The Chemical Evolution of a Travertine-Depositing Stream: Geochemical Processes and Mass Transfer Reactions

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This field study focuses on quantitatively defining the chemical changes occurring in Falling Spring Creek, a travertine-depositing stream located in Alleghany County, Virginia. The processes of CO_2 outgassing and calcite precipitation or dissolution control the chemical evolution of the stream. The observed chemical composition of the water was used with the computerized geochemical model WATEQF to calculate aqueous speciation, saturation indices, and CO_2 partial pressure values. Mass balance calculations were performed to obtain mass transfers of CO_2 and calcite. Reaction times, estimated from stream discharge, were used with the mass transfer results to calculate rates of CO_2 outgassing and calcite precipitation between consecutive sampling points. The stream, which is fed by a carbonate spring, is supersaturated with respect to CO_2 along the entire 5.2-km flow path. Outgassing of CO_2 drives the solution to high degrees of supersaturation with respect to calcite. Metabolic uptake of CO_2 by photosynthetic plants is insignificant, because the high supply rate of dissolved carbon dioxide and the extreme agitation of the stream at waterfalls and rapids causes a much greater amount of inorganic CO_2 outgassing to occur. Calcite precipitation is kinetically inhibited until near the crest of a 20-m vertical waterfall. Calcite precipitation rates then reach a maximum at the waterfall where greater water turbulence allows the most rapid escape of CO_2. Physical evidence for calcite precipitation exists in the travertine deposits which are first observed immediately above the waterfall and extend for at least 1.0 km below the falls. Net calcite precipitation occurs at all times of the year but is greatest during low-flow conditions in the summer and early fall.

INTRODUCTION

The relationship between carbon dioxide flux and calcite solubility is a critical control on the geochemical evolution of carbonate water systems. The carbon dioxide content in carbonate groundwater typically reaches values ten to one hundred times greater than normal atmospheric CO_2 partial pressure P_{CO_2}, which is $10^{-3.5}$ atm [*Pearson et al.*, 1978; *Butler*, 1982]. If this groundwater emerges at the earth's surface, the water loses CO_2 in an attempt to equilibrate with the lower CO_2 concentration in the air [*Jacobson and Langmuir*, 1970; *Langmuir*, 1971]. Carbon dioxide outgassing is the dominant cause of supersaturation with respect to calcite and subsequent precipitation of the mineral in many carbonate waters. Although carbon dioxide outgassing and calcite precipitation have been extensively studied from a theoretical and experimental approach, field-based investigations of the interplay of these processes are still lacking. Travertine-depositing streams, which are fed by carbonate springs, offer an excellent field setting to monitor carbon dioxide outgassing and calcite precipitation. This paper describes the geochemical evolution of Falling Spring Creek, a travertine-depositing stream located in Alleghany County, Virginia.

The degree of supersaturation with respect to calcite increases as the P_{CO_2} of the water decreases downstream of a spring [*Barnes*, 1965; *Shuster and White*, 1971; *Jacobson and Usdowski*, 1975]; however, calcite does not precipitate immediately as supersaturation is reached. Both laboratory and field studies have shown that calcite precipitation is initially kinetically inhibited. The formation of a crystal by precipitation from solution initially requires an increase in free energy because of the excess energy needed to create new surface area [*Nielsen*, 1964; *Berner*, 1980]. A certain critical degree of supersaturation must be achieved to pass this nucleation barrier [*Stumm and Morgan*, 1981]. Laboratory kinetic studies have shown that the critical concentration, above which nucleation and growth occurs, can be as much as 10 times the equilibrium calcite solubility value [*Reddy*, 1983].

Foreign ions in solution can inhibit precipitation. Phosphate acts as an extremely strong inhibitor of calcite growth rate by adsorbing onto the crystal surface and blocking active growth sites [*Reddy*, 1977; *Morse*, 1983]. Calcite crystallization rates also decrease with increasing magnesium ion concentration in solution [*Berner*, 1975; *Morse*, 1983]. Some organic compounds, such as humic and fulvic acids and organic phosphates, retard calcite growth by poisoning the surfaces of particles which could have acted as nucleation sites [*Reddy*, 1975; *Morse*, 1983]. Because of one or more of these inhibiting factors, high degrees of supersaturation with respect to calcite can be maintained in a solution without noticeable calcite precipitation taking place.

Several studies of surface water systems show significant supersaturation with respect to calcite. *Suarez* [1983] reports that calcite precipitation is not detectable in the Colorado River system although the water reaches 4–6 times supersaturation with respect to calcite. Precipitation is inhibited by the combination of short residence times and unavailability of reactive calcite to act as nucleation sites. The calcite in the river sediment is apparently coated by inhibiting organic material. Two field studies of travertine-depositing streams show that carbon dioxide outgassing must continue until 5 times [*Jacobson and Usdowski*, 1975] and 10 times [*Dandurand et al.*, 1982] supersaturation with respect to calcite is reached. The nucleation barrier can then be passed, and calcite can precipitate [*Dandurand et al.*, 1982]. Calcite precipitation is most rapid in turbulent zones of the stream where CO_2 can

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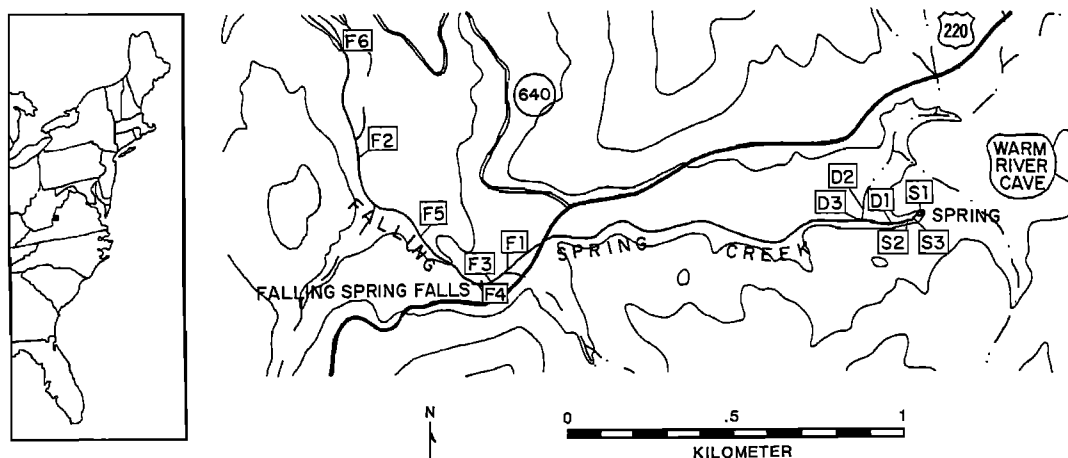[1]Now at U.S. Geological Survey, Towson, Maryland.

Fig. 1.   Map showing location of Falling Spring Creek, Alleghany County, Virginia, and location of sample collection points.

degas more rapidly [*Jacobson and Usdowski*, 1975; *Usdowski et al.*, 1979; *Dandurand et al.*, 1982].

Although the kinetics of the $CaO-CO_2-H_2O$ system have been considered extensively under controlled laboratory conditions, few researchers have quantified reaction rates in field studies. Several investigators have used mass transfer calculations and flow velocity measurements to determine rates of carbonate mineral-water interactions from groundwater geochemical data [*Plummer*, 1977; *Nadler et al.*, 1980; *Plummer and Back*, 1980; *Back et al.*, 1983]. Relative rates of calcite precipitation along travertine-depositing streams have been determined by measuring changes in Ca^{2+} concentration with distance [*Jacobson and Usdowski*, 1975; *Dandurand et al.*, 1982]. *Jacobson and Usdowski* [1975] also give rates estimated from the mass of calcite that precipitated on objects placed in a stream. Although several researchers have noted that agitation of stream water at cascades allows a great amount of CO_2 outgassing to occur [*Dandurand et al.*, 1982], no previous study has quantified the mass transfer and rate of removal of CO_2 in a natural field setting.

Controversy has existed for years over the relative importance of inorganic and organic processes in removing CO_2 from travertine-precipitating streams. Some researchers believe organisms such as bacteria, algae, moss, and other photosynthetic plants uptake significant amounts of CO_2 from the stream water during metabolic processes [*Emig*, 1917; *Mathews*, 1962]. Photosynthetic activity is known to deplete the CO_2 content of lakes to the point of supersaturation with respect to calcite [*Stumm*, 1985]. However, several studies show that in spring-fed streams the combination of a high supply rate of dissolved carbon dioxide and agitation of the water at cascades and rapids allows a great amount of inorganic CO_2 outgassing to occur. Thus metabolic CO_2 uptake becomes an insignificant factor in travertine precipitation in streams [*Usdowski et al.*, 1979; *Dandurand et al.*, 1982; *Chafetz and Folk*, 1984]. Organisms may indirectly aid in formation of these travertine deposits, however, by trapping microparticulate calcite and providing a substrate for calcite growth [*Golubic*, 1969; *Pentecost*, 1978; *Dennen and Diecchio*, 1984].

The present field investigation of the geochemical evolution of a travertine-depositing stream focuses on quantifying rates of carbon dioxide outgassing and calcite precipitation. Reac-

tion rates are obtained by calculating the mass transfers of CO_2 and calcite along the flow path and by using flow velocity to estimate reaction time. Both downstream and seasonal variations in the mass transfers and reaction rates are defined. Diurnal variations in stream water chemistry are also studied to assess the importance of biological activity on travertine precipitation.

FIELD SITE DESCRIPTION

The field site for this study lies in the thermal springs area of Virginia, which stretches along the folded and faulted western anticlines of the Valley and Ridge province (Figure 1). The local geologic section mainly consists of a thick sequence of Lower Ordovician dolomites and Middle and Upper Ordovician limestones, many of which contain significant shale interbeds [*Rader and Gathright*, 1984].

Falling Spring, which feeds Falling Spring Creek, actually consists of several discrete springs emerging from a large breakdown pile that closes off Warm River Cave. Falling Spring represents a mixture of thermal carbonate groundwater and cold carbonate groundwater. Deeply circulated meteoric water, which has been heated under a normal geothermal gradient to a temperature that may exceed 38°C, issues as a thermal spring inside the cave. The thermal water converges with a cold stream derived from shallow groundwater, and this mixed stream resurges as Falling Spring on the surface [*Rader and Gathright*, 1984; *Herman and Lorah*, 1986]. Approximately 0.8 km downstream from Falling Spring, the stream breaches a small Tuscarora sandstone ridge and flows over a 20-m vertical waterfall. The vertical cliff is covered in travertine, and more travertine deposits are evident in the streambed immediately above and below the waterfall.

METHODS

Field Methods and Sample Collection

Seven field trips to collect water samples along Falling Spring Creek were made between June 1984 and April 1985. A 24-hour sampling trip was also made in June 1985 to determine if diurnal variations occurred in the stream water chemistry. Samples of the thermal, cold, and mixed streams inside

Warm River Cave were obtained, but the cave study is reported elsewhere [*Herman and Lorah*, 1986, 1987; *Lorah*, 1987].

Twelve sampling sites were established along a 5.2-km stretch of Falling Spring Creek (Figure 1). Three of the distinct springs emerging from the breakdown pile that closes off Warm River Cave were sampled (S-1, S-2, S-3). The springs combine to form Falling Spring Creek upstream of site D-1. Below site D-1 water was collected from a small tributary (D-2) during the months that it flowed. Site D-3 is downstream of the junction of the tributary with Falling Spring Creek. Samples were also collected near the crest of Falling Spring Falls (F-1, F-3), immediately below the falls (F-4), and downstream from the falls (F-5, F-2, F-6). The last sampling site (F-6) is approximately 4 km downstream of the falls.

During each field trip samples for anion and cation analyses were collected in acid-washed 250-mL polyethylene bottles. Samples for laboratory alkalinity titrations were collected in acid-washed 250-mL glass bottles with ground glass stoppers. All samples were immediately placed on ice.

Temperature, pH, conductivity, and discharge were determined in the field. A portable pH meter was calibrated with pH 4.00 and 7.00 buffers, which were in thermal equilibrium with the stream water, and then duplicate pH measurements were made on samples immediately after collection in a beaker [*Wood*, 1976]. The pH measurements were reproducible within ± 0.02 units. Conductivity was measured with a YSI model 33 conductivity-salinity meter and probe. Discharge was obtained by measuring the flow velocity with a portable water current meter and by determining the cross-sectional area of the stream. Discharge was measured near site D-3 on each trip and at additional sites, near F-1 and F-6, during four of the sampling trips.

On three trips, alkalinity titrations were performed in the field at several sites and compared to alkalinites determined in the laboratory. Titrations were performed on a 10-mL sample with 0.02 N Baker HCl added with a Gilmont micrometer buret. Titration endpoints were taken to be the inflection points in the cumulative acid added versus pH curve. Alkalinity values were converted to HCO_3^-, which was assumed to be the only species contributing significantly to alkalinity. The largest error found between field and laboratory alkalinity titrations was 10%, while the average error was 4%.

A location approximately 500 m below F-2 was chosen for the diurnal variations study because it offered a convenient camping site and was similar to the established sampling sites in the amount of sunlight the stream received for plant photosynthesis. At 2-hour intervals, a sample was collected for cation analysis, and temperature, pH, alkalinity, and conductivity were measured.

Laboratory Methods

Filtered, acidified samples were analyzed for the cations Ca^{2+}, Mg^{2+}, Na^+, and K^+ by standard atomic absorption procedures [*Lorah*, 1987]. Only Ca^{2+} was determined for the samples collected for the diurnal variations study. Replicate dilutions and analyses were performed to determine the maximum relative standard deviations for concentration values: 4.0% for Ca^{2+}, 3.4% for Mg^{2+}, 6.8% for Na^+, and 3.5% for K^+. Unacidified samples were analyzed for SO_4^{2-}, F^-, Cl^-, NO_3^-, and PO_4^{3-} by ion chromatography. EPA standards for F^- and SO_4^{2-} were analyzed, and the concentrations were within the range given for a 95% confidence interval.

Alkalinity titrations were performed with 0.02 N Baker HCl on 50 mL of each sample within 36 hours of returning to the laboratory. Duplicate titrations showed that analytical errors in HCO_3^- concentrations were usually less than 1% with a maximum error of 2%. Titrations were performed on both an unfiltered and filtered portion of several samples after the first field trip. Since the differences between these alkalinites were within the error of titration, all subsequent measurements were performed on unfiltered samples.

Data Analysis

The data analysis can be divided into three parts: (1) defining the saturation state of the waters with respect to calcite and carbon dioxide, (2) determining mass transfers of calcite and carbon dioxide gas along the flow path, and (3) calculating the rates of calcite precipitation and carbon dioxide outgassing. A computerized geochemical model, WATEQF [*Plummer et al.*, 1976], was used to determine the saturation state of the water.

The raw chemical concentration data and the field pH and temperature for each sample were input to WATEQF using the program WATIN [*Moses and Herman*, 1986] to create input files. The WATEQF computer code, based on thermochemical data, calculates the activities of all species in solution and the saturation state of the water with respect to solid mineral phases. The saturation index for calcite SI_c is the logarithm of the ratio of the ion activity product $IAP(T)$ to the equilibrium solubility product $K_c(T)$ at sample temperature: $SI_c = \log [IAP(T)/K_c(T)]$. The value of the saturation index indicates whether the solution is undersaturated (negative SI_c), supersaturated (positive SI_c), or at equilibrium ($SI_c = 0$) with respect to calcite. Given the errors in the pH values, the Ca^{2+} and HCO_3^- concentrations, and the thermodynamic data, the SI_c values can be reported to ± 0.05 units. The theoretical CO_2 partial pressure P_{CO_2} of a hypothetical coexistent gas phase with which the water sample is in equilibrium is also calculated by WATEQF using the HCO_3^- concentration and pH of the sample. The stream samples were considered to be supersaturated with carbon dioxide if P_{CO_2} values were greater than the normal atmospheric P_{CO_2} of $10^{-3.50}$ atm. The error in calculated log P_{CO_2} values is ± 0.03 log P_{CO_2}.

Complete chemical analyses are needed to run WATEQF, but only Ca^{2+} and HCO_3^- concentrations were determined for the samples collected on the diurnal variations study. Concentrations of other cations and anions were estimated using the ratio of concentrations observed for past samples. WATEQF was then run to obtain SI_c and P_{CO_2} values.

Calcite was the only $CaCO_3$ mineral considered for the mass transfer and rate calculations. Some very fresh solid travertine was collected from a wire mesh cage that had been emplaced in Falling Spring Creek near the waterfall. This material was identified by powder X-ray diffraction to be calcite with a trace amount of detrital quartz (R. S. Mitchell, personal communication, 1986).

The calcite and CO_2 mass transfers were determined by using a mass balance on the total calcium Ca_T and the total inorganic carbon C_T between each final and initial point: (1) $Ca_T = $ calcite and (2) $C_T = $ calcite $+ CO_2$. Thus the calcite mass transfer is simply the change in calcium molal concentrations between two sampling sites. The CO_2 mass transfer is the change in total inorganic carbon concentration

TABLE 1. Selected Chemical Analyses of Falling Spring Creek

Sample	T, °C	Conductivity, $\mu S\ cm^{-1}$	pH	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	F^-	Cl^-	SO_4^{2-}
				October 14, 1984							
S-1	24.3	700	7.32	308.	165.	25.4	5.1	14.2	1.0	3.3	283.
S-3	24.6	730	7.23	316.	168.	28.0	3.9	14.8	1.1	3.5	291.
S-2	24.7	720	7.20	315.	169.	26.2	3.9	14.3	1.1	5.8	296.
D-1	24.3	730	7.24	310.	168.	26.0	3.4	14.2	1.1	3.2	283.
D-3	23.6		7.43	314.	168.	26.2	2.8	12.9	1.2	3.5	288.
F-1	21.4	695	7.79	312.	166.	25.6	3.5	13.9	1.2	3.4	286.
F-3	20.5	695	8.06	311.	164.	25.2	3.7	14.0	1.0	3.5	283.
F-4	19.7	690	8.27	278.	160.	25.6	3.6	14.3	1.0	3.8	286.
F-5	19.6	690	8.28	273.	157.	25.5	3.1	14.1	1.1	3.4	283.
F-2	18.4	660	8.37	264.	151.	25.6	3.2	14.3	1.0	3.4	283.
F-6	14.4	442	8.25	210.	122.	21.3	3.3	11.4	0.7	4.0	246.
				April 6, 1985							
S-1	20.0	590	6.98	234.	102.	17.0	2.5	6.8	0.5	3.3	150.
S-3	20.0	600	6.91	239.	105.	17.1	2.9	7.3	0.6	3.9	159.
S-2	20.0	600	6.89	240.	106.	16.6	2.4	6.9	0.6	3.8	159.
D-1	19.5	600	7.01	237.	103.	17.2	3.0	7.1	0.6	3.6	158.
D-3	17.0	595	7.19	237.	104.	16.6	2.4	6.6	0.6	3.8	158.
F-1	17.0	600	7.41	235.	104.	16.9	2.5	6.5	0.6	3.7	160.
F-3	16.5	520	7.83	234.	102.	16.5	2.8	6.9	0.6	3.8	162.
F-4	13.0	510	7.98	224.	100.	16.3	2.7	6.6	0.6	3.7	162.
F-5	13.5	488	7.92	220.	99.	16.2	2.5	6.7	0.6	3.8	162.
F-2	13.5	461	7.98	209.	97.	16.7	2.3	6.4	0.6	3.9	164.
F-6	11.0	393	8.08	183.	83.	15.0	2.5	5.8	0.6	4.3	142.

All concentrations are given in milligrams per liter.

minus the change in calcium concentration, which accounts for the loss or gain of HCO_3^- due to calcite precipitation or dissolution. Negative mass transfers indicate calcite precipitation and CO_2 outgassing; positive mass transfers indicate calcite dissolution and CO_2 ingassing. Mass transfers (moles per kilogram H_2O) were determined for each pair of successive points along the flow path and for each month that samples were collected.

Rates of calcite precipitation or dissolution and carbon dioxide outgassing were calculated using the mass transfers and estimates of reaction time. The average stream velocity v (meters per second) was calculated from $v = Q/A$, where Q (cubic meters per second) is the discharge and A (square meters) is the cross-sectional area of the stream. An average uniform velocity was assumed to exist along the stream for each sampling trip. Distances (meters) between sampling sites were read from a topographic map. Reaction time (seconds) between successive sampling sites was then computed from distance divided by velocity. Finally, reaction rates (moles per kilogram H_2O per second) were calculated by dividing the

mass transfers of $CaCO_3$ and CO_2 between two sites by the reaction time.

RESULTS

Chemical Data

The results of the chemical analyses (Table 1) show that Ca^{2+} and HCO_3^- dominate the chemical character of Falling Spring Creek. The other important ions are SO_4^{2-} and Mg^{2+}. K^+ is elevated relative to Na^+ concentrations with $Na^+:K^+$ molar ratios generally being 1:2 to 1:4. Cl^- and F^- are present in low concentrations. NO_3^- and PO_4^{3-} concentrations were determined to be below 5 and 1 mg L^{-1}, respectively. The pH of the waters ranged from near neutral to values as high as 8.50. The complete results of this study are reported in the work by Lorah [1987].

For each month that samples were collected, Ca^{2+} and HCO_3^- concentrations generally decreased downstream (Figures 2 and 3). Large decreases in Ca^{2+} and HCO_3^- concentrations occurred between the crest of the falls (F-3) and
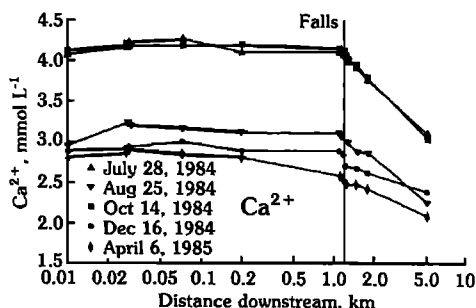

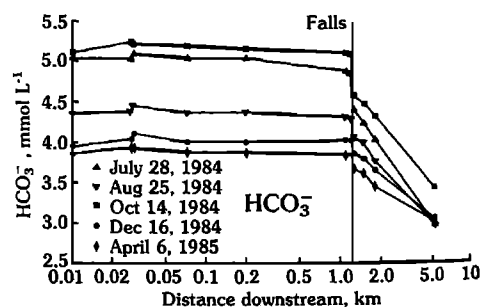Fig. 2. Millimolar Ca^{2+} concentration versus distance along the flow path.

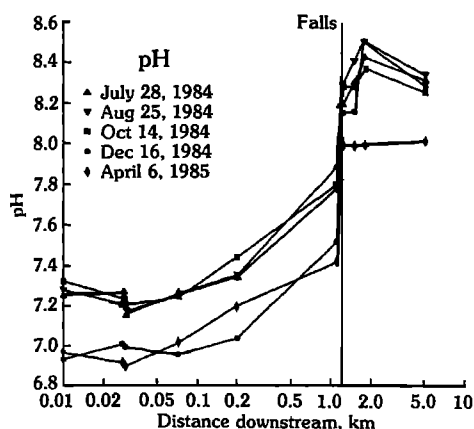Fig. 3. Millimolar HCO_3^- concentration versus distance along the flow path.

Fig. 4. The pH versus distance along the flow path.

the last sampling site (F-6). These downstream changes were more pronounced in the summer and fall than in the spring and winter months (Figures 2 and 3). For example, HCO_3^- concentrations dropped by 48% from site F-3 to F-6 in October, 1984, while in April 1985 a 28% decrease was observed. The pH increased downstream except for a drop between the last two sampling sites (Figure 4). The most rapid change in pH occurred near the crest of the falls (F-1 to F-3) and directly at the waterfall (F-3 to F-4).

The downstream changes in Ca^{2+} and HCO_3^- concentrations are much greater than the effect of dilution by inputs of groundwater to the stream. Concentrations of conservative constituents such as F^- and Cl^-, which can act as indicators of dilution, do not show a significant decrease along the flow path (Table 1). In addition, discharge measurements did not indicate significant groundwater recharge or surface runoff entering the stream (Table 2). On the October sampling trip, discharge differed by 12% between site D-3 and the last sampling site, F-6. This difference is probably within the error of the flow measurements. Only a 3% difference is seen in the discharges measured on the February trip. The December flow measurements show a greater variation (23%); however, the measurements do not reflect a pattern of increasing discharge downstream, as might be expected if groundwater recharge is occurring. Instead, the random differences appear to represent errors in the measurement technique. A small intermittent tributary (D-2) did flow during part of the sampling period,

TABLE 2. Flow Data for Falling Spring Creek

Date	Location	Discharge, $m^3 s^{-1}$	Cross-Sectional Area, m^2	Velocity, $m s^{-1}$
June 23, 1984	D-3	0.366	2.35	0.156
July 28, 1984	D-3	0.323	1.77	0.182
Aug. 25, 1984	D-3	0.372	1.77	0.210
Oct. 14, 1984	D-3	0.217	1.78	0.122
Oct. 14, 1984	F-1	0.228	1.72	0.133
Oct. 14, 1984	F-6	0.243	2.20	0.110
Dec. 16, 1984	D-3	0.345	1.76	0.196
Dec. 16, 1984	F-1	0.266	2.25	0.118
Dec. 16, 1984	F-6	0.438	2.66	0.165
Feb. 16, 1985	D-3	0.508	1.68	0.302
Feb. 16, 1985	F-6	0.521	2.53	0.206
April 6, 1985	D-3	0.441	1.56	0.283
April 6, 1985	F-6	0.476	2.48	0.192

TABLE 3. Chemical Analyses and WATEQF Results for the Diurnal Variations Study

Sampling Time	T, °C	Conductivity, μS cm^{-1}	pH	HCO_3^-, $mg L^{-1}$	Ca^{2+}, $mg L^{-1}$	$\log P_{CO_2}$	SI_c
			June 18, 1985				
1:15 P.M.	21.7	430	8.04	225.	121.	−2.75	+0.86
3:00 P.M.	21.8	445	8.08	232.	122.	−2.78	+0.92
5:00 P.M.	21.6	445	8.09	234.	121.	−2.78	+0.92
7:00 P.M.	20.7	440	8.07	239.	122.	−2.76	+0.90
9:00 P.M.	20.0	430	8.08	243.	120.	−2.77	+0.90
11:00 P.M.	19.4	430	8.06	240.	124.	−2.75	+0.88
			June 19, 1985				
1:00 A.M.	19.2	425	8.07	244.	129.	−2.76	+0.91
5:00 A.M.	19.0	410	8.07	243.	126.	−2.76	+0.90
7:00 A.M.	19.0	420	8.06	243.	127.	−2.75	+0.89
9:00 A.M.	19.1	427	8.06	243.	129.	−2.75	+0.90
11:00 A.M.	19.6	430	8.08	248.	125.	−2.76	+0.92
1:00 P.M.	20.2	437	8.09	243.	126.	−2.78	+0.94

but the volume of water that it contributes to the main stream is negligible.

Seasonally, concentrations of dissolved ions were higher in the summer and fall than in the spring and winter. The Ca^{2+} and HCO_3^- concentrations were highest in the July and October samples (Figures 2 and 3). Conductivities reached a peak in July 1984 and decreased by approximately 60% in December 1984 and February 1985.

The small changes observed in the stream chemical composition over a 24-hour period do not show an obvious time pattern (Table 3). The pH values fluctuated within 0.05 units, and Ca^{2+} and HCO_3^- concentrations varied within 0.3 mmol L^{-1}.

Saturation States

The results of the WATEQF calculations show that the stream was always supersaturated with CO_2 and usually supersaturated with respect to calcite (Table 4). Downstream and seasonal changes occurred in the P_{CO_2} and SI_c values; however, only a small variation in these values was observed over a 24-hour period (Table 3).

The calculated P_{CO_2} of the springs ranged from $10^{-2.02}$ to $10^{-1.56}$ atm throughout the year. The P_{CO_2} values then decreased downstream, except between the last two sampling sites for several of the months (Table 4, Figure 5). The most rapid decrease in P_{CO_2} along the stream occurred in the vicinity of the waterfall on each sampling trip. However, the P_{CO_2} did not fall as low as normal atmospheric P_{CO_2} ($10^{-3.50}$ atm) anywhere along the 5.2-km stretch of Falling Spring Creek that was studied.

During summer and fall, Falling Spring Creek was supersaturated with respect to calcite along the entire studied flow path (Table 4, Figure 6). In contrast, the three springs were undersaturated in the spring and winter months, although the stream water then reached supersaturation with calcite before site F-1 was reached. In the summer and fall the stream water was between 11 and 16 times supersaturated with calcite at the crest of the falls (F-3), but in the spring and winter months the water was only 3–6 times supersaturated at this site. The most rapid increases in the saturation indices occurred from near the crest of the waterfall to below the waterfall (F-1 to F-4). The saturation indices generally continued to increase

TABLE 4. Results of the WATEQF Calculations

Sample	June 23, 1984	July 28, 1984	Aug. 25, 1985	Oct. 14, 1984	Dec. 16, 1984	Feb. 16, 1985	April 6, 1985
			Calcite Saturation Indices SI_c				
S-1	+0.18	+0.35	+0.17	+0.42	−0.24	−0.22	−0.24
S-3	+0.20	+0.36	+0.15	+0.34	−0.15	−0.16	−0.29
S-2	+0.15	+0.28	+0.11	+0.32	−0.16	−0.11	−0.30
D-1	+0.20	+0.37	+0.16	+0.34	−0.20	−0.11	−0.21
D-2	−0.06	+0.12					
D-3	+0.27	+0.44	+0.26	+0.53	−0.14	−0.06	−0.06
F-1	+0.70	+0.94	+0.69	+0.84	+0.34	+0.09	+0.15
F-3	+1.06	+1.20	+1.08	+1.08	+0.80	+0.50	+0.55
F-4	+1.13	+1.15	+1.11	+1.21	+0.90	+0.60	+0.62
F-5	+1.21	+1.27	+1.21	+1.21	+0.90	+0.72	+0.56
F-2	+1.23	+1.30	+1.25	+1.25	+1.14	+0.84	+0.58
F-6	+0.80	+0.98	+0.90	+0.92	+0.81	+0.57	+0.54
			Theoretical Partial Pressure of Carbon Dioxide Gas log P_{CO_2}				
S-1	−1.80	−1.80	−1.91	−1.87	−1.60	−1.74	−1.66
S-3	−1.80	−1.81	−1.83	−1.77	−1.66	−1.77	−1.58
S-2	−1.72	−1.69	−1.78	−1.74	−1.65	−1.81	−1.56
D-1	−1.79	−1.80	−1.86	−1.79	−1.62	−1.83	−1.69
D-2	−1.91	−1.98					
D-3	−1.86	−1.89	−1.97	−1.98	−1.70	−1.89	−1.88
F-1	−2.30	−2.46	−2.41	−2.36	−2.18	−2.05	−2.11
F-3	−2.69	−2.77	−2.85	−2.64	−2.67	−2.51	−2.54
F-4	−2.92	−2.83	−2.97	−2.92	−2.86	−2.69	−2.73
F-5	−3.02	−3.02	−3.11	−2.94	−2.88	−2.83	−2.67
F-2	−3.10	−3.14	−3.23	−3.05	−3.20	−2.97	−2.76
F-6	−3.01	−3.14	−3.15	−3.04	−3.12	−3.00	−2.92

below the falls but decreased between the last two sites (F-2 to F-6).

Mass Transfers

Calcite precipitation and CO_2 outgassing characterized the chemical changes along Falling Spring Creek throughout the year (Table 5). Positive mass transfers of calcite, which indicate dissolution, only occurred upstream of the waterfall between sites D-1 to D-3 and sites D-3 to F-1 on a few dates. Calcite precipitation was always observed from near the crest of the waterfall (F-1) to the last sampling site (F-6). The July and August data showed calcite precipitating between every sampling site. All values for CO_2 mass transfer along Falling Spring Creek were negative, indicating that outgassing occurred consistently each date that samples were collected.

The total amount of calcite precipitated along Falling Spring Creek varied throughout the sampling period (Figure 7). Calcite precipitation reached a peak on the July trip (1.18 × 10^{-3} mol kg^{-1} H_2O) and remained high through October 1984. Compared to the July trip, calcite precipitation dropped by more than 50% on the February and April 1985 sampling trips (0.56 × 10^{-3} and 0.50 × 10^{-3} mol kg^{-1} H_2O, respectively).

Reaction Rates

By combining discharge measurements (Table 2) with the mass transfer calculations, rates of calcite precipitation or dissolution and of carbon dioxide outgassing were determined (Table 5, Figure 8). The chemical data for the springs could not be averaged and treated as a single sampling site along the
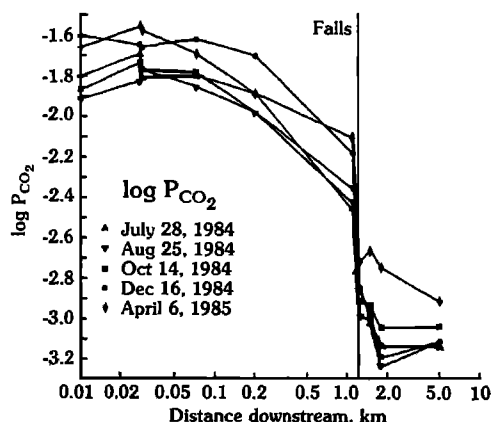

Fig. 5. Calculated partial paressure of carbon dioxide gas P_{CO_2} versus distance along the flow path.
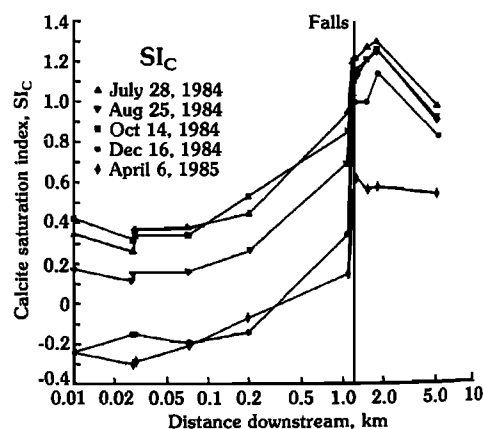

Fig. 6. Saturation state with respect to calcite SI_c versus distance along the flow path.

TABLE 5. Selected Calculated Mass Transfers and Reaction Rates Along Falling Spring Creek

Sampling Sites (Initial to Final)	Mass Transfers		Reaction Rates	
	Calcite, mol kg^{-1} H_2O	CO_2 Gas, mol kg^{-1} H_2O	Calcite, mol kg^{-1} H_2O s^{-1}	CO_2 Gas, mol kg^{-1} H_2O s^{-1}
	October 14, 1984			
D-1 to D-3	$+2.00 \times 10^{-5}$*	-1.58×10^{-4}	$+1.91 \times 10^{-8}$*	-1.50×10^{-7}
D-3 to F-1	-4.99×10^{-5}	-2.22×10^{-4}	-6.62×10^{-9}	-2.94×10^{-8}
F-1 to F-3	-6.87×10^{-5}	-7.05×10^{-5}	-8.38×10^{-8}	-8.60×10^{-8}
F-3 to F-4	-9.25×10^{-5}	-5.29×10^{-4}	-5.64×10^{-7}	-3.22×10^{-6}
F-4 to F-5	-6.13×10^{-5}	-2.16×10^{-5}	-2.99×10^{-8}	-1.05×10^{-8}
F-5 to F-2	-1.51×10^{-4}	-2.20×10^{-5}	-6.14×10^{-8}	-8.95×10^{-9}
F-2 to F-6	-7.38×10^{-4}	-5.76×10^{-5}	-2.64×10^{-8}	-2.06×10^{-9}
	April 6, 1985			
D-1 to D-3	$+1.37 \times 10^{-5}$	-2.68×10^{-4}	$+2.55 \times 10^{-8}$	-4.98×10^{-7}
D-3 to F-1	0.00	-2.66×10^{-4}	0.00	-6.88×10^{-8}
F-1 to F-3	-4.49×10^{-5}	-1.96×10^{-4}	-1.07×10^{-7}	-4.67×10^{-7}
F-3 to F-4	-6.24×10^{-5}	-1.43×10^{-4}	-7.43×10^{-7}	-1.70×10^{-6}
F-4 to F-5	-1.30×10^{-6}	-4.82×10^{-5}	-1.24×10^{-9}	-4.59×10^{-8}
F-5 to F-2	-6.62×10^{-5}	-1.35×10^{-4}	-5.25×10^{-8}	-1.07×10^{-7}
F-2 to F-6	-3.37×10^{-4}	-1.09×10^{-4}	-2.35×10^{-8}	-7.64×10^{-9}

Negative signs denote calcite precipitation or CO_2 outgassing; positive signs denote calcite dissolution or CO_2 ingassing.

*Suspect because they contradict the saturation state of the water with respect to calcite.

flow path because both the chemical composition and the flow volume of the springs differ from one another. In addition, several smaller springs enter the stream before site D-1. Therefore all reaction rate simulations along Falling Spring Creek begin slightly downstream of the springs (D-1) and end at the last site (F-6).

For each sampling trip, calcite precipitation and CO_2 outgassing rates varied over two or three orders of magnitude along Falling Spring Creek (Figure 8). The lowest calcite precipitation rates or small dissolution rates were seen at the beginning of the stream, commonly between sites D-1 to D-3 or sites D-3 to F-1. Calcite precipitation rates reached a distinct maximum at the waterfall throughout the sampling period, varying between 151×10^{-9} and 2280×10^{-9} mol kg^{-1} H_2O s^{-1}. The rates dropped again downstream of the falls but generally remained higher than those seen above the falls (D-1 to F-1).

The CO_2 outgassing rates also increased significantly as the stream flowed over the waterfall (Figure 8). Outgassing rates at the falls varied between 403×10^{-9} and 4180×10^{-9} mol kg^{-1} H_2O s^{-1} throughout the sampling period. At all other sampling locations along Falling Spring Creek, outgassing rates were only between 0.57×10^{-9} and 781×10^{-9} mol kg^{-1} H_2O s^{-1}. Outgassing rates dropped to a minimum between the last two sites (F-2 to F-6) on each sampling date.
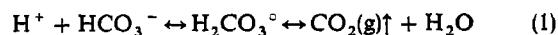
DISCUSSION

Carbon dioxide outgassing and calcite precipitation or dissolution are the two major processes controlling the chemical changes along Falling Spring Creek. The combined evidence of the water chemistry data, the saturation state of the waters relative to carbon dioxide gas and calcite, and the mass transfer and reaction rate data help define these processes and their effect on the surface water system.

Carbon Dioxide Outgassing

The three springs emerging from Warm River Cave have a high concentration of CO_2 throughout the year. A state of

disequilibrium with respect to CO_2 often exists between carbonate springs and the normal atmosphere. Other thermal springs in western Virginia have P_{CO_2} values as high as $10^{-0.56}$ atm [*Helz and Sinex*, 1974; *Hobba et al.*, 1979]. Fourteen carbonate springs in the Central Appalachians were found to contain about an order of magnitude more CO_2 than the atmospheric partial pressure [*Shuster and White*, 1971]. Subsequently, outgassing occurs during surface flow as the stream water tries to reach equilibrium with the atmosphere.

The decrease in HCO_3^- concentration (Figure 3) and increase in pH downstream (Figure 4) reflect the loss of CO_2 along Falling Spring Creek. The following reaction explains these changes in the chemical composition of the water:

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3° \leftrightarrow CO_2(g)\uparrow + H_2O \qquad (1)$$

Thus H^+ ions are consumed during degassing to give a rise in pH, and an equal amount of HCO_3^- ions is lost from solution.

Rates of CO_2 transfer out of solution (Figure 8) are relatively high immediately downstream of the springs, between sites D-1 to D-3 (85×10^{-9} to 498×10^{-9} mol kg^{-1} H_2O
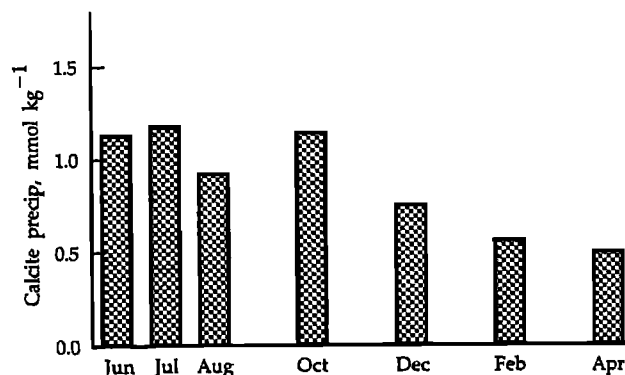

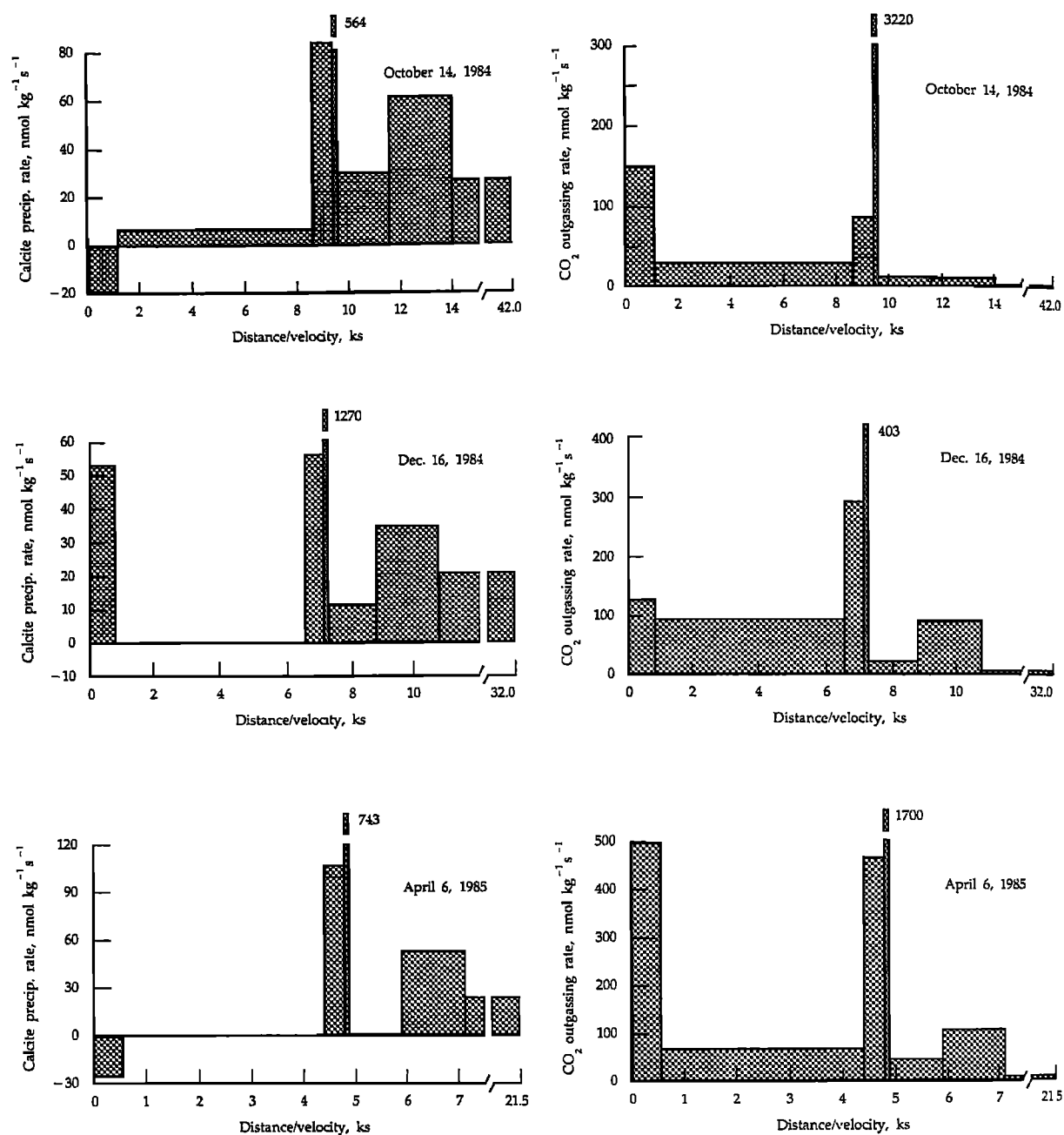Fig. 7. Total amount of calcite precipitated along the stream versus the sampling date.

Fig. 8. Calcite precipitation and CO_2 outgassing rates along the flow path versus reaction time (distance/velocity) between sampling points. Three representative sampling dates are shown.

s^{-1}). However, no distinct decrease in HCO_3^- concentration occurs between these sites (Figure 3). Concentration of HCO_3^- is a less sensitive parameter than pH to changes in the partial pressures of CO_2 [Shuster and White, 1971; Jacobson and Usdowski, 1975]. For example, a pH change from 8.0 to 8.5 by loss of CO_2 to the atmosphere results in a change in H^+ concentration of 7×10^{-9} mol L^{-1}. By the requirements of stoichiometry in (1), there is a corresponding change of 7×10^{-9} mol L^{-1} or only 4.3×10^{-4} mg L^{-1} HCO_3^- [Barnes, 1965].

Although the water is still highly supersaturated with CO_2, outgassing rates drop significantly along the next 920 m of Falling Spring Creek (D-3 to F-1). Between these sampling locations the stream flows along a fairly smooth and straight path. As the stream encounters the small riffles near the top of

the falls (F-1 to F-3) and the waterfall itself (F-3 to F-4), water turbulence forces a more rapid flux of CO_2. The water chemistry changes even more dramatically as the stream forms a cascade over the 20-m high vertical cliff. Carbon dioxide gas escapes from the turbulent water as fast as 4180×10^{-9} mol kg^{-1} H_2O s^{-1} (Figure 8). The first distinct decrease in HCO_3^- concentration is seen at the waterfall (Figure 3).

This study clearly shows the direct relationship between rapid CO_2 outgassing and turbulent areas in carbonate streams. Several other researchers have observed this relationship [Jacobson and Usdowski, 1975; Dandurand et al., 1982], but none have quantified the outgassing rates. Turbulence causes water to become dispersed, which increases the surface area of solution in contact with the atmosphere and allows a high rate of CO_2 escape at the liquid-gas interface. Dandurand
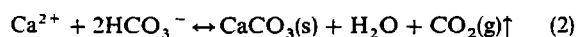
et al. [1982] show that the surface area of the water at a 24-m cascade is a function of the discharge of the stream. During high-flow conditions the water in the cascade is less dispersed; consequently, outgassing rates are slower. When discharge is lower, a small amount of water is well dispersed at the falls. High-flow conditions at Falling Spring Creek occur during the winter and spring, while low flow is seen in summer and fall (Table 2). Outgassing rates at the waterfall averaged 920 $\times$ 10^{-9} mol kg^{-1} H_2O s^{-1} from the December, February, and April 1985 sampling trips. Rates were higher between June and October 1984, with an average of 2970 $\times$ 10^{-9} mol kg^{-1} H_2O s^{-1}. These results support the conclusions of *Dandurand et al.* [1982].

Outgassing rates generally drop to a minimum between the last two sampling sites (F-2 to F-6), because the CO_2 concentration gradient between the solution and the air is at a minimum (Figure 8). Temperature is another factor that could slow down the outgassing rates. Water temperatures drop by as much as $10°C$ along the flow path (Table 1), as the thermal spring water adjusts to the cooler air temperature and as evaporative cooling occurs. Even during the summer, the air temperature was slightly lower than the spring-water temperature and then became cooler in the wooded area between the waterfall and the last sampling site. Because CO_2 solubility increases with lower temperatures, the rate of degassing would decrease downstream.

The stream is still slightly supersaturated with CO_2 at the last sampling site, which lies approximately 5.2 km downstream of the surface springs. Carbonate waters are known to remain supersaturated with CO_2 after many hours of contact with the open atmosphere [*Barnes*, 1965; *Jacobson and Langmuir*, 1970]. Approximately 6–12 hours, depending on the flow velocity on a sampling date, elapse as a volume of water flows from the surface springs to the last sampling site.

Calcite Precipitation

Calcite precipitation is extensive along Falling Spring Creek because the low P_{CO_2} of the open atmosphere and the turbulence of the stream water allows extensive CO_2 degassing. Calcite precipitation can be shown by the reaction

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3(s) + H_2O + CO_2(g)\uparrow \quad (2)$$

Calcite does not precipitate instantaneously as supersaturation is reached. The Ca^{2+} and HCO_3^- concentrations remain nearly constant for the first 1120 m along Falling Spring Creek (S-1 to F-1), even though the water becomes more and more supersaturated with calcite (Figures 2 and 3). In the summer and fall months the water has attained between 5 and 9 times supersaturation with respect to calcite by the time site F-1 is reached (Table 4), but mass transfer and reaction rate calculations indicate that calcite precipitation is very low or nonexistent upstream of this sampling location (Figure 8).

In the turbulent areas near the crest of the falls and at the waterfall itself, the rapid increase in CO_2 outgassing rates and in calcite supersaturation allows the kinetic inhibitions on calcite crystallization to be overcome. A large decrease in the Ca^{2+} and HCO_3^- concentration provides chemical evidence that significant calcite precipitation begins in the vicinity of the waterfall (Figures 2 and 3). The HCO_3^- concentrations drop more dramatically than Ca^{2+}, as both calcite precipitation and CO_2 outgassing now act as removal mechanisms for HCO_3^-. High calcite precipitation rates (Figure 8) are first

seen near the crest of the falls (F-1 to F-3), but the rates reach a maximum at the waterfall (F-3 to F-4).

Physical evidence for calcite precipitation exists in the travertine deposits observed in some areas of the stream. Travertine is not noticeable between the springs and site F-1. However, near the crest of the falls buildups of travertine have formed small rimstone dams and coatings over rocks, twigs, bottles, and other materials in the streambed. Travertine covers the vertical cliff at the falls in thick "cascade-type" deposits, characterized by draped and stalactitelike forms that are layered due to successive coatings of travertine [*Chafetz and Folk*, 1984; *Dennen and Diecchio*, 1984]. At the base of the falls, fresh white calcite crusts were observed on everything, including undecomposed leaves and twigs. Travertine deposits are most extensive at and immediately below the falls, but more rimstone dams are evident for at least 1.0 km downstream of the falls. Thus the combined chemical and physical evidence suggests that calcite precipitation begins and reaches its maximum rate in the highly turbulent area of the waterfall.

The pattern of calcite precipitation observed along Falling Spring Creek demonstrates the kinetic inhibition to nucleation and crystal growth that has been noted in many laboratory studies and in several other field studies of travertine-depositing streams [*Jacobson and Usdowski*, 1975; *Usdowski et al.*, 1979; *Dandurand et al.*, 1982]. Besides the energy barrier to calcite nucleation [*Berner*, 1980; *Stumm and Morgan*, 1981], a lack of suitable nucleation sites [*Suarez*, 1983] and the presence of dissolved magnesium or phosphate ions [*Berner*, 1975; *Reddy*, 1977; *Morse*, 1983] are factors that can strongly inhibit the precipitation of calcite. One field study has shown that close contact of stream water with previously deposited travertine accelerates calcite precipitation rates in the vicinity of waterfalls [*Steidtmann*, 1936]. Contact with calcite as a nucleation site does not seem necessary for deposition at Falling Spring Creek, as travertine coatings are found on any material in the water's path. Particles in suspension and material on the channel bottom and sides could act as nucleation sites at every site along the stream; therefore the availability of nucleation sites probably does not retard calcite precipitation in this stream.

Although phosphate was not detectable, magnesium was present in fairly high concentrations (Table 1). There does not appear to be, however, a strong relationship between the magnesium concentration and the critical degree of supersaturation observed in the stream. Near the crest of the falls (F-1) where calcite precipitation mainly begins, the water was between 1 and 9 times supersaturated with respect to calcite between June 1984 and April 1985 (Table 4). Yet the molar ratio of Mg^{2+} : Ca^{2+} in the stream water was nearly constant throughout this period, ranging between 0.21 and 0.30. In a travertine-depositing stream studied by *Jacobson and Usdowski* [1979] the Mg^{2+} : Ca^{2+} ratio was much higher (approximately 0.45), but the critical degree of calcite supersaturation was not any higher than the values observed in Falling Spring Creek. Several laboratory experiments have shown that Mg^{2+} does not inhibit calcite precipitation at Mg^{2+} : Ca^{2+} ratios lower than approximately 1 [*Katz*, 1973; *Berner*, 1975].

The energy barrier to nucleation is probably the major factor inhibiting calcite precipitation in Falling Spring Creek. The rapid degassing of CO_2 and subsequent rise in the calcite supersaturation state at the waterfall allow this barrier to be passed, even at the relatively low degree of supersaturation observed in the winter and early spring (Table 4). It is not

clear why precipitation can begin at lower supersaturation levels during these months. Possibly, the high-flow conditions in winter and spring increase the amount of particles in suspension in the stream. These particles could act as seeds on which the critical nuclei could form so that the nucleation energy needed is decreased [Nielsen, 1964; Berner, 1980].

Although the rate of precipitation is not as high as at the waterfall, calcite deposition continues along the 4 km of stream that was studied below the falls (Figure 8). Despite this prolonged precipitation, the water remains far from equilibrium with calcite at the last sampling site. As calcite precipitates, more CO_2 is produced (equation (2)) and must be simultaneously removed from solution to maintain the high level of calcite supersaturation observed. The pH and calcite saturation index decrease significantly between the last two sampling sites (Figures 4 and 6), showing that here calcite precipitation finally begins to outpace the loss of CO_2 from the stream water. Once the driving force of CO_2 outgassing has been decreased, Falling Spring Creek can begin to adjust toward equilibrium with calcite.

Seasonally, the amount of calcite precipitated along Falling Spring Creek is tied to the mixing of the two carbonate waters inside Warm River Cave [Herman and Lorah, 1986, 1987; Lorah, 1987]. During low-flow conditions in summer and fall (Table 2), less shallow groundwater is available to dilute the highly concentrated thermal water inside the cave, and the mixed stream emerges at the surface already supersaturated with calcite. Outgassing of CO_2 can then drive the stream water to a higher degree of supersaturation than observed during the spring and winter. Consequently, more calcite must be precipitated per unit volume of water to move toward equilibrium with calcite. On the July trip when travertine deposition was at a maximum, a total of 11.8×10^{-4} mol $CaCO_3$ kg^{-1} H_2O, or 0.118 g $CaCO_3$ kg^{-1} H_2O, was precipitated along the studied section of Falling Spring Creek (Figure 7). During the spring and winter months high-flow conditions existed, causing the thermal cave stream to become greatly diluted by shallow groundwater. In April 1985 the net amount of calcite precipitated was 5.0×10^{-4} mol $CaCO_3$ kg^{-1} H_2O, or 0.050 g $CaCO_3$ kg^{-1} H_2O. Thus net calcite precipitation does occur throughout the year at Falling Spring Creek but decreases by more than 50% during times of high flow.

Only one other study of the travertine deposition along Falling Spring Creek has been conducted. Dennen and Diecchio [1984] collected water samples at three locations along the stream during March and April 1984 but did not find evidence of active calcite precipitation. They postulated that active precipitation would be expected in the late summer when the stream would not be diluted by surface runoff. The amount of calcite precipitation is instead largely controlled by the degree of mixing and dilution occurring inside Warm River Cave. Dennen and Diecchio also expected the zone of maximum deposition to be farther downstream in the early spring than in late summer; however, the present study indicates that calcite precipitation reaches a maximum at the waterfall throughout the year.

Biologic Effects on Calcite Precipitation

Biologic processes are not an important influence on calcite precipitation in Falling Spring Creek. If metabolic removal of dissolved carbonate species by organisms such as algae, fungae, and bacteria is significant, a diurnal cycle should show a minimum for HCO_3^- and P_{CO_2} and a maximum for pH

during the daytime [Barnes, 1965; Stumm, 1985]. The daytime uptake of CO_2 would be reflected in increased supersaturation with respect to calcite; at night the situation would reverse. However, a 24-hour study at Falling Spring Creek did not reveal any significant variations in the P_{CO_2} or SI_c values (Table 3). The variations that are seen are generally within the error in the calculated log P_{CO_2} and SI_c values (± 0.03 and ± 0.05 units, respectively).

With a high concentration of dissolved CO_2 in a stream, a great amount of $CaCO_3$ can precipitate inorganically upon degassing; therefore biologic processes become relatively unimportant in removing CO_2 from solution [Chafetz and Folk, 1984]. In a calcite-depositing stream in the Pyrenees of southern France, carbonate springs supply HCO_3^- at a rate of approximately 25 g HCO_3^- s^{-1}. In that system metabolic effects are not strong enough to influence calcite precipitation [Dandurand et al., 1982]. The same conclusion is reported for a stream that has a supply rate of 1.2 g HCO_3^- s^{-1} [Jacobson and Usdowski, 1979]. In comparison, the average supply rate in Falling Spring Creek is 101 g HCO_3^- s^{-1}, as determined from the average HCO_3^- concentration of the three springs and the average discharge throughout the year. Thus 4–100 times more dissolved CO_2 flows through Falling Spring Creek than seen in previous studies where biologic processes were shown to be negligible.

Errors in the Reaction Rates

The reaction rate calculations are affected by errors in the chemical analyses and in the hydrologic data used to obtain the reaction times. Some of the mass transfer results are certainly suspect because they contradict the saturation state of the water with respect to calcite (Table 5). These contradictory results were only seen immediately downstream of the springs between sites D-1 to D-3 or sites D-3 to F-1. The Ca^{2+} concentrations often stayed the same or differed only slightly from the initial to the final water in this area of the stream. Because very small changes in Ca^{2+} concentrations were being subtracted, relatively small errors in the chemical analyses would have become more noticeable. Thus a small amount of calcite dissolution could easily be shown rather than a small amount of calcite precipitation.

Errors in the reaction times, which were estimated from the discharge measurements, could also lead to errors in the rates. When discharge was measured at several points along Falling Spring Creek on a sampling trip, the values differed by 3–23% (Table 2), and most of this variation in the discharge is caused by analytical error. A large error in the reaction time probably occurs from assuming a uniform velocity along the stream on each sampling date. As the cross-sectional area of a stream changes, the flow velocity changes if a constant discharge is assumed. However, it would have been impractical to determine the cross-sectional area and flow velocity at every sampling location. The assumption of uniform velocity is probably accurate upstream of the waterfall where the stream flows along a fairly straight uniform channel. A large degree of error in the reaction time is most likely at the waterfall and for a short distance downstream of the falls where the stream forms a series of pools and small travertine dams.

CONCLUSIONS

The processes of carbon dioxide outgassing and calcite precipitation or dissolution control the chemical evolution of the travertine-depositing stream in this study. When the carbonate

groundwater issues from Warm River Cave to the surface and feeds Falling Spring Creek, a large amount of CO_2 outgassing occurs as the stream water tries to reach equilibrium with the low CO_2 content of the open atmosphere. Outgassing forces the solution to high degrees of supersaturation with respect to calcite. By using mass balance calculations and estimated reaction times, we were able to quantify the rates of CO_2 outgassing and calcite precipitation along the flow path.

Calcite precipitation rates are low or nonexistent along the first 1120 m of Falling Spring Creek where the stream flows along a quiet smooth path. Rapid CO_2 outgassing and increased calcite supersaturation in the vicinity of the waterfall are needed to overcome the kinetic inhibitions on calcite nucleation and growth. Travertine deposits are first observed near the crest of the falls, providing physical evidence that calcite precipitation mainly begins in this area. At all times of the year CO_2 degasses most rapidly at the 20-m high waterfall where water turbulence is greatest. Outgassing rates varied from 403×10^{-9} to 4180×10^{-9} mol kg^{-1} H$_2$O s^{-1} at the falls. Consequently, calcite precipitation rates also reach a distinct maximum at the waterfall, ranging from 151×10^{-9} to 2280×10^{-9} mol kg^{-1} H$_2$O s^{-1} throughout the year. Biological uptake of CO_2 by organisms such as algae or moss has an insignificant effect on travertine precipitation compared to the large amount of inorganic CO_2 outgassing. Although outgassing and calcite precipitation continues below the falls, the stream water does not attain equilibrium with respect to either CO_2 or calcite by the time the last sampling point, which lies 4 km downstream of the waterfall, is reached. Net calcite precipitation occurs along Falling Spring Creek throughout the year but decreases by more than 50% during the high-flow conditions in the spring and winter.

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