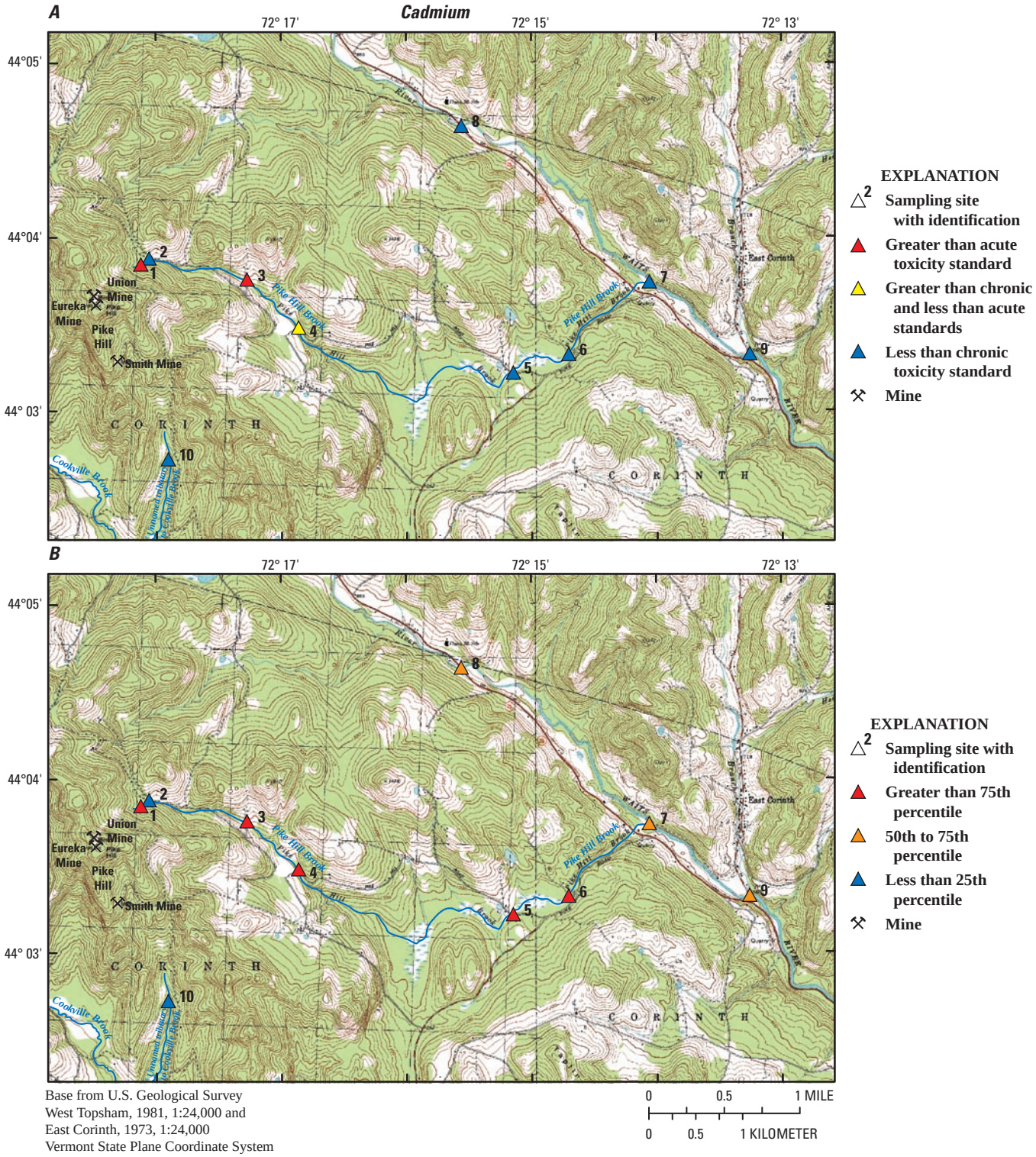

Figure 15. (*A*) Median concentrations of cadmium in relation to U.S. Environmental Protection Agency National Recommended Water Quality Criteria, and (*B*) mean instantaneous loads of cadmium relative to percentiles of the data at synoptic sampling sites in the Pike Hill, VT, study area.

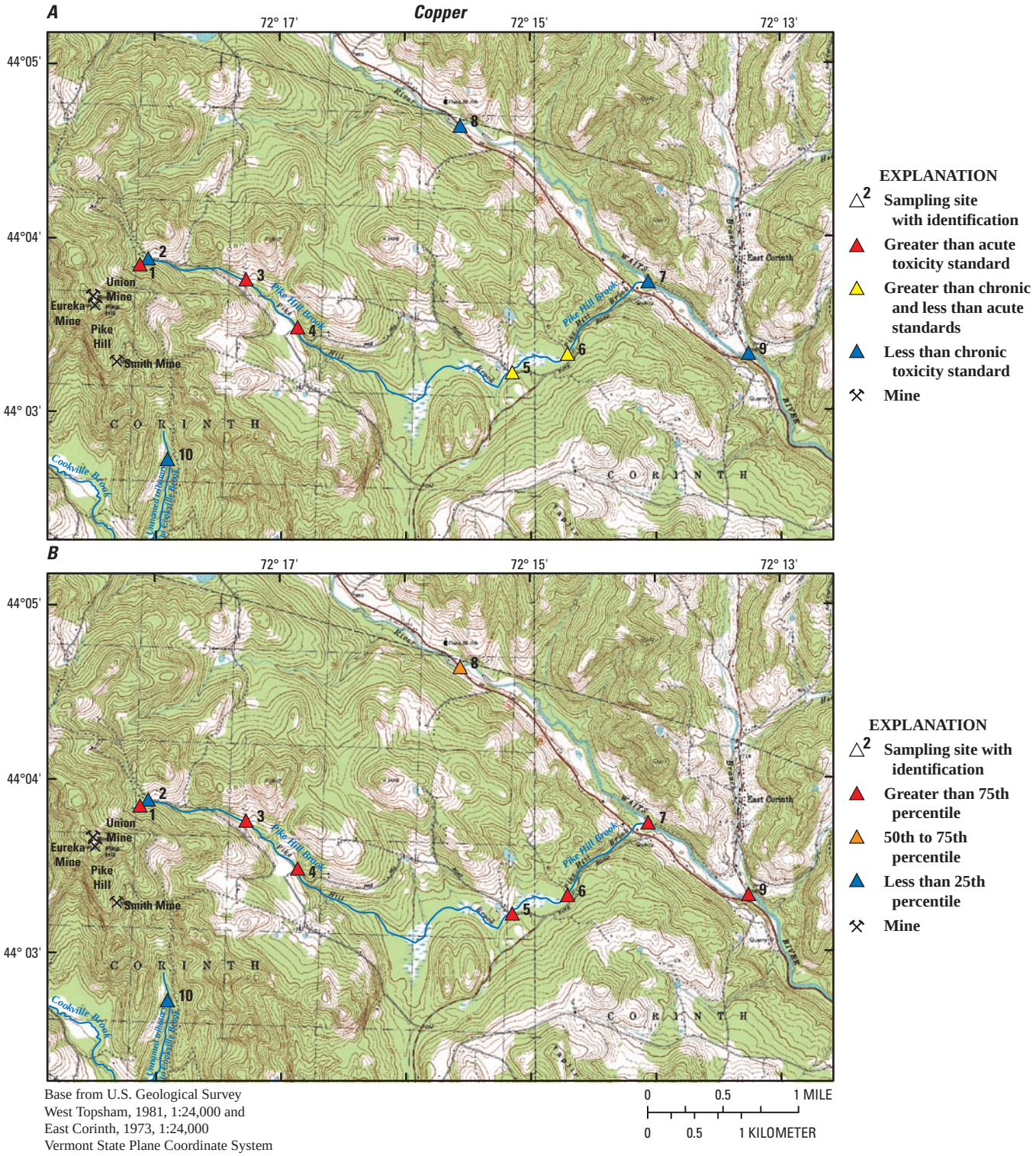

Figure 16. (*A*) Median concentrations of copper in relation to U.S. Environmental Protection Agency National Recommended Water Quality Criteria, and (*B*) mean instantaneous loads of copper relative to percentiles of the data at synoptic sampling sites in the Pike Hill, VT, study area.

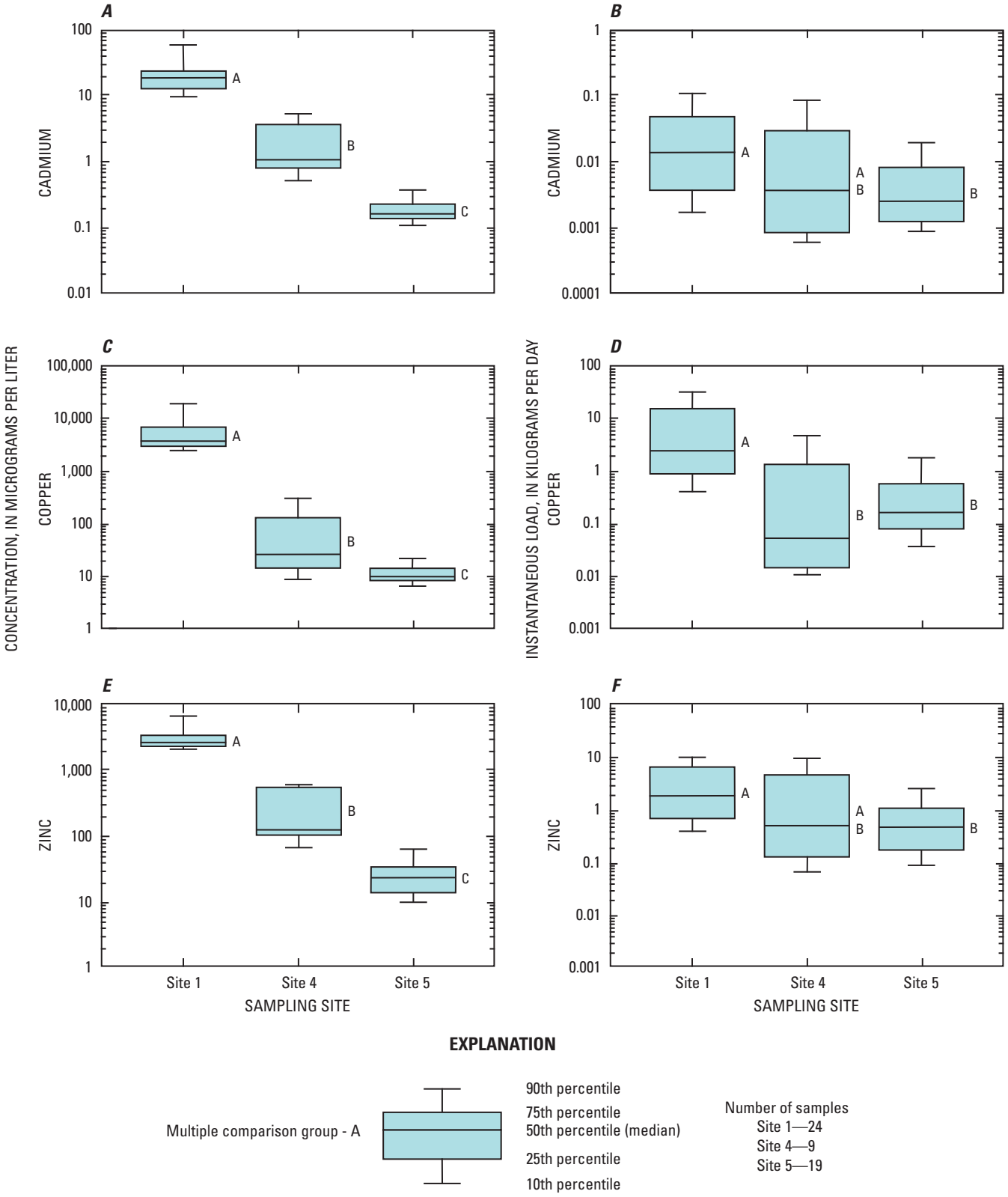

Figure 17. A comparison of (*A*) concentrations of cadmium, (*B*) instantaneous loads of cadmium, (*C*) concentrations of copper, (*D*) instantaneous loads of copper, (*E*) concentrations of zinc, and (*F*) instantaneous loads of zinc among the three continuously monitored sites in the Pike Hill, VT, study area.

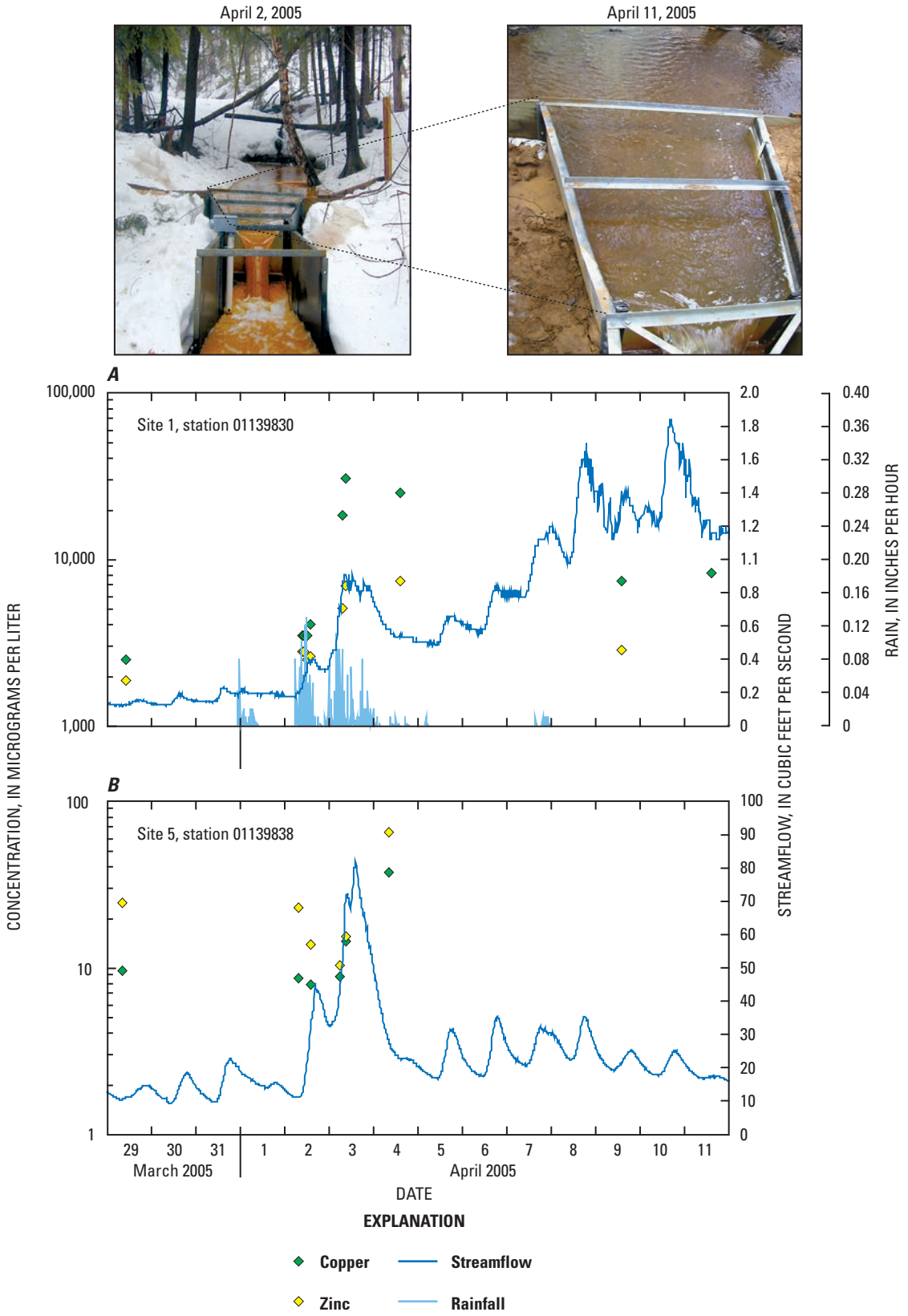

Figure 18. Streamflow conditions at site 1 during early snowmelt and rain (April 2, 2005) and snowmelt (April 11, 2005), and graphs showing the distribution of concentrations of copper and zinc in relation to maximum streamflows resulting from early snowmelt and rain (April 2 to 4, 2005), and from snowmelt (April 5 to 11, 2005) at (*A*) Pike Hill Brook above Richardson Road near Bradford, VT, station 01139830, site 1; and (*B*) Pike Hill Brook at Pike Hill Road near Bradford, VT, station 01139838, site 5.

Concentrations of Cu and Zn in relation to the instantaneous streamflow at site 1 from March 29, 2005 to April 11, 2005 are graphically shown in figure 18A. Hourly rain totals recorded at USGS streamflow-gaging station 01139800 East Orange Branch at East Orange, VT, are also shown in figure 18A. Concentrations of Cu and Zn in relation to the instantaneous streamflow at site 5 from March 29, 2005 to April 11, 2005 are graphically shown in figure 18B.

Samples were collected on March 29, 2005 to document conditions before the spring snowmelt. Samples were collected on April 2 and 3, 2005 to document conditions during the rise in streamflow resulting from early spring snowmelt and rain. Samples were collected on April 4, 2005 to document conditions during the recession in streamflow. Samples were collected at site 1 on April 9 and 11, 2005 to document conditions during the rise in streamflow resulting from snowmelt only.

At sites 1 and 5, the maximum concentrations of Al, Fe, Cd, Cu, and Zn were observed during the early spring rains and snowmelt (April 3 and 4, 2005). At site 1 the maximum concentrations were not at the maximum streamflow sampled, whereas at site 5 the maximum concentrations were at the maximum streamflow sampled (fig. 18). Samples collected at high streamflows at site 1 (April 9 and 11, 2005) had lower concentrations of trace elements than those observed during early spring rains and snowmelt, most likely the result of flushing of the efflorescent sulfate salts from the waste rock during early spring snowmelt and rains and dilution from snowmelt during high streamflows. Maximum concentrations of SO_4, Fe, and Cu were observed during the maximum streamflow sampled on April 3, 2005, whereas the maximum Al, Cd, and Zn concentrations were observed during the recession in streamflow on April 4 for site 1. Early spring rains probably flushed the mine wastes and pooled mine waters, thus increasing the trace-element concentrations in Pike Hill Brook. The difference in timing for the maximum observed Al and Fe concentrations at site 1 was likely the result of changes in pH and its effects on the precipitation of these elements. The timing of the maximum concentrations of Cd, Cu, and Zn at site 1 may be related to the order of adsorption or desorption to Fe hydroxides with changes in pH. The timing of the maximum observed concentrations of Al, Cd, Cu, Fe, Zn, and SO_4 at site 5 may reflect the travel time required for waters from site 1 to reach site 5.

Measured and Estimated Constituent Concentrations and Loads

Concentrations of SO_4, Ca, Al, Fe, Cd, Cu, and Zn at site 1 and Ca at sites 4 and 5 were estimated using multiple linear regressions. Regression equations were developed using streamflow, specific conductance, pH, and water temperature as variables to estimate concentrations of SO_4, Ca, Al, Fe, Cd, Cu, and Zn at site 1. The regression equations are listed in table 7. In general, the estimated concentrations were similar to the measured concentrations (fig. 19). The R^2 for the regression equations ranged from 0.82 to 0.96, whereas the MSE for regression equations ranged from 0.031 to 0.17 (table 7).

The regression analysis was applied to the continuous water-quality data recorded at site 1 to compute estimated daily mean concentrations of SO_4, Ca, Al, Fe, Cd, Cu, and Zn, and at sites 4 and 5 to compute estimated daily mean concentrations of Ca (fig. 20, table 8). All estimated Al, Cd, Cu, and Zn concentrations were above acute and chronic toxicity standards. All estimated Fe concentrations were above chronic toxicity standards.

Seasonal and annual loads were estimated for SO_4, Ca, Al, Fe, Cd, Cu, and Zn at site 1 using the estimated daily mean concentrations and the daily mean streamflow record. Seasonal and annual loads were estimated at site 5 using LOADEST for the dissolved and total SO_4, Al, Fe, Cd, Cu, and Zn phases and using the estimated daily mean concentrations and daily mean streamflow record for Ca. Summer and fall loads were estimated at site 4 using LOADEST for the dissolved and total SO_4, Al, Fe, Cd, Cu, and Zn phases and using the estimated daily mean concentrations and daily mean streamflow record for Ca. The LOADEST regression equations are listed in table 9. Annual loads were estimated for the period of January to December 2005.

Annual loads for dissolved SO_4 and Ca were greater at site 5 than at site 1 (fig. 21, table 10). The ratio of total to dissolved annual loads was about 1 for Al, Cd, Cu, and Zn at site 1 (table 10). Annual loads for dissolved Al and Fe were greater at site 1 than at site 5 (fig. 20, table 10). Annual loads for total Al, however, were similar at sites 1 and 5, whereas the annual loads for total Fe were greater at site 1 than at site 5 (fig. 21, table 10). Annual loads for dissolved Cd and Zn at site 1 were about four to five times greater than at site 5, whereas the annual load for dissolved Cu at site 1 was about seventeen times greater than at site 5 (fig. 21, table 10). Annual loads for total Cd and Zn at site 1 were about three times greater than at site 5, whereas the annual load for total Cu at site 1 was about six times greater than at site 5.

Dissolved and total loads for SO_4, Ca, Al, Fe, Cd, Cu, and Zn varied seasonally. Minimum seasonal loads were estimated for the summer except for dissolved Al at site 5, which was estimated for the winter (fig. 21, table 10). The maximum seasonal loads were estimated for the spring and fall except for SO_4 at site 5, which was estimated for the winter (fig. 21, table 10). The ratio of dissolved to total loads at site 5 for Al, Fe, Cd, Cu, and Zn sharply decreased during the spring relative to the other seasons. Dissolved SO_4 loads increased from site 1 to 4 and decreased from site 4 to site 5 during the summer and fall (fig. 21, table 10). An increase in dissolved loads was estimated from site 4 to site 5 for the summer and fall for Al and for the summer for Fe. Total Al and Fe loads, however, decreased with distance from site 1 during the summer and fall (fig. 21, table 10). Total and dissolved Cd, Cu, and Zn loads generally decreased with distance from site 1 during the summer and fall (fig. 21, table 10).

Table 7. Regression equations for estimating concentrations of sulfate, calcium, aluminum, iron, cadmium, copper, and zinc at the three continuously monitored sites in the Pike Hill, VT, study area.

[MSE, mean square error; R^2, coefficient of determination; *SC*, specific conductance; *Q*, streamflow; *Temp*, water temperature; log, logarithm. Location for sites is shown on figure 1]

Constituent	Phase	Equation	MSE	R^2
Concentration		Pike Hill Brook above Richardson Road near Bradford, VT (station 01139830, site 1)		
Sulfate (SO_4)	Dissolved	$\log_{10}(SO_4) = 1.12\log_{10}(SC) - 0.683$	0.033	0.94
Calcium (*Ca*)	Dissolved	$\log_{10}(Ca) = 0.299\log_{10}(SC) - 0.137\log_{10}(Q) + 0.868$	.042	.96
Aluminum (*Al*)	Dissolved	$\log_{10}(Al) = 1.346\log_{10}(SC) + 0.068\log_{10}(Q) + 2.542\log_{10}(pH) - 1.3$	.04	.89
Aluminum (*Al*)	Total	$\log_{10}(Al) = 1.341\log_{10}(SC) + 0.075\log_{10}(Q) + 2.23\log_{10}(pH) - 1.106$	.031	.94
Iron (*Fe*)	Dissolved	$\log_{10}(Fe) = 2.686\log_{10}(SC) + 0.355\log_{10}(Q) - 3.163$	.15	.85
Iron (*Fe*)	Total	$\log_{10}(Fe) = 2.455\log_{10}(SC) + 0.393\log_{10}(Q) - 2.383$	.17	.82
Cadmium (*Cd*)	Dissolved	$\log_{10}(Cd) = 1.905\log_{10}(SC) + 0.282\log_{10}(Q) - 0.008(Temp) - 3.99$	.077	.94
Cadmium (*Cd*)	Total	$\log_{10}(Cd) = 1.909\log_{10}(SC) + 0.341\log_{10}(Q) - 4.013$	.09	.91
Copper (*Cu*)	Dissolved	$\log_{10}(Cu) = 1.919\log_{10}(SC) + 0.462\log_{10}(Q) - 1.589$	.086	.94
Copper (*Cu*)	Total	$\log_{10}(Cu) = 1.954\log_{10}(SC) + 0.459\log_{10}(Q) - 1.687$	.084	.94
Zinc (*Zn*)	Dissolved	$\log_{10}(Zn) = 1.418\log_{10}(SC) + 0.118\log_{10}(Q) - 0.558$	.04	.95
Zinc (*Zn*)	Total	$\log_{10}(Zn) = 1.447\log_{10}(SC) + 0.122\log_{10}(Q) - 0.638$	.04	.96
Concentration		Pike Hill Brook at Pike Hill Road west crossing near Bradford, VT (station 01139833, site 4)		
Calcium (*Ca*)	Dissolved	$\log_{10}(Ca) = 0.299\log_{10}(SC) - 0.137\log_{10}(Q) + 0.868$	.042	.96
Concentration		Pike Hill Brook at Pike Hill Road near Bradford, VT (station 01139838, site 5)		
Calcium (*Ca*)	Dissolved	$\log_{10}(Ca) = 0.299\log_{10}(SC) - 0.137\log_{10}(Q) + 0.868$	.042	.96

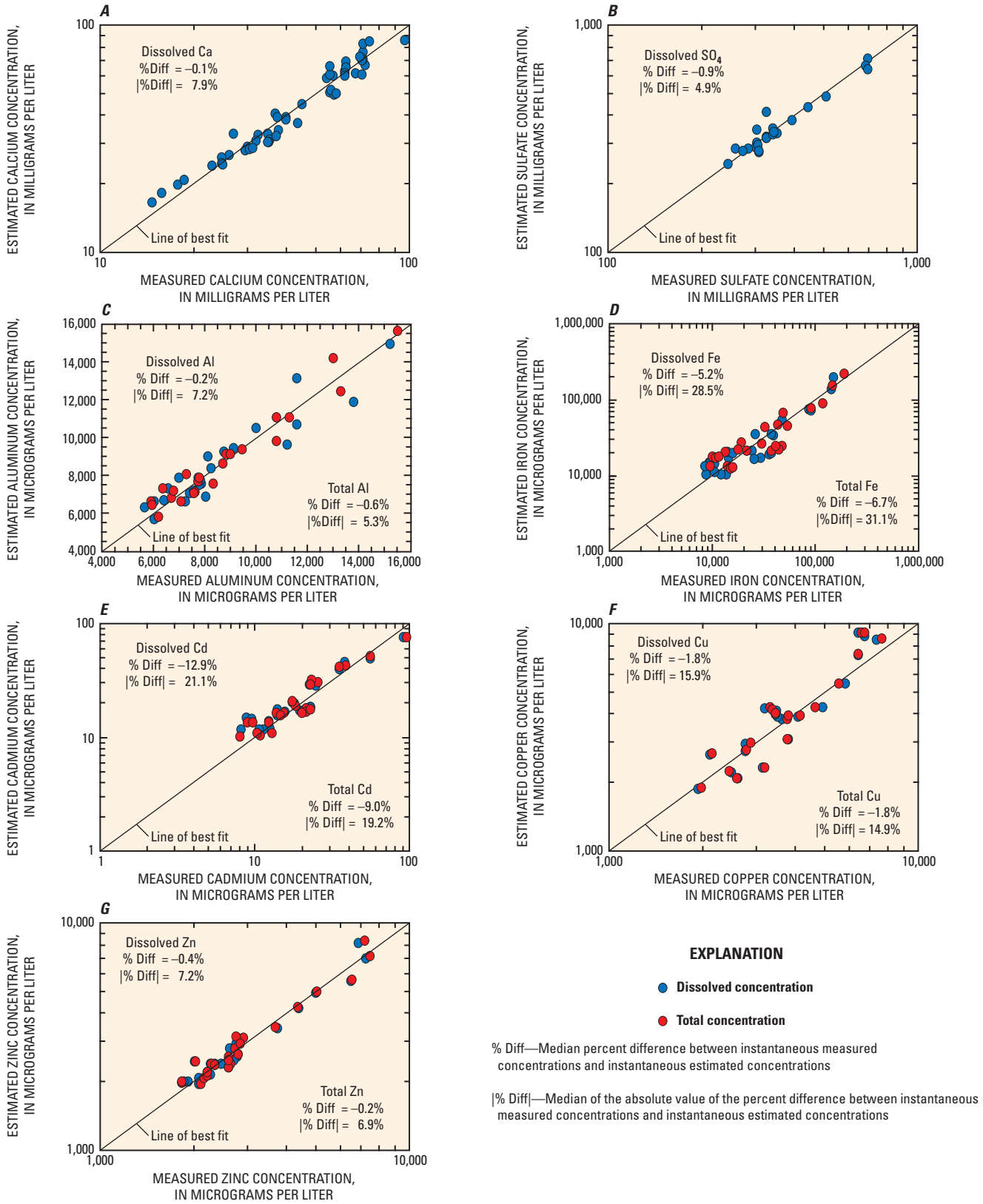

Figure 19. The relation of measured to estimated concentrations of (*A*) calcium at the three continuously monitored sites in the Pike Hill, VT, study area; and (*B*) sulfate; (*C*) aluminum; (*D*) iron; (*E*) cadmium; (*F*) copper; and (*G*) zinc at Pike Hill Brook above Richardson Road near Bradford, VT, station 01139830, site 1.

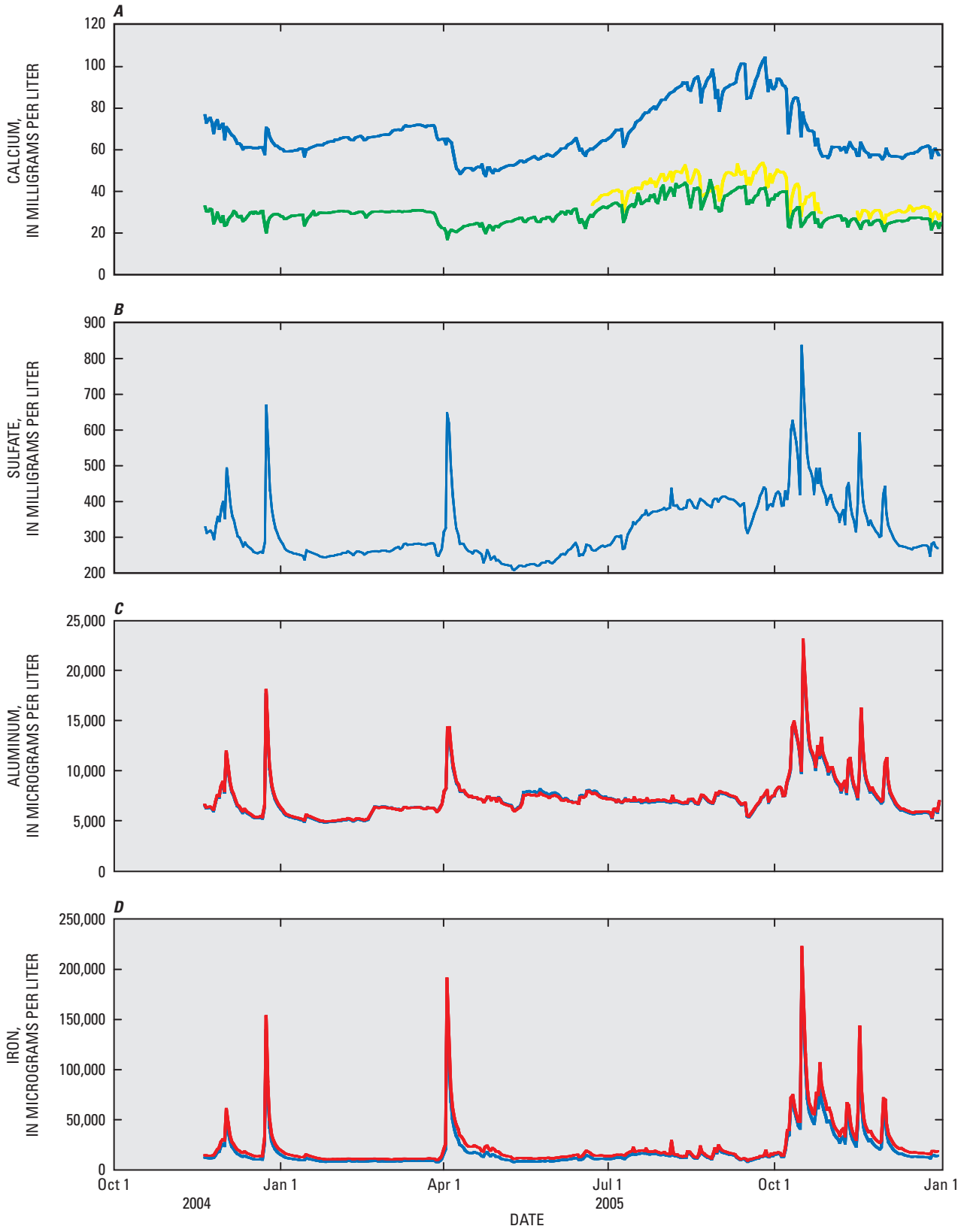

Figure 20. Estimated daily mean concentrations of (*A*) calcium at the three continuously monitored sites in the Pike Hill, VT, study area; and (*B*) sulfate; (*C*) aluminum; (*D*) iron; (*E*) cadmium; (*F*) copper; and (*G*) zinc at Pike Hill Brook above Richardson Road near Bradford, VT, station 01139830, site 1, from November 2004 to December 2005.

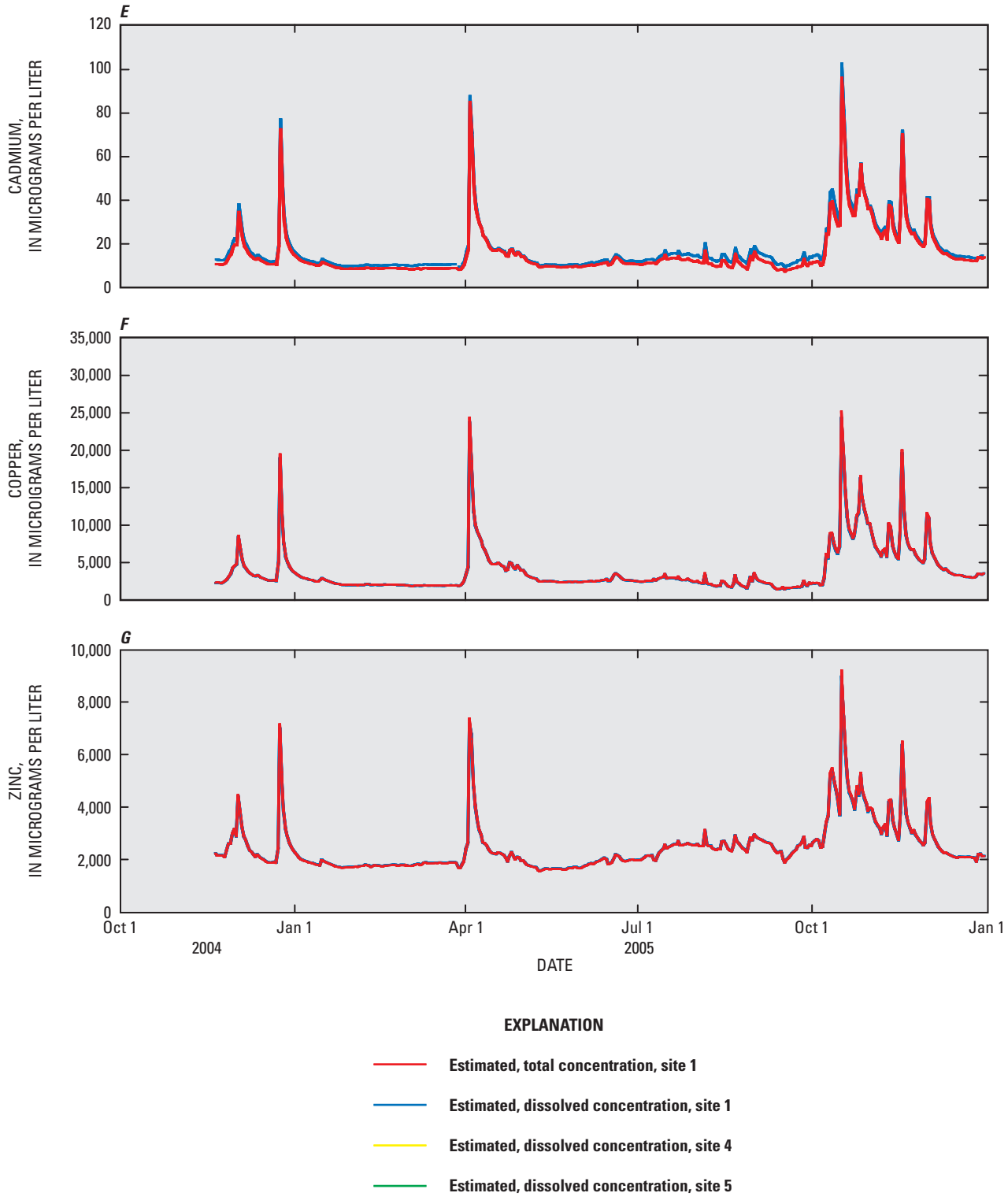

Figure 20. Estimated daily mean concentrations of (*A*) calcium at the three continuously monitored sites in the Pike Hill, VT, study area; and (*B*) sulfate; (*C*) aluminum; (*D*) iron; (*E*) cadmium; (*F*) copper; and (*G*) zinc at Pike Hill Brook above Richardson Road near Bradford, VT, station 01139830, site 1, from November 2004 to December 2005.—Continued

Table 8. Summary statistics for estimated daily mean concentrations of sulfate, calcium, aluminum, iron, cadmium, copper, and zinc from regression models at the three continuously monitored sites in the Pike Hill, VT, study area.

[mg/L, milligrams per liter; µg/L, micrograms per liter. Location for sites is shown on figure 1]

Constituent	Phase	Concentration			
		Minimum	Mean	Median	Maximum
Pike Hill Brook above Richardson Road near Bradford, VT (station 01139830, site 1)					
Sulfate (mg/L)	Dissolved	208	323	283	836
Calcium (mg/L)	Dissolved	48	68	64	104
Aluminum (µg/L)	Dissolved	4,840	7,330	6,940	22,600
Aluminum (µg/L)	Total	4,940	7,400	7,040	23,000
Iron (µg/L)	Dissolved	7,830	19,800	13,000	213,000
Iron (µg/L)	Total	9,320	24,100	15,800	222,000
Cadmium (µg/L)	Dissolved	9.2	17.2	14	102
Cadmium (µg/L)	Total	7.4	15.9	12	95.8
Copper (µg/L)	Dissolved	1,340	3,820	2,570	24,200
Copper (µg/L)	Total	1,370	3,870	2,580	25,100
Zinc (µg/L)	Dissolved	1,570	2,490	2,190	9,000
Zinc (µg/L)	Total	1,560	2,500	2,190	9,240
Pike Hill Brook at Pike Hill Road, west crossing, near Bradford, VT (station 01139833, site 4)					
Calcium (mg/L)	Dissolved	25	40	40	54
Pike Hill Brook at Pike Hill Road near Bradford, VT (station 01139838, site 5)					
Calcium (mg/L)	Dissolved	17	30	29	46

Table 9. Regression equations for estimating loads of sulfate, aluminum, iron, cadmium, copper, and zinc at Pike Hill Brook at Pike Hill Road, west crossing, and Pike Hill Brook at Pike Hill Road near Bradford, VT.

[MSE, mean square error; R^2, coefficient of determination; *Q*, centered streamflow; ln, natural logarithm; *dtime*, centered decimal time, in years. Location for sites is shown on figure 1]

Constituent	Phase	Equation	MSE	R^2
Load		Pike Hill Brook at Pike Hill Road, west crossing, near Bradford, VT (station 01139833, site 4)		
Sulfate (SO_4)	Dissolved	$\ln(SO_4) = 5.6564 + 0.8410\ln(Q) - 0.0323\ln(Q^2) - 0.198\sin(2\pi dtime) - 0.758\cos(2\pi dtime) - 0.1184 dtime + 2.7005 dtime^2$	0.061	0.98
Aluminum (*Al*)	Dissolved	$\ln(Al) = -3.3902 + 0.3929\ln(Q) - 0.3465\ln(Q^2) + 0.0825\sin(2\pi dtime) + 0.3768\cos(2\pi dtime) + 0.4758 dtime$	.159	.80
Aluminum (*Al*)	Total	$\ln(Al) = -0.2799 + 2.1387\ln(Q) + 0.8506 dtime$	.349	.95
Iron (*Fe*)	Dissolved	$\ln(Fe) = -2.4362 + 2.2209\ln(Q) + 0.8039\ln(Q)^2 - 1.0391 dtime$	.613	.92
Iron (*Fe*)	Total	$\ln(Fe) = 1.0884 + 2.194\ln(Q)$	.626	.90
Cadmium (*Cd*)	Dissolved	$\ln(Cd) = -5.5781 + 1.5989\ln(Q) + 0.2501\ln(Q)^2$	.337	.91
Cadmium (*Cd*)	Total	$\ln(Cd) = -5.4561 + 1.6028\ln(Q) + 0.2199\ln(Q)^2$	.336	.91
Copper (*Cu*)	Dissolved	$\ln(Cu) = -2.9096 + 2.335\ln(Q) + 0.5036\ln(Q^2) + 0.7047\sin(2\pi dtime) + 0.1365\cos(2\pi dtime)$	.221	.97
Copper (*Cu*)	Total	$\ln(Cu) = -0.5698 + 2.3372\ln(Q)$	.599	.91
Zinc (*Zn*)	Dissolved	$\ln(Zn) = -0.422 + 1.5776\ln(Q)$	.44	.87
Zinc (*Zn*)	Total	$\ln(Zn) = -0.2725 + 1.5759\ln(Q)$	.399	.88
Load		Pike Hill Brook at Pike Hill Road near Bradford, VT (station 01139838, site 5)		
Sulfate (SO_4)	Dissolved	$\ln(SO_4) = 5.8695 + 0.8644\ln(Q) - 0.1243\ln(Q^2) - 0.3077\sin(2\pi dtime) - 0.2965\cos(2\pi dtime)$	.082	.94
Aluminum (*Al*)	Dissolved	$\ln(Al) = -1.7750 + 1.397\ln(Q) + 0.1172\ln(Q^2) + 0.6302\sin(2\pi dtime) + 0.1686\cos(2\pi dtime)$	.069	.97
Aluminum (*Al*)	Total	$\ln(Al) = 0.4339 + 2.3288\ln(Q) + 0.3748\ln(Q^2) - 0.5015\sin(2\pi dtime) - 0.543\cos(2\pi dtime)$	.333	.97
Iron (*Fe*)	Dissolved	$\ln(Fe) = 0.1137 + 0.7294\ln(Q) - 1.1607 dtime$	.415	.68
Iron (*Fe*)	Total	$\ln(Fe) = 1.7552 + 1.9065\ln(Q) + 0.4655\ln(Q)^2 - 0.6532 dtime$	.336	.95
Cadmium (*Cd*)	Dissolved	$\ln(Cd) = -5.3819 + 1.0413\ln(Q) - 0.1435\ln(Q)^2$	.193	.89
Cadmium (*Cd*)	Total	$\ln(Cd) = -5.3218 + 1.4706\ln(Q) + 0.2197\ln(Q)^2 - 0.3042\sin(2\pi dtime) - 0.072\cos(2\pi dtime)$	.066	.98
Copper (*Cu*)	Dissolved	$\ln(Cu) = -1.3764 + 1.1708\ln(Q) + 0.6534 dtime$	.182	.91
Copper (*Cu*)	Total	$\ln(Cu) = -0.6892 + 1.8529\ln(Q) + 0.2599\ln(Q)^2 + 0.3985 dtime$	.091	.98
Zinc (*Zn*)	Dissolved	$\ln(Zn) = -0.6342 + 0.9074\ln(Q) - 0.1523\ln(Q)^2 - 0.6475\sin(2\pi dtime) - 0.1409\cos(2\pi dtime)$	.213	.91
Zinc (*Zn*)	Total	$\ln(Zn) = -0.4285 + 1.4581\ln(Q) + 0.1638\ln(Q)^2 - 0.6199\sin(2\pi dtime) - 0.1558\cos(2\pi dtime)$	.073	.98

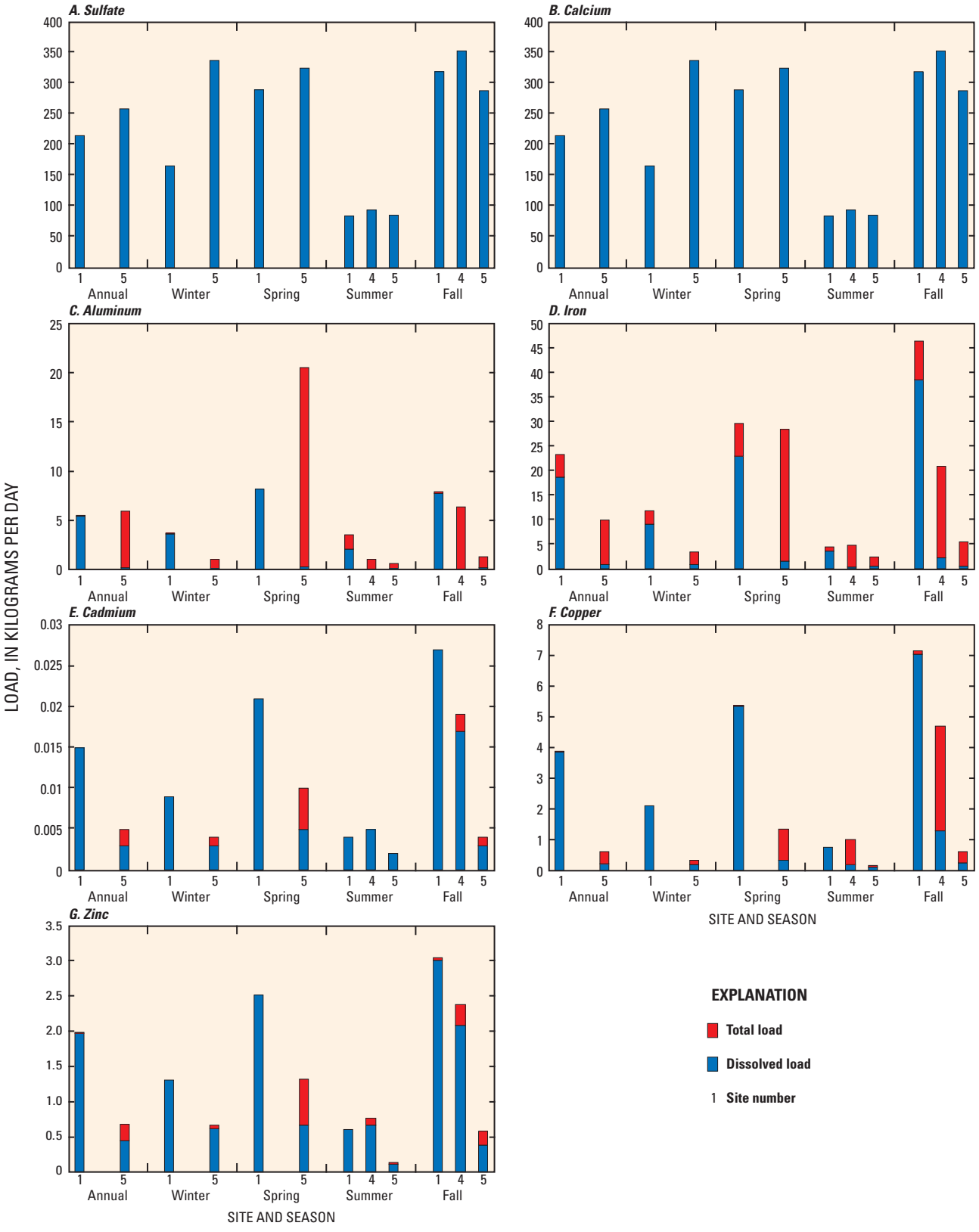

Figure 21. Annual and seasonal loads for (*A*) sulfate, (*B*) calcium, (*C*) aluminum, (*D*) iron, (*E*) cadmium, (*F*) copper, and (*G*) zinc at the three continuously monitored sites in the Pike Hill, VT, study area.

Table 10. Annual and seasonal loads estimated for the three continuously monitored sites in the Pike Hill, VT, study area.

[Winter, December to February; Spring, March to May; Summer, June to August; Fall, September to November; --, no data. Refer to figure 1 and table 1 for site name, station number, and location]

Season site	Load, in kilograms per day											
	Sulfate dissolved	Calcium dissolved	Aluminum		Iron		Cadmium		Copper		Zinc	
			Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total
Annual												
Site 1	216	40	5.43	5.50	18.7	23.3	0.015	0.015	3.85	3.88	1.87	1.88
Site 5	259	416	.13	5.91	.87	9.98	.003	.005	.22	.62	.44	.68
Winter												
Site 1	166	36	3.60	3.68	9.10	11.8	.009	.008	2.11	2.12	1.31	1.31
Site 5	338	391	.06	1.00	.92	3.41	.003	.004	.19	.33	.62	.66
Spring												
Site 1	290	57	8.14	8.15	22.9	29.6	.021	.020	5.35	5.37	2.51	2.51
Site 5	326	608	.25	20.56	1.54	28.4	.005	.010	.33	1.36	.67	1.32
Summer												
Site 1	84	19	2.10	2.08	3.54	4.43	.004	.003	.76	.76	.61	.61
Site 4	95	65	.03	1.07	.41	4.83	.005	.005	.19	1.02	.67	.76
Site 5	86	246	.10	.64	.50	2.41	.002	.001	.10	.18	.11	.13
Fall												
Site 1	320	47	7.72	7.92	38.6	46.4	.028	.026	7.04	7.15	3.01	3.04
Site 4	353	145	.02	6.33	2.27	20.8	.017	.019	1.30	4.70	2.08	2.38
Site 5	289	414	.13	1.30	.53	5.48	.003	.004	.25	.61	.38	.58

Effect of Wetlands on Chemical Constituents

Wetlands can interact chemically with ARD through aerobic and anaerobic pathways. The aerobic pathway is dominated by the oxidation of reduced iron, with the potential for precipitation of ferric hydroxides and the associated adsorption of metals. The anaerobic pathway is dominated by sulfate-reducing bacteria, which consume sulfate and organic matter to produce sulfide and alkalinity. The resultant sulfide is available to remove metals through the precipitation of sulfide minerals in the wetlands. The anaerobic pathway also offers the possibility of reducing previously formed hydrated ferric hydroxides.

A series of wetlands occurs along Pike Hill Brook between the mine site and the confluence with the Waits River (fig. 1). Throughout the wetlands, Pike Hill Brook maintains a discrete channel. Thus, water that discharges from the wetlands includes both ground and surface waters that have interacted with the wetlands, and surface waters in Pike Hill Brook that have flowed through with minimal interaction. To evaluate the potential of aerobic and anaerobic pathways, water was sampled in August 2005 from Pike Hill Brook upstream and downstream from the wetlands during base-flow conditions to maximize geochemical signatures attributable to the wetlands (fig. 1, table 1). Additional surface waters unrelated to the mine site that were contributing to the wetlands also were sampled. The Pike Hill Brook tributary at Brook Road (site 5A) was the only tributary to have significant streamflow during the sampling (fig. 1, table 11). Streamflows for sites 1, 4, and 5 were measured at the continuous streamflow-gaging stations. Streamflows for sites 3, 6, and 7 were estimated on the basis of drainage area. Streamflow measurements were made at Pike Hill Brook at Pike Hill Road, northwest crossing (site 2A) and at site 5A (table 11). Streamflows at sites 4, 5, and 6 indicated that ground water contributes over half of the discharge from the wetlands.

The concentrations of dissolved Fe entering the wetlands were low, and it appears unlikely that oxidation of ferrous Fe and precipitation of ferric hydroxides have a significant effect on trace metals in the wetlands through sorption (fig. 22). Total Fe concentrations, however, were about three times the dissolved Fe concentrations entering the wetlands. Therefore, a large amount of the Fe entering the wetlands is in particulate form and may have transported sorbed copper and other trace metals. Thus, aerobic activity related to oxidation of iron within the wetlands is not likely to play an important role in metal cycling in the watershed.

Table 11. Selected parameters for sampling sites associated with the wetlands in the Pike Hill, VT, study area, August 3, 2005.

[ft³/s, cubic feet per second; µg/L, micrograms per liter; mg/L, milligrams per liter; --, no value; <, less than; e, estimated. Refer to figure 1 and table 1 for site name, station number, and location]

Site number (table 1; figure 1)	Streamflow (ft³/s)	Dissolved concentrations		
		pH	Iron[1] (µg/L)	Sulfate (mg/L)
0	--	4.2	717	373
1	0.04	3.2	10,600	342
2A	.11	6.8	<20	125
3	e.14	6.8	<20	95
4	.24	6.9	59	50
5A	.14	8.2	<20	11
5	.92	7.3	130	8.0
6	e1.1	7.4	163	5.7
7	e1.2	8.3	52	6.7

[1] Analyzed using Inductively Coupled Plasma.

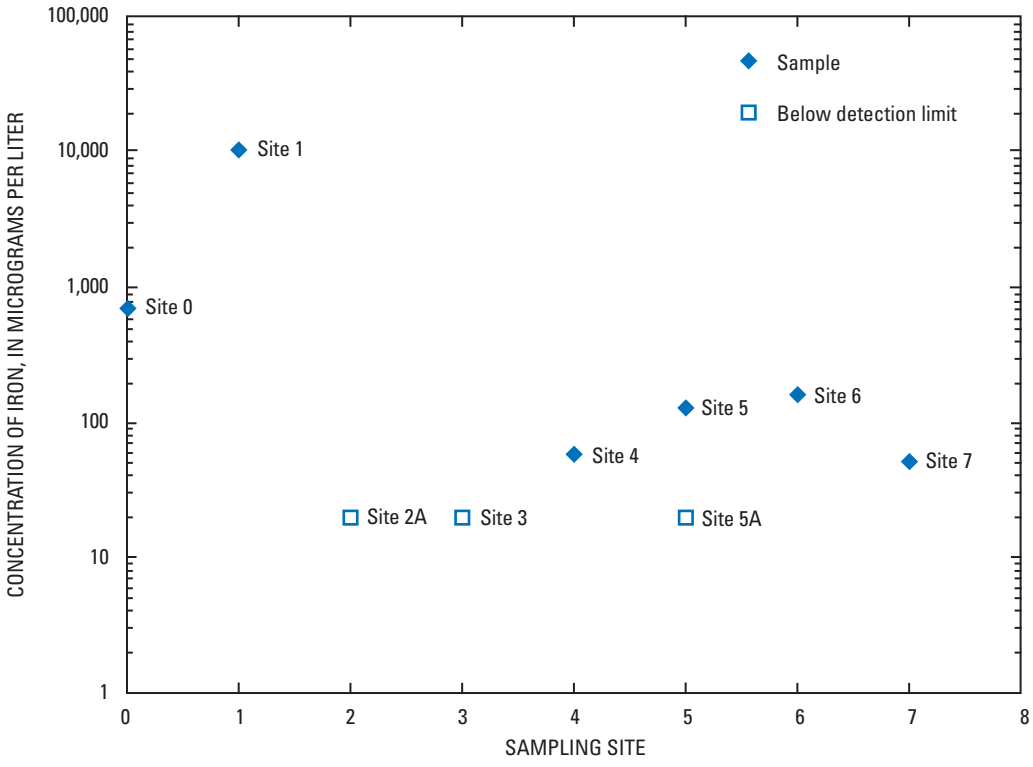

Figure 22. Concentrations of dissolved iron at synoptic sampling sites in the Pike Hill, VT, study area, August 3, 2005.

Concentrations of SO_4 showed a steady decrease downstream (fig. 23). Unaffected tributaries (sites 2 and 5A) had sulfate concentrations that were comparable to those in Pike Hill Brook downstream from the wetlands at sites 5, 6, and 7. Therefore, concentrations and loads of SO_4 may be unlikely to define unequivocally the role of the wetlands with regard to anaerobic bacterial sulfate reduction. However, sites 1, 2A, 3, and 4 had similar loads. Sites 5, 6, and 7 had similar, but lower loads that indicated sulfate removal. Therefore, bacterial sulfate removal may have affected loads of SO_4.

Concentrations of Cu and Zn also decreased in Pike Hill Brook with distance downstream from the Eureka and Union mines (site 0) (figs. 24 and 25). Cu loads increased at site 5, downstream from the wetlands, whereas Zn loads decreased. Total concentrations of Cu were about twice the dissolved concentrations at site 4, upstream from the wetlands, but total and dissolved Zn concentrations were similar. The increase in Cu loads may reflect the reductive dissolution of ferric hydroxide particulates in anaerobic parts of the wetlands. Dissolved Fe concentrations increased at site 5, downstream from the wetlands (fig. 22), which is consistent with this hypothesis. The lack of a similar increase in Zn loads is consistent with most of the Zn load being in the dissolved form rather than the total form.

Biological Assessment of the Pike Hill Brook Watershed

To determine the effects of ARD on the macroinvertebrate assemblages at sites in the study area, the benthic macroinvertebrate data were compared with hazard quotients (HQ), which were based on median metal concentrations at the sampling sites. The HQ for each synoptic sampling site was calculated by dividing median concentrations of Cd, Cu, and Zn by their respective chronic toxicity value, then these HQ values were summed to provide a single Hazard Index value for each site (table 12). A Hazard Index often is used to represent the cumulative toxicity of multiple contaminants (U.S. Environmental Protection Agency, 1986). In this study, a Hazard Index greater than 1 indicates the median concentrations of Cd, Cu, and Zn exceed their additive chronic toxicity values. The relative toxicity of the ARD, therefore, is represented by the Hazard Index.

Benthic Macroinvertebrate Assemblages

Macroinvertebrate samples were collected at the 10 synoptic water-quality sites and at an additional site (4A) on Pike Hill Brook about 0.5 mi below site 4 and immediately above the dominant wetland in the basin. This wetland confines the flow of Pike Hill Brook for approximately 1.25 mi and is between site 4A and site 5 (fig. 1, table 1). Site 4A was added to allow a comparison of the macroinvertebrate assemblages above and below the wetland (sites 4A and 5, respectively). The difference in the macroinvertebrate assemblages between sites 4A and 5, when compared to changes between other consecutive sites along Pike Hill Brook, could indicate the relative degree that the wetland reduced the affects of ARD on the macroinvertebrate assemblages. Because site 4A was not part of the initial site network for water-quality sampling, the Hazard Index for site 4A was estimated by interpolation, based on the drainage area of the site and the relation between the drainage area and the median concentration of metals at sites 3, 4, and 5.

An ordination of the macroinvertebrate assemblage data was done with the use of correspondence analysis to determine the differences among sites based on patterns in the assemblage structure (taxa richness and abundance of organisms). The correspondence analysis indicated that the assemblage structure of the macroinvertebrates was related to drainage area as well as contamination at the sites, determined from correlations of the first-axis site scores of the correspondence analysis with the drainage area (spearman rho = 0.936) and with the Hazard Index (spearman rho = 0.505). These results also indicated that stream size (= drainage area) affected the assemblage structure most strongly. The consequence of comparing macroinvertebrate assemblages among sites with dissimilar drainage areas is that the streams are ecologically very different, and this difference is a primary factor in the structure of the macroinvertebrate assemblage at a site. For example, sites 8 and 9 have relatively wide channels with open canopy, which can contribute to the production of benthic algae as a primary food base. Conversely, site 2 is a closed canopy headwater stream that is not shown on a USGS 1:24,000-scale map, has summer flows in a channel that is typically less than 3.28 ft (1 m) wide, and has a food base that comes mainly from fallen leaf litter. Among the sites, therefore, physical differences related to watershed size as well as the chemical differences caused by ARD were factors that would likely affect the macroinvertebrate assemblages.

To investigate the effects of ARD on changes in the macroinvertebrate assemblages, it is important to take into account that the sites not directly affected by ARD were the smallest (2) and largest (8 and 9) among all the study sites in terms of drainage areas and stream size. Although these sites were appropriate for use as water-quality indicators to characterize relatively uncontaminated sites in this study, the biological assemblages at these sites were not directly comparable to the sites affected by ARD. Furthermore, a comparison of site 2 with sites 8 and 9 showed they had very different macroinvertebrate assemblages (appendix 1), which are likely a result of stream size and not ARD. Therefore, to determine the effect of ARD on macroinvertebrate assemblages, several comparisons were made only among the sites most affected by ARD (sites 1, 3–7, and 10). It is important to note, however, that the macroinvertebrate data collected at site 2 (appendix 1) indicated the potential for a diverse macroinvertebrate assemblage at a headwater stream, such as site 1, if ARD was absent. In this context,

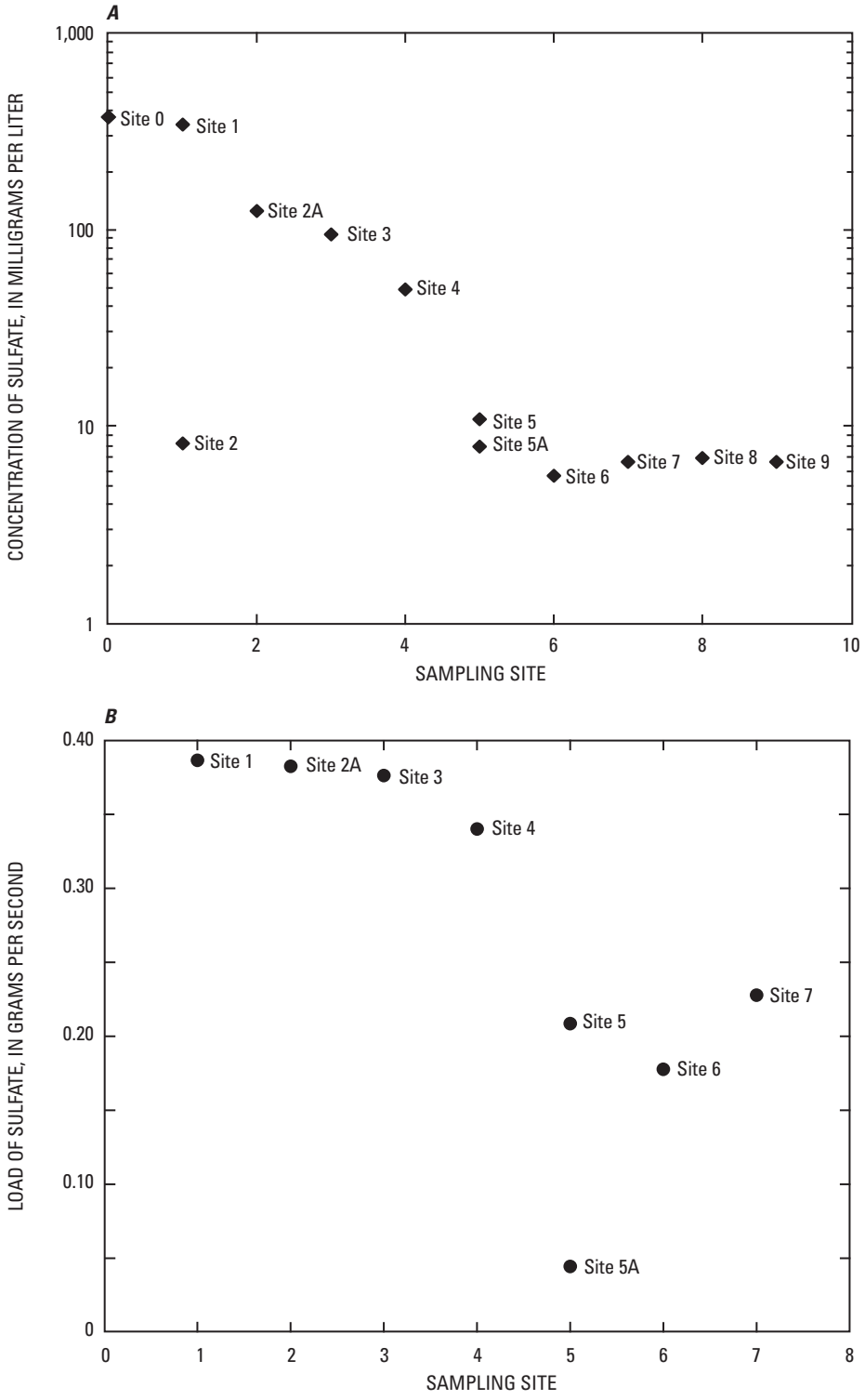

Figure 23. (*A*) Concentrations of dissolved sulfate, and (*B*) instantaneous loads of sulfate at sampling sites in the Pike Hill, VT, study area, August 3, 2005.

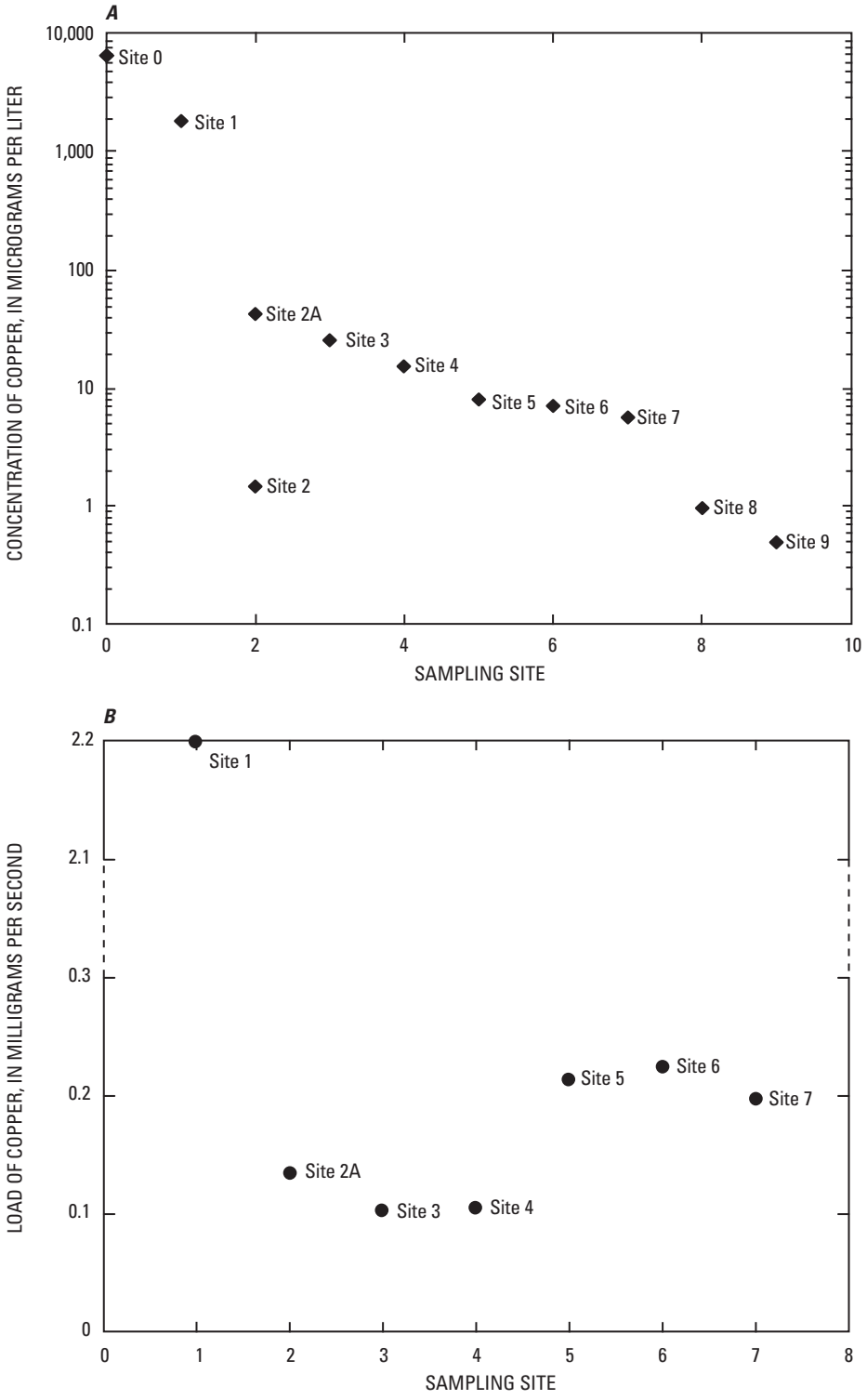

Figure 24. (*A*) Concentrations of dissolved copper, and (*B*) instantaneous loads of copper at sampling sites in the Pike Hill, VT, study area, August 3, 2005.

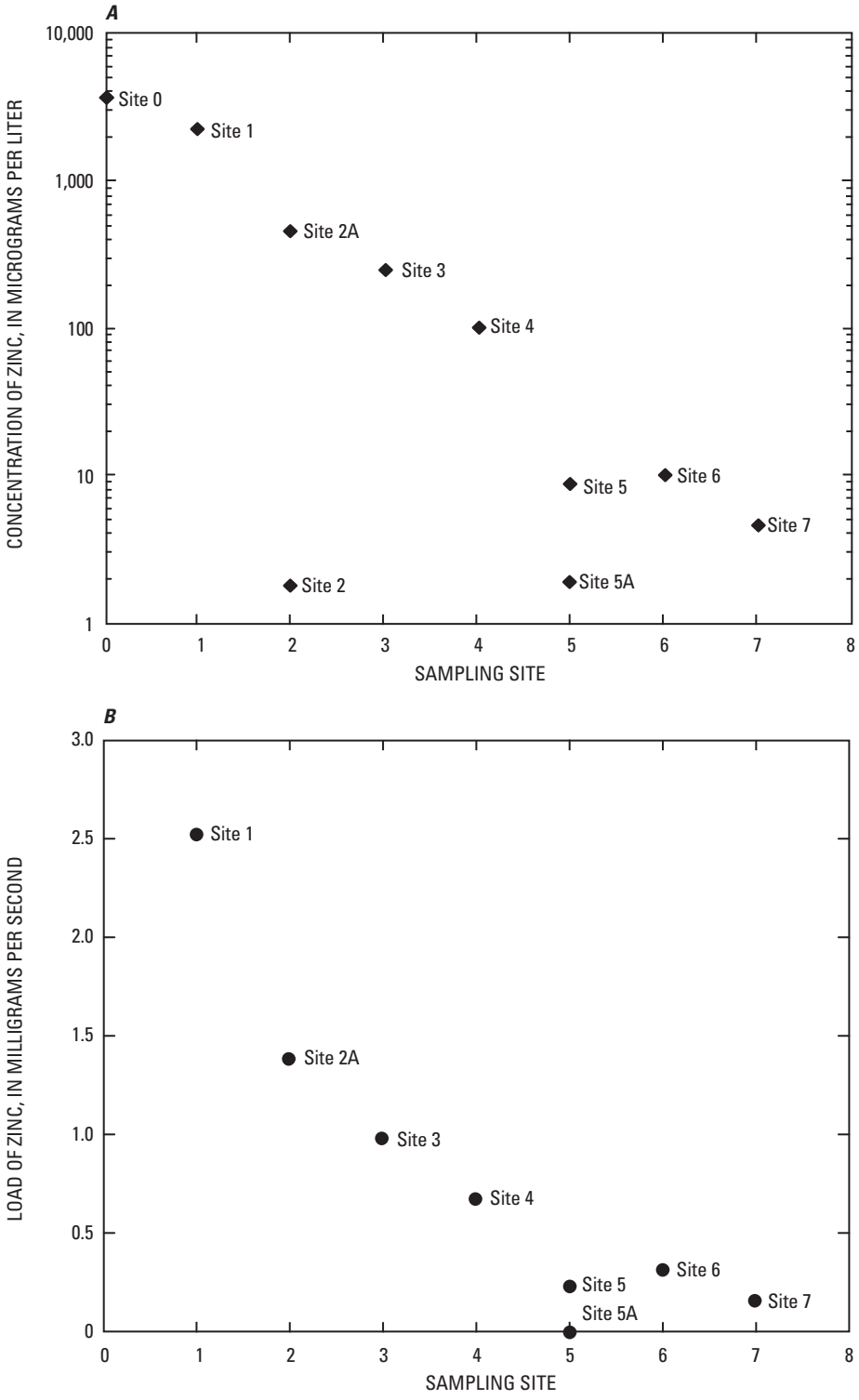

Figure 25. (*A*) Concentrations of dissolved zinc, and (*B*) instantaneous loads of zinc at sampling sites in the Pike Hill, VT, study area, August 3, 2005.

the comparison between sites 1 and 2 is relevant because the change in the macroinvertebrate assemblages moving downstream on Pike Hill Brook was more a function of ARD than basin area.

The most apparent effects on the macroinvertebrate assemblages caused by high contaminant levels from ARD (represented by Hazard Index values) were seen in the abundance of organisms and richness of taxa. Although other metrics and indices indicted a response to ARD, additional investigation showed that these responses were correlated to a general decrease in macroinvertebrate density (abundance) and richness. For example, an increase in the Hazard Index resulted in a decrease in three functional-group richness metrics that represent Filterers, Gatherers, and Predators; however, these three metrics were responding because taxa richness, in general, was decreasing, and not because a specific taxonomic group was being displaced by another.

A decrease in the macroinvertebrate abundance was strongly correlated to increasing values of the Hazard Index (rho = -0.929). This response was clearly indicated by the progressive decrease in Hazard Index with a concurrent increase in macroinvertebrate abundance among the Pike Hill Brook sites as their distance increased from the waste piles; the site closest to the waste piles (site 1) had the highest Hazard Index value and lowest abundance, whereas the site farthest from the waste piles (site 7) had the lowest Hazard Index value and highest abundance (fig. 26A). Site 1 was the most affected by ARD (Hazard Index = 503), and this site had an abundance value of 30 individuals (lowest of all sites), which was markedly less than the abundance of 539 individuals at site 2. Although sites 1 and 2 are not directly comparable (as explained above), a higher abundance would be expected at site 1, in the absence of ARD, because of its larger drainage area. Of the stations along Pike Hill Brook, site 7 was the most downstream and least affected by ARD, and had the highest macroinvertebrate abundance of 814 individuals.

In addition to a general decrease in taxa abundance with increasing ARD, the richness of certain taxonomic groups also decreased. The EPT (Ephemeroptera, Plecoptera, Trichoptera) richness is a metric commonly used to indicate the level of increased disturbance based on the loss of mayfly, stonefly, and caddisfly taxa (Barbour and others, 1999). At the ARD sites, however, the stoneflies appeared not quite as sensitive as the mayflies and the caddisflies. The likely reason for this is that stoneflies can be somewhat resistant to metals contamination and low pH, and the mayflies are typically the most sensitive to ARD (Earle and Callaghan, undated, accessed on March 15, 2006 at *http://www.leo.lehigh.edu/envirosci/enviroissue/amd/links/wildlife1.html*). An example of this type of tolerance to ARD was seen at site 1, where two of the six taxa collected were stoneflies. The ET Richness (Ephemeroptera + Trichoptera), therefore, responded more strongly to the Hazard Index than did EPT Richness (rho = -0.884 and -0.771, respectively). Neither mayflies nor caddisflies were present at site 1, and although downstream caddisfly richness increased steadily to site 5, mayflies were not present until site 4A (fig. 26B). Compared to the mayflies and caddisflies, Chironomids, as a group, often are regarded as more tolerant to disturbance, although the reason for this categorization has primarily been based on a relatively greater tolerance to organic pollution (Barbour and others, 1999). In contrast, however, Chironomid richness was fairly well correlated with the Hazard Index (rho = -0.837), indicating that some midge taxa were sensitive to ARD (fig. 26C). This finding was supported by the Chironomid richness of 19 at site 2, which was a value that was not reached until site 5.

Table 12. Hazard Index values and the Vermont Department of Environmental Conservation (VT-DEC) assessment of U.S. Geological Survey macroinvertebrate assemblage data for sites in the Pike Hill, VT, study area.

[Values in **BOLD** are downgradient from mines. Refer to figure 1 and table 1 for site name, station number, and location]

Site number (table 1; fig. 1)	Hazard Index	VT-DEC assessment
1	**503**	Poor
2	.2	Good
3	**17**	Poor
4	**7.9**	Poor
4A	**6.9**	Poor
5	**1.9**	Fair
6	**1.7**	Good-fair
7	**1.2**	Fair
8	.1	Very good
9	.2	Very good
10	**1.0**	Good

Comparison of Assemblages with Vermont Bioassessment Metrics

The VT-DEC has conducted biological assessments of streams near Pike Hill mines since 1997 to determine the extent of effects from ARD. These assessments have evaluated macroinvertebrate and fish assemblages, and have consistently indicated that the standards for Class B Aquatic Life Support have not been met for the entire length of Pike Hill Brook (S. Fiske and R. Langdon, Vermont Department of Environmental Conservation, and J.F. Coles, U.S. Geological Survey, written commun., 2006). These ratings are most likely a direct result of the ARD because no other major stressor to the aquatic community was identified in the watershed. As a component of these assessments, the VT-DEC evaluated the

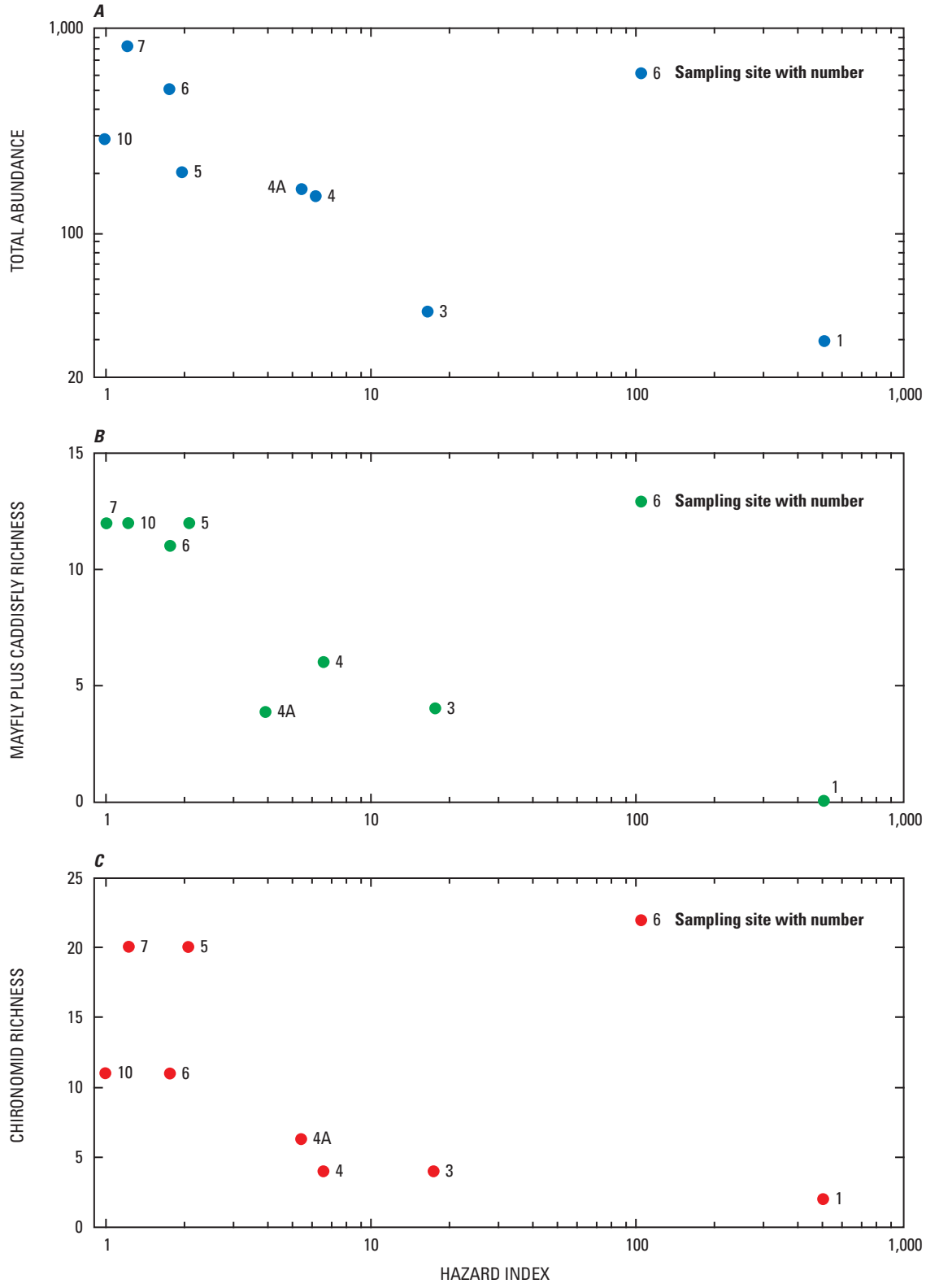

Figure 26. The relation of Hazard Index and (*A*) total abundance, (*B*) Mayfly plus caddisfly richness, and (*C*) Chironomid richness at sampling sites in the Pike Hill, VT, study area.

macroinvertebrate-assemblage data collected on August 29, 2005 by the USGS (table 12). As typically done by VT-DEC, these assessments are based primarily on how the macroinvertebrate assemblage data compare to threshold values of eight biocriteria metrics, which are regarded by VT-DEC (appendix 2) as responsive to various stream impairments.

In addition, fish surveys by VT-DEC have been conducted along reaches of Pike Hill Brook that were near USGS sites 4 (in 1997 and 2002), 5 (in 1997), and 7 (in 2002 and 2005), and all have been assessed as "Poor" on the basis of fish assemblages. Cookville Brook was surveyed for fish at USGS site 10, concurrent to the USGS macroinvertebrate sampling (in 2005), and it was assessed as "Excellent" on the basis of the fish assemblage.

To characterize the macroinvertebrate assemblages among sites in a way that was relevant to the biological assessments made by VT-DEC (S. Fiske and R. Langdon, Vermont Department of Environmental Conservation, and J.F. Coles, U.S. Geological Survey, written commun., 2006), five of the eight metrics used by VT-DEC were applied to the USGS macroinvertebrate data and then compared to median values of the metrics from Vermont reference sites. The metrics used were Density, Richness, EPT Index, Percent Model Affinity of Orders, and Pinkham-Pearson Coefficient of Similarity-Functional Groups (appendix 2). Metrics not used were EPT/EPT+Chironimidae, percent Oligochaeta, and Hilsenhoff Biotic Index, because they were likely to be more responsive to organic enrichment than to ARD. Based on information provided by VT-DEC, the USGS sites represented three stream types (headwaters = sites 1, 2, 3, 10; small high-gradient streams (SHG) = sites 4, 4A, 5, 6, 7; and medium high-gradient streams (MHG) = sites 8, 9). By the use of this classification method, the assessment threshold values of the metrics were specific to the stream type. This approach, therefore, overcomes some of the problems associated with the influence of stream size on macroinvertebrate assemblages, as discussed previously.

The macroinvertebrate characterizations were made by first calculating the five metric values for the macroinvertebrate data (site metrics), then dividing each of these values by the respective metric value for reference sites (reference metrics). For this purpose, each reference metric was the median of the metric values from reference streams for the specific type (headwaters, SHG, or MHG). The quotient that resulted from dividing the site metric by the reference metric was multiplied by 100, which resulted in a standardized percentage value that was not, therefore, dependent on the stream type. To provide a single comprehensive value to relate the site metrics with reference metrics, the geometric mean was calculated for the five metric quotients, from which 100 was subtracted. This single value was termed the "site deviation from reference," which characterized the difference between a sampling site and its respective reference site by deriving the average of the percentage difference between site-metric values and reference-metric values. A zero value would, therefore, result when the values of the site metrics were the same as the reference metrics; a positive or negative value would indicate the percent deviation above or below the reference metric.

The results of this analysis from the 11 sampling sites indicated that site deviation from reference values were highly correlated with the Hazard Index values (rho = -0.936) (fig. 27). This relation indicated a trend of gradually improving conditions in Pike Hill Brook along the continuum of sites from the waste-rock headwaters (site 2) to the end of the brook (site 7) before it enters the Waits River (fig. 28). Additionally, the wetland between sites 4A and 5 may have a mitigating effect on the water quality of Pike Hill Brook, possibly because it traps much of the sediment that was transported from the waste rock. A comparison between the qualitative assessment categories provided by VT-DEC and values of site deviation from reference indicates relative agreement among all sites. These results help confirm consistency in the evaluations of the sites, which increases the confidence in recognizing the level of ecological risk associated with each site.

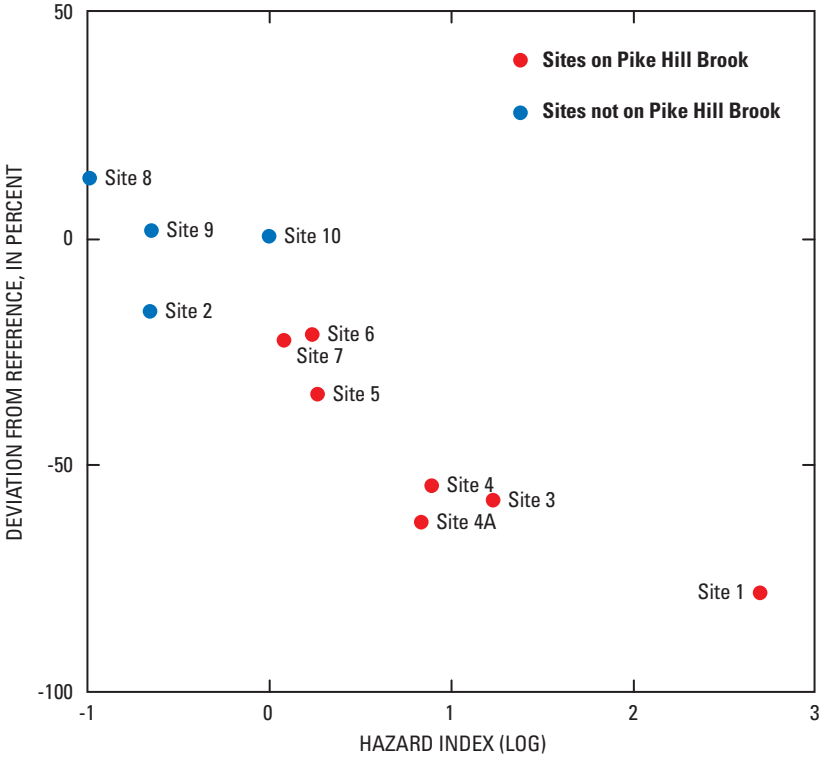

Figure 27. The relation between values of site deviation from reference and the Hazard Index values (log) at sampling sites in the Pike Hill, VT, study area.

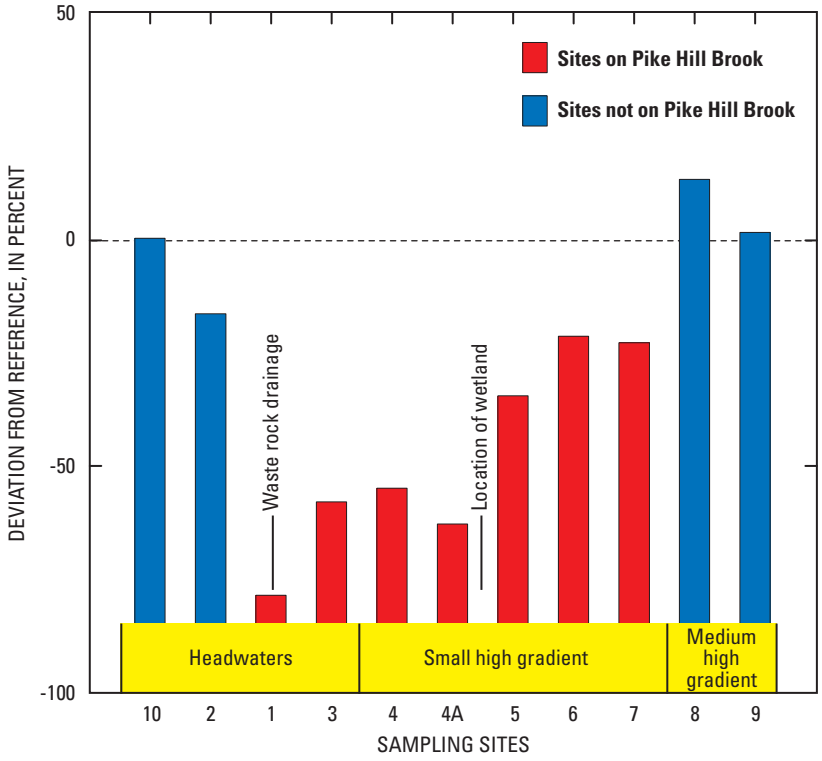

Figure 28. The relation of macroinvertebrate data at the Pike Hill, VT, study area to data from Vermont reference streams.

Summary and Conclusions

The Pike Hill Superfund Site, placed on the U.S. Environmental Protection Agency (USEPA) National Priorities List in 2004, consists of three abandoned mines, the Eureka, the Smith, and the Union mines, and is in the town of Corinth, VT. The site is contributing trace elements to Pike Hill Brook and an unnamed tributary to Cookville Brook. The U.S. Geological Survey (USGS), in cooperation with USEPA, used an integrated (physical, chemical, and biological) approach to assess the current water-quality conditions in and around the Pike Hill Brook watershed and describe the fate and transport of contamination associated with the acid rock drainage (ARD).

A combination of continuous monitors and water-quality sampling was used to characterize the surface-water hydrology and water quality of Pike Hill Brook over an annual cycle. Continuous monitors were used at three sites on Pike Hill Brook to measure streamflow, specific conductance, pH, and water temperature from October 2004 to December 2005. Water samples were collected monthly for analysis of trace elements and major ions at the three continuously monitored sites from October 2004 to December 2005.

Water samples from the three continuously monitored sites showed that some concentrations of aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), and zinc (Zn) exceeded the USEPA National Recommended Water Quality Criteria for acute and chronic toxicity. Concentrations of sulfate (SO_4), Al, Cd, Cu, Fe, and Zn decreased with distance from a site on Pike Hill Brook directly downstream from the mines (site 1) as a result of dilution and through sorption and precipitation of the trace metals. Significant statistical differences among the three continuously monitored sites were found for concentrations of SO_4, Ca, Cd, Cu, and Zn; however, instantaneous loads of Cd, Cu, and Zn at some of the three continuously monitored sites were statistically similar. Instantaneous loads of SO_4 also were statistically similar among the three sites.

Synoptic water-quality samples were collected for major ions and trace elements at 10 sites in November 2004, April 2005, and June 2005 and at 13 sites in August 2005 to describe the spatial and seasonal variability in the water quality of streams in and around the Pike Hill Brook watershed. Synoptic sites represented conditions in Pike Hill Brook, a tributary to Cookville Brook, the Waits River below the confluence with Pike Hill Brook, and background conditions. Concentrations of Al, Fe, Cd, Cu, and Zn at background sites generally were lower than those observed at other synoptic sites. Some concentrations of Al, Fe, Cd, Cu, and Zn were above acute and chronic toxicity standards at sites in Pike Hill Brook (sites 1, 3, 4, 5, 6, and 7). The concentration of Cu from one sample was above the chronic standard at a tributary to Cookville Brook (site 10). No concentrations of Al, Fe, Cd, Cu, or Zn were above toxicity standards at background sites (sites 2 and 8) or in the Waits River below the confluence with Pike Hill Brook (site 9).

Estimates of annual and seasonal loads at the three continuously monitored sites showed that loads of Cd and Zn in Pike Hill Brook directly below the mines (site 1) were about five times greater than at a site about 3 mi downstream (site 5), whereas the annual load for Cu at site 1 was about seventeen times greater than at site 5. The annual load for SO_4 was greater at site 5 than at site 1.

Wetlands can interact chemically with ARD through both aerobic and anaerobic pathways. Samples collected from Pike Hill Brook upstream and downstream from a series of wetlands during low flows in August 2005 showed that oxidation of ferrous Fe and precipitation of Fe-hydroxides were probably not affecting trace metals in the wetlands through sorption. A significant portion of the iron entering the wetlands was in particulate form, however, and may transport sorbed copper and other trace metals. Thus, aerobic activity in the wetlands probably is not affecting metal cycling in the watershed. Anaerobic bacterial sulfate reduction, however, may have affected loads of SO_4. Loads of Cu increased downstream from the wetlands and may reflect the reductive dissolution of ferric hydroxide particulates in anaerobic parts of the wetlands.

The most apparent effects on the macroinvertebrate assemblages caused by high levels of ARD were seen in the abundance of organisms and richness of taxa. A decrease in the macroinvertebrate abundance was strongly correlated to increasing values of the Hazard Index. This response was clearly indicated by the progressive decrease in Hazard Index with a concurrent increase in macroinvertebrate abundance among the Pike Hill Brook sites as the distance increased from the waste piles. In addition to a general decrease in taxa abundance with increasing ARD, a decrease in the richness of certain taxonomic groups also occurred. At the ARD sites, stoneflies were not quite as sensitive as the mayflies and the caddisflies. Neither mayflies nor caddisflies were present at site 1, and although downstream caddisfly richness increased steadily to site 5, mayflies were not present until a site about 2.5 mi downstream of site 1 (site 4A). In contrast, Chironomids as a group are typically regarded as relatively tolerant organisms, but their richness values were fairly well correlated with the Hazard Index, indicating that some midge taxa were sensitive to ARD. Results of this investigation will aid water-resources managers in determining what additional studies may be necessary for a remedial investigation and feasibility study for cleanup of the Pike Hill Superfund Site.

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Appendixes 1–2

Appendix 1. Taxa and total number of macroinvertebrates for samples collected in the Pike Hill, VT, study area.

[Refer to figure 1 and table 1 for site names, station numbers, and locations. Cells with no values (blank) indicate no individuals of the taxon were collected at the site]

Taxa	Site number										
	1	2	3	4	4A	5	6	7	8	9	10
Ephemeroptera											
Acentrella turbida								5	132	48	
Baetis flavistriga								5	756	151	41
Baetis intercalaris									144	119	
Baetis sp.					2			2	48	8	1
Epeorus sp.									72	24	
Ephemera sp.									12		
Ephemerella sp.		5							84	48	
Heptageniidae									36	16	
Isonychia sp.										71	
Leptophlebiidae										8	
Leucrocuta sp.									12	24	
Paraleptophlebia sp.									12		
Plauditus sp.									216	71	
Procloeon sp.						1					
Rhithrogena sp.									24		
Stenonema sp.									156	40	
Odonata											
Boyeria grafiana				3				2		8	
Boyeria sp.							1				
Boyeria vinosa								2			
Coenagrionidae						1					
Cordulegaster sp.			6	5	3		7	2			5
Gomphidae		2		2	1		3				5
Ophiogomphus sp.										8	
Plecoptera											
Acroneuria abnormis						1		2		8	
Agnetina capitata							1				
Chloroperlidae						1		2			
Leuctridae		7				1					
Malirekus sp.		12			1						
Paragnetina immarginata							7			56	
Paragnetina sp.						1		53	12		
Peltoperlidae				1							
Perlidae				1							
Perlodidae	3					1	1	26			4
Pteronarcys sp.				1					12	8	
Soyedina sp.		33	7				1	2			1
Sweltsa sp.	1	7		2			3				35
Coleoptera											
Anacaena sp.				1							
Helichus sp.		5		1							4
Hydrobius sp.		2									
Optioservus ovalis				58	7		25	2	156		5

Appendix 1. Taxa and total number of macroinvertebrates for samples collected in the Pike Hill, VT, study area.—Continued

[Refer to figure 1 and table 1 for site names, station numbers, and locations. Cells with no values (blank) indicate no individuals of the taxon were collected at the site]

Taxa	Site number										
	1	2	3	4	4A	5	6	7	8	9	10
Coleoptera—Continued											
Optioservus sp.										63	
Optioservus trivittatus						3					
Oulimnius latiusculus		9		4	2		4				1
Promoresia tardella				2	1		6				
Psephenus herricki									132	32	
Stenelmis sp.						3	22		12	24	
Megaloptera											
Nigronia serricornis							7		12		
Sialis sp.	3					1					1
Diptera-Chironomidae											
Brillia sp.		4	2	2	3	1		7	12		6
Brundiniella sp.		4									
Chaetocladius sp.		4									
Chironomini						1		5			
Cladotanytarsus sp.									12	24	
Corynoneura sp.		5						26	12	16	1
Cricotopus bicinctus gr.					1	1		2	12		
Cricotopus sp.						1	4	36			
Cricotopus trifascia gr.									12		
Diamesa sp.	1	12				1					
Diplocladius sp.		7									
Eukiefferiella brehmi gr.										8	
Eukiefferiella claripennis gr.											10
Eukiefferiella coerulescens gr.							1	24			
Heleniella sp.		23									
Heterotrissocladius marcidus gr.		2									
Krenopelopia sp.		2									
Limnophyes sp.	20	14		1		7	1	10	12		4
Micropsectra sp.		4	1			1	3		24	16	
Microtendipes pedellus gr.									12	40	
Microtendipes rydalensis gr.							12	2	36		
Nanocladius sp.										8	
Orthocladius (Symp.) lignicola		2				1	1		12		
Orthocladius Complex				2		1		5	24		4
Orthocladius sp.										8	
Pagastia sp.									24		
Parachaetocladius sp.		7									
Parakiefferiella sp.						5					
Parametriocnemus sp.		2				8	27	22	48	8	
Paraphaenocladius sp.						2		2			
Pentaneurini					1						
Phaenopsectra sp.											1
Polypedilum aviceps								2	348	135	

Appendix 1. Taxa and total number of macroinvertebrates for samples collected in the Pike Hill, VT, study area.—Continued

[Refer to figure 1 and table 1 for site names, station numbers, and locations. Cells with no values (blank) indicate no individuals of the taxon were collected at the site]

Taxa	Site number										
	1	2	3	4	4A	5	6	7	8	9	10
Diptera-Chironomidae—Continued											
Polypedilum illinoense gr.						1					
Polypedilum sp.						1			36	16	
Polypedilum tritum				5	6			12			6
Potthastia gaedii gr.					97	2		10			
Procladius sp.						1					
Psilometriocnemus sp.		16									
Rheocricotopus sp.		12	1								1
Rheotanytarsus exiguus gr.							1		12	24	
Rheotanytarsus pellucidus gr.								2	144	16	
Stempellinella sp.									24	8	
Stenochironomus sp.		2				2		2			6
Stilocladius sp.		2									
Sublettea sp.								12			
Tanytarsus sp.							7		36		
Thienemanniella sp.								5	36	16	1
Thienemannimyia gr. sp.					1	6	19	2	24		8
Tribelos jucundum						2					
Tvetenia bavarica gr.		14	1			7	1	302	72		
Tvetenia discoloripes gr.										8	
Diptera - non Chironomidae											
Antocha sp.					2				24		
Atrichopogon sp.						1					
Bezzia/Palpomyia sp.		84		2	3	12	15	2		32	17
Cryptolabis sp.							1				
Culicidae						2					
Dasyhelea sp.						6					
Dicranota sp.		11	1		2						1
Diptera							1				
Dixidae						1	1				
Empididae		5									
Hemerodromia sp.							3	17	12		
Hexatoma sp.		35		6	1	1	4	2	36	32	
Limonia sp.								2			
Molophilus sp.		12		2		1					
Neoplasta sp.											3
Pedicia sp.		7	1								
Simulium sp.						6	6	5	24	8	3
Stilobezzia sp.		23									1
Tabanidae						1	1				
Tipula sp.	2					1	10				1
Tipulidae		2	6	1					12		3
Wiedemannia sp.		7				1	1	22		8	3

Appendix 1. Taxa and total number of macroinvertebrates for samples collected in the Pike Hill, VT, study area.—Continued

[Refer to figure 1 and table 1 for site names, station numbers, and locations. Cells with no values (blank) indicate no individuals of the taxon were collected at the site]

Taxa	Site number										
	1	2	3	4	4A	5	6	7	8	9	10
Trichoptera											
Brachycentrus appalachia								2	24	63	
Ceraclea sp.									24		
Cheumatopsyche sp.						1	21		84	143	1
Chimarra aterrima				4		6	151				
Diplectrona sp.		2	3	1	2	1	6	7			7
Dolophilodes sp.						28		12		8	
Glossosoma sp.									24		
Glossosomatidae								2		127	
Helicopsyche borealis									300	975	
Hydropsyche betteni						11	66				
Hydropsyche bronta										8	
Hydropsyche morosa									84	95	
Hydropsyche morosa gr.						28	1				8
Hydropsyche slossonae								74			
Hydropsyche ventura				26	13						
Lepidostoma sp.								2	216	56	31
Limnephilidae		23	1			1	1				
Mystacides sp.						1	10		12		
Neophylax sp.									24		
Oecetis avara										8	
Oxyethira sp.						1	1				
Parapsyche apicalis				3							2
Parapsyche sp.		21	2								
Philopotamidae		2									
Phryganeidae			1								1
Polycentropus sp.							1	5		24	
Psilotreta sp.				1					12		
Ptilostomis sp.						1	1				
Rhyacophila acutiloba								5			
Rhyacophila atrata				1							
Rhyacophila fuscula					1			7		8	3
Rhyacophila invaria gr.		28									8
Rhyacophila minora											9
Rhyacophila sp.						1	1			8	2
Setodes sp.									84	16	
Lepidoptera											
Lepidoptera			2							8	3
Pyralidae				1							
Gastropoda											
Lymnaeidae									24	16	
Physa (Physella) sp.							1		12		
Bivalvia											
Sphaeriidae			2								

Appendix 1. Taxa and total number of macroinvertebrates for samples collected in the Pike Hill, VT, study area.—Continued

[Refer to figure 1 and table 1 for site names, station numbers, and locations. Cells with no values (blank) indicate no individuals of the taxon were collected at the site]

Taxa	Site number										
	1	2	3	4	4A	5	6	7	8	9	10
Annelida											
Oligochaeta		21	4		1	7	3	19	132	16	20
Acari											
Acari										8	
Atractides sp.									12		
Hygrobates sp.		2									
Lebertia sp.		2			1		4	2			2
Oribatei		9	1	7	2	3	3	17	12	8	4
Panisus sp.		2		2							1
Protzia sp.									12		
Sperchon sp.		2						5	12		
Crustacea											
Hyalella sp.							6				
Other											
Nematoda		25		2	1	9	1	2	24		3
Turbellaria				2							1
Total abundance	**30**	**539**	**42**	**152**	**155**	**198**	**504**	**814**	**4,262**	**2,855**	**289**
Taxa richness	**6**	**49**	**17**	**31**	**24**	**55**	**51**	**52**	**65**	**57**	**47**

Appendix 2. Vermont Department of Environmental Conservation (VT-DEC) bioassessment metrics for macroinvertebrate assemblages.

[The evaluation that is the basis for figure 28 used metrics 1–5 because they appeared to be more responsive to acid rock drainage, whereas metrics 6–8 appear to generally be more representative to changes in organic pollution]

1. **Density** - The relative abundance of invertebrates in a sample.
2. **Richness** - The number of taxa in a sample.
3. **EPT Index** - A subset of the richness measure, it is the number of taxa in the generally more environmentally sensitive orders of Ephemeroptera, Plecoptera, and Trichoptera.
4. **Percent Model Affinity of Orders** - (PMA-O) - A measure of order-level similarity that is based on finding the percentage composition for each major order in the sample and comparing these values to the percentage values for an appropriate reference stream.
5. **Pinkham-Pearson Coefficient of Similarity - Functional Groups** - (PPCS-F) - A measure of functional-feeding group similarity to a model based on an appropriate reference stream. It is similar in concept to the PMA-O in that a site is compared to a model of the composition of the functional feeding groups.
6. **EPT/EPT & Chironomidae** - A measure of the ratio of the abundance of the intolerant EPT orders to the generally tolerant Diptera family Chironomidae.
7. **Percent Oligochaeta** - A measure of the percent of the macroinvertebrate community made up of the Oligochaeta.
8. **Hilsenhoff Biotic Index** - HBI (0–10) - A measure of the macroinvertebrate assemblage tolerance toward organic (nutrient) enrichment. The HBI is metric that is an indicator of sensitive taxa as well as functional groups, because taxa that become more dominant in moderately enriched streams are usually responding to changes in the available food base.

Prepared by Publications Service Center 1

For more information concerning the research in this report, contact:
Keith W. Robinson, Director
U.S. Geological Survey
New Hampshire-Vermont Water Science Center
361 Commerce Way
Pembroke, NH 03275

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Scientific Investigations Report 2007–5003

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