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Geochemical and Biogeochemical Interactions in a Hot Spring

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Southeast Harney Lake Hot Spring and its effluent channel were examined for spatial and temporal variations in the concentrations of several chemical species, viz. dissolved oxygen, pH, alkalinity, phosphate-phosphorous, nitrate and nitrite-nitrogen, conductivity, chloride, flouride, temperature, calcium, magnesium, potassium, and sodium. Phosphate-phosphorous and nitrate-nitrogen both exhibited downstream increases in concentration. pH and alkalinity increased also, mainly due to CO_2 evolution and temperature mediated carbon species redistribution. The diurnal pH and alkalinity curves exhibited depressions during the daylight hours due to the oxidation of ammonia to nitrate within the pool and effluent stream.

GEOCHEMICAL AND BIOGEOCHEMICAL INTERACTIONS IN A HOT SPRING

by

WILLIAM DELIS KNOX

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
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TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of William Delis Knox presented October 23, 1980.

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INTRODUCTION

The chemical, physical, and biological characteristics of a great many thermal springs throughout the world have been published. Waring (1965) published an annotated bibliography of the thermal springs in the United Stated, a small portion of a world wide bibliography of over 3700 thermal springs in open files with the U.S. Geological Survey. Castenholz (1969) published an extensive review of the thermophilic blue-green algae.

With few exceptions there has been little work done on the spatial and temporal variations of the chemical components of a thermal spring, most of the work being focused on the biological components.

World wide spatial distribution of algal species of hot springs appears to be fairly uniform. Species found growing in Yellowstone National Park can also be found growing in Indonesia (Castenholz, 1969). The spatial distribution of algae within a particular thermal system has also received a lot of attention but is usually expressed in terms of temperature distributions. Once the heated water leaves the ground, atmospheric and flow conditions determine its temperature distribution and thus that of the biota.

Above approximately 57°C no eucaryotic organisms have been found and above 74°C blue-green algae cease to be found (Castenholz, 1969). Sulfur bacteria have been found growing at 93°C but their temperature for optimum uptake of various labeled organic compounds was between 80°C and 90°C (Brock, et al., 1971). Below 57°C the number of different types of organisms that are found in thermal springs increases and primary consumers start to appear at about 50°C (Castenholz, 1969).

Seasonal variation in the biological component can be pronounced, usually due to seasonal variation of light (Stockner, 1968a; Sperling, 1975; Naiman, 1975) and variation in predatator density (Collins, et al, 1976; Stockner, 1971).

Stockner (1968b), working on a portion of an effluent channel of Ohanapecosh hot spring, reported a very regular cyclic change in the relative abundance of diatoms, although neither absolute numbers nor biomass were reported. He attributed these changes to light adaption.

Submerged algal mats of Mastigocladus laminosa in Icelandic hot springs were found by Sperling (1975) to exhibit a dramatic decrease in biomass from their summer maximum. Portions of the mat with a southern exposure exhibitied greater rates of production than portions with northern exposures.

Monthly standing crop in Topeka Bore, Mojave Desert (Naiman, 1975), exhibited cyclic behavior over the course of a year and a half. It was lowest during the winter months, 522 kcal/m^2 (56 gC/m^2) in October, 1972 and reached a peak of 1056 kcal/m^2 (113 gC/m^2) in April, 1973. Primary production reached a minimum of 1.16 gC/m^2/day in December, 1972 and a peak of 4.86 gC/m^2/day in May, 1973. For each sampling station along the stream there were large differences between minimum and maximum rates but the mean annual rate was fairly constant at 3.5 gC/m^2/day along the middle portion of the length of the stream. The temperature varied from 38°C to 45°C.

Collins, Mitchell, and Wiegert (1976) suggest that seasonal increases in primary production may be due in part to predation upon the algal mat material by primary consumers. By predation of Paracoenia turbida (Diptera) larvae upon senescent patches of algal material these areas were converted to areas of higher productivity, probably by the elimination of mechanical barriers to nutrient flow. Brock (1967) has shown that algal photosysthesis is more efficient per unit chlorophyll in habitats with flies than in higher temperature habitats without flies.

Variation in stream length standing crop and primary productivity as well as diurnal variation in productivity along a thermal stream were studied by Brock (1967) in Mushroom Spring, Yellowstone National Park. The stream was approximately 53 meters long and the temperature varied from 72°C to 33°C.

Peak standing crop was found between 50° to 60°C regardless of the terms in which it was measured, i.e., chlorophyll content, DNA content or protein content. From 33° to 45°C, chlorophyll A content remained constant and then increased to its maximum value (100% of the greatest value) at 58.5°C, then dropped sharply between 65° and 68°C. C^{14} uptake reached a maximum value at around 48°C and remained constant to 58.5°C, thereafter it too dropped off rapidly. Sunrise to sunset variation in photosynthetic efficiency was also measured at various stations along the stream. These results indicate, generally, that the integrated photosynthetic efficiency (in cpm/ug chlorophyll A/hour) was highest at 68°C and decreased with decreasing temperature.

Stockner (1968a) reports an example of diurnal variation in net primary productivity in Ohanapecosh hot spring. A maximum value of 97 mg O_2/m^2/hour was measured for the 1230 to 1330 hours interval and decreased to 31 mg O_2/m^2/hour before sunset. Changes in calcium and magnesium concentrations were also measured. Calcium varied inversely with productivity, attributed to CO_2 removal during photosynthesis.

There was no significant variation in magnesium.

Other than the above mentioned references to calcium and magnesium diurnal variation, no other reports of diurnal variation of other chemical components of biological interest have been found, although Stockner (1968a) did report periodic values of nutrient concentrations, alkalinity, and total dissolved solids (TDS) throughout the four year period of the study. Nitrate-nitrogen ranged from 0.035 mg/l to 0.064 mg/l; total phosphorous, .068 mg/l to 0.095 mg/l; dissolved ortho-phosphate, 0.041 mg/l to 0.061 mg/l; alkalinity (bicarbonate alkalinity as $CaCO_3$) 817 mg/l to 834 mg/l; and total dissolved solids, 2.6 gm/l to 2.76 gm/l.

Brock (1967) reported no change in phosphate concentration, 2.7 mg/l between the source and the foot of Mushroom Spring, a distance of 53 meters. In the same distance however, ammonia and nitrate concentrations increases: 0.012 mg/l to 0.026 mg/l in the case of ammonia and 0.001 mg/l to 0.008 mg/l in the case of nitrate. These increases in nitrate and ammonia were attributed to nitrogen fixation (Brock, 1967; Stewart, 1970).

Castenholz (1969) reports an increase in phosphate-phosphorous from less than 0.040 mg/l at the source to over 0.100 mg/l 20 meters downstream of Hunters Hot Springs, Oregon. Similarly, nitrate-nitrogen increased from zero at one source to from 0.042 mg/l to 0.142 mg/l in the same distance.

Wiegert and Fraliegh (1972), using four boards as an artificial stream bed, found no change in concentration in approximately 8 meters of dissolved ortho phosphate (0.17 mg/l), nitrate-nitrogen (less than 0.05 mg/l) and average alkalinity (bicarbonate) (238 mg/l) in

Serendipity Springs in Yellowstone National Park.

The present study was undertaken to examine the relationship between the geochemical and biolgocial activity of Southeast Harney Lake Hot Spring. Evident in the studies cited above, the geochemical characteristics of a hot spring set the stage for the kinds of organisms that may exist and the activities they may partake in. The current study demonstrates that in addition to the chemical and physical changes in the water that occur upon exposure to atmospheric conditions, the biological activity mediates some of the chemical changes. This study then is an examination of the geochemical and biogeochemical changes in the spring water downstream from a hot spring and an estimation of the chemical, physical, and biological processes which bring about these changes.

DESCRIPTION OF STUDY AREA

South Harney Lake Hot Spring (unofficial name; 4°11' North, 119° 2' West) is located in the northcentral portion of Harney County in southeastern Oregon (Figure 1). The study area is located at the east end of the High Lava Plains Province and is characterized by young lava flows of moderate relief. There is abundant evidence of extensive volcanic activity during the Pliestocene and Recent times. The soils in the immediate area of the spring are formed from lacustrine deposits in old lake beds. The soils are deep and silty, with a subsurface clay horizon and extensive sodium accumulations. The vegetation in the basin area is characterized as shrubland, Artemesia sp. being the most abundant plant. The climate is characterized by warm dry summers and cold winters (Franklin and Dyrness, 1973).

The spring is typical of the numerous alkaline hot springs in the Harney Basin area. Numerous small springs at the base of a hill discharge directly into a common pool of approximately 450 square meters. From this pool a stream flows southwesterly down a gentle slope, taking on a meandering character. Approximately 450 meters from the source pool the stream flows into a marshy area and from there eventually flows into Harney Lake (Figure 2).

The water issues from the ground at a temperature of about 60°C and with a total discharge rate of 6 to 10 liters/sec., depending upon the hydraulic conditions.

Within the pool there is an extensive algal and bacterial mat very similar to that described by Brock (1969) in Yellowstone National Park. The upper 3mm of the mat is composed of the green filamentous bacterium

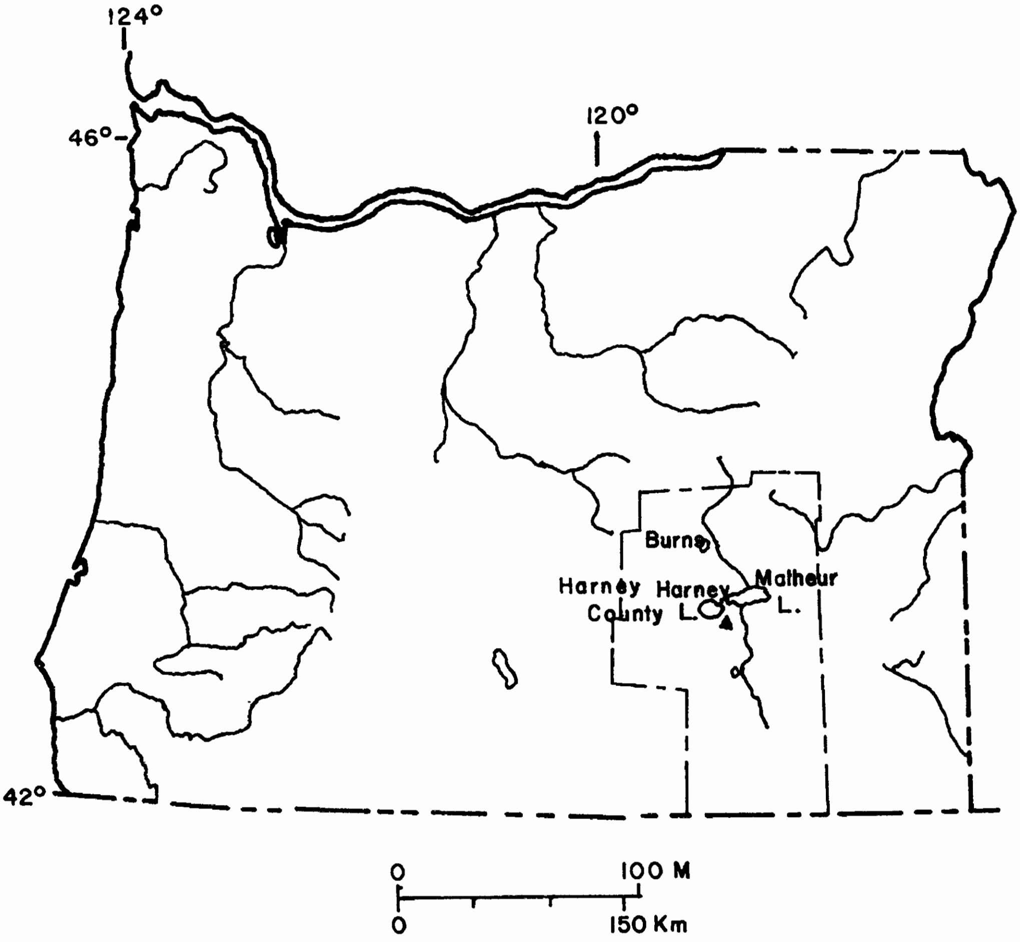

Figure 1. Location of study site (triangle) in Harney County, Oregon

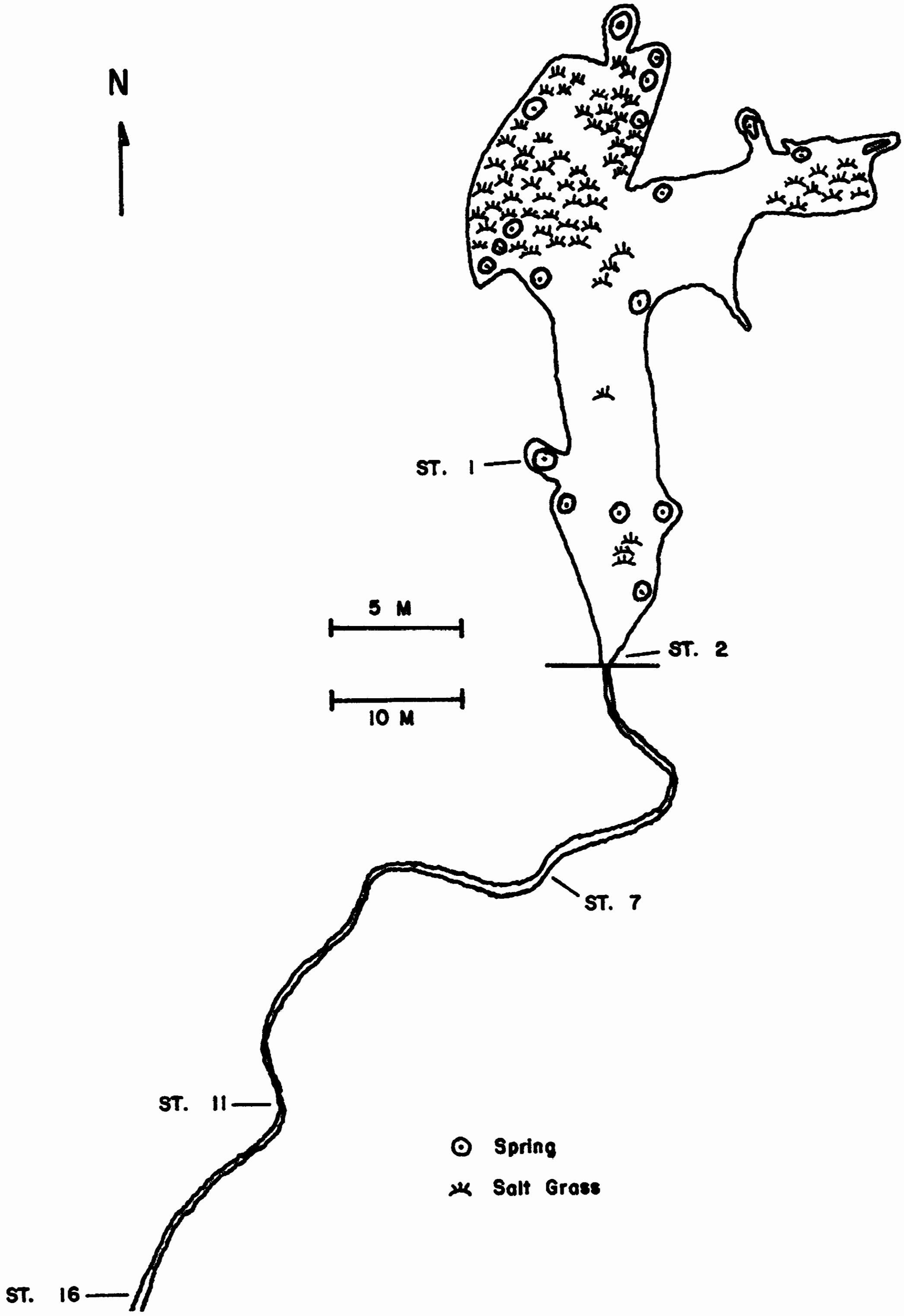

Figure 2. Southeast Harney Lake Hot Spring

Chloroflexus aurantiacus and the rod shaped blue-green alga *Synechococcus lividus*. The more coccoid shaped *Synechococcus minerva* is also present but not very abundant. Other less common algae in the mat are *Pseudanabaena* sp. and *Spirulina labyrinthiformis*.

The lower portion of the mat is composed of layers of amorphous material and high densities of rod shaped bacteria. Throughout the lower portion of the mat and especially at the mat-sediment interface there are extensive sulfide deposits. For the most part the mat extends to the surface of the pool and even slightly above the water surface. The mat averages about 2 cm thick and the water reaches a maximum depth of about 15 to 20 cm. There are areas where the mat is not sitting on the substrate but floats, typically in the neighborhood of the throat of a spring. The interior temperature of the mat is about 45°C. The water courses through channels cut in the mat.

Russel (1903), in a survey of artesian basins in portions of Idaho and Oregon, published a short description of the spring. Piper et al. (1939) also published a description of the spring along with a photograph and a chemical analysis of the water (Table II). The present physical appearance of the spring and its chemical composition of the water is not very different from those reported by Russel (1903) and Piper et al. (1939).

Station 2, the station at which the diurnal measurements were made, is located at the start of the effluent channel. The width of the channel is 45 cm and has a maximum depth of 15 cm, representing a cross-sectional area of 415 cm^2 and a discharge rate of 10 liters/sec. The algal flora at Station 2 is represented almost entirely by *Synechococcus lividus* arranged into streamers.

Appendix I presents the spatial distribution of algal species along the length of the stream.

MATERIALS AND METHODS

The spatial variation in pH, alkalinity, dissolved orthophosphate-phosphorous, nitrate-nitrogen, dissolved oxygen, Ca^{++}, Mg^{++}, Na^{+}, K^{+}, Si, Cl^{-}, F^{-}, conductivity, and temperature were measured on 1 and 2 May, 1976.

The diurnal variations in dissolved orthophosphate-phosphorous, total phosphorous, nitrate-nitrogen, alkalinity, pH, dissolved oxygen, and temperature were measured during 2 and 3 April, 1977.

The diurnal measurements were made at Station 2 (Figure 2). This is the point where the effluent channel began and it was assumed that this point represented an integration of all the chemical and biological activity within the pool.

The discharge rate was measured on 2 May, 1976 using a Gurly meter at a well defined, smooth flowing portion of the effluent channel. The discharge rate on 3 April, 1977 was measured by the time of passage of a float between two measured marks for each transverse subdivision of the effluent channel.

Temperature was measured with a mercury bulb thermometer and a Yellowsprings Instrument Co. Telethermometer. Although the telethermometer registered a maximum temperature of 50°C there was a -3°C error. Throughout the period of measurement the telethermometer did not register greater than 50°C. The measured temperature plus the correction factor agreed with the mercury thermometer at all times.

Conductivity was measured at the U.S. Geological Survey Laboratory, Portland, Oregon, with a Leeds and Northrup Co. specific conductance meter. Values are adjusted to 25°C.

pH was measured in the field with a Chemtrix Model 31 pH meter with a combination electrode. The meter was calibrated with buffer solutions at the local temperature of the water on 2-3 April, 1977 and on 1 May, 1976 it was calibrated at air temperature and manual temperature adjustments were made as needed.

Sodium and potassium concentrations were determined according to Standard Procedures (Annon., 1971) with a Perkin Elmer 305B Atomic Absorption Spectrophotometer.

Total hardness and calcium concentration were determined by EDTA titration as outlined in "Standard Methods" (APHA, 1971). Total hardness was assumed to be due to calcium and magnesium only and magnesium was determined by difference. Reference to literature on similar types of water indicates that this is a good approximation although it will exaggerate the Mg concentration (Castenholz, 1969).

Nitrate and nitrite-nitrogen were determined in the field colorimetrically with a HACH Kit, using HACH chemicals and methods with modifications. Instead of using the supplied scales for NO_3-N and NO_2-N, the percent transmittance scale was used. Standard solutions were taken into the field and standard curves were made at the time of analysis.

Chloride was determined by mercuric nitrate titration as outlined in "Standard Methods" (APHA, 1971).

Flouride and sulfate were measured in the laboratory using HACH Kit. The procedure was the same as that used for nitrate and nitrite-nitrogen.

Silicon (reactive silica as Si) concentration was determined using the method of H.L. Golterman (1969). Due to the high silica content of the water, a 1 to 50 dilution was used. Absorbance was measured on a Beckman Spectrophotometer 20 with a 1 cm cell.

Dissolved orthophosphate-phosphorous concentration was measured using Shapiro's (1973) modification of the method of Strickland and Parsons (1968). Particulate phosphorous was determined by boiling 100 ml of sample with 5 ml concentrated sulfuric acid. Orthophosphate-phosphorous was then measured as above. Particulate phosphorous was assumed to be the difference between this measurement and the dissolved orthophosphate-phosphorous measurement. Total phosphorous was measured in the laboratory using the EPA ascorbic acid method.

Dissolved oxygen on 2 May, 1976 and 4 April, 1977 was measured with a YSI Model 51A Dissolved Oxygen Meter equipped with a stirring electrode. The diurnal oxygen measurements were made on 2 to 3 April, 1977 with a Chemtrix Dissolved Oxygen Meter.

Alkalinity was determined by potentiometric titration. The end point was found by a linear regression of a Gran plot (Stumm and Morgan, 1970).

With the exception of temperature, pH, dissolved oxygen, dissolved orthophosphate-phosphorous extraction, nitrate and nitrite-nitrogen all chemical analyses were done in the laboratory within two weeks of sample collection.

The CO_2 (H_2CO_3*), HCO_3^-, and CO_3^{-2} concentrations were calculated assuming a closed system for all stations considered. Even though the stream and the pool are not closed to the atmosphere this is not an untoward assumption. Station 1, a source spring within the pool, was sampled below the water surface within the throat of the spring, presumably before any appreciable shift in equilibrium can take place. Calculations show that the water is supersaturated with CO_2. Thus the system does not start out equilibrated with the atmosphere. The later diurnal measurements at Station 1 show that the stream is in a state approaching dynamic equilibrium; alkalinity is constant and the pH varies cyclically and slowly in time. Thus the effects of atmospheric CO_2 intrusion can be neglected and the system considered closed and each point in the system can be considered at steady state through time.

In the calculations involving the buffering system, corrections were made for temperature and ionic strength. Activity coefficients were calculated using the Guntelberg equation:

$$\log f = -AZ^2 \frac{\sqrt{I}}{\sqrt{1 + I}}$$

where I is the ionic strength, $A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$ (T in degrees Kelvin) and Z is the ion charge. The effect of temperature on the dielectric constant of water (ε) was also taken into account. Data for ε versus temperature was obtained of the Handbook of Chemistry and Physics, 42nd edition (CRC, 1960). Data for the various equilibrium constants were obtained from Stumm and Morgan (1970).

The equilibrium constants used in the buffering system calculations are:

$$K_1' = \frac{(H^+)(HCO_3^-)\ f_{H^+}\ f_{HCO_3^-}}{(H_2CO_3^*)\ f_{H_2CO_3^*}} = K_1 \frac{f_{H^+}\ f_{HCO_3^-}}{f_{H_2CO_3^*}}$$

$$K_2' = \frac{(H^+)(CO_3^=)\ f_{H^+}\ f_{CO_2^-}}{(HCO_3^-)\ f_{H_2CO_3^*}} = K_2 \frac{f_{H^+}\ f_{CO_3^=}}{f_{HCO_3^-}}$$

H^+ was measured with a pH meter and assuming pH = p^aH then $f_{H^+} = 1$; the ionic charge on $H_2CO_3^*$ is zero thus $f_{H_2CO_3^*} = 1$. The above equations become:

$$K_1' = K_1 f_{HCO_3^-}$$

$$K_2' = K_2 \frac{f_{CO_3^=}}{f_{HCO_3^-}}$$

Changing to pK

$$pK_1' = pk_1 - \log f_{HCO_3^-}$$

$$pK_2' = pk_2 - \log f_{CO_3^=} + \log f_{HCO_3^-}$$

or

$$pK_.' = pk_1 + AZ^2_{HCO_3^-} \frac{\sqrt{I}}{1+\sqrt{I}} = pK_1 + A \frac{\sqrt{I}}{1+\sqrt{I}}$$

$$pK_2' = pk_2 + A(Z^2_{CO_3^=} - Z^2_{HCO_3^-}) \frac{\sqrt{I}}{1+\sqrt{I}} = pK_2 + 3A \frac{\sqrt{I}}{1+\sqrt{I}}$$

The data for the dielectric constant were fit with a second degree polynomial that is in excellent agreement with the published values. pK_2 values published by Stumm and Morgan (1970) were fit with a third degree polynomial and pK_1 was regressed against the reciprocal of the temperature.

RESULTS AND DISCUSSION

Table I presents a summary of the streamlength distribution of temperature for three seasons, late winter, spring, and late summer. The mean and standard deviation exclude the data for 1 May, 1976 to avoid bias in the spring data. The 1 May, 1976 temperature data is also presented in Table I. As seen from the standard deviations, the source at Station 1 is less variable than any downstream station. A hint of seasonality can be seen as the temperature for all seasons increases through the summer, from March, 1975 to September, 1975. The diurnal temperature data (Figure 7) also illustrates the effect of variation in atmospheric conditions upon the stream temperature. Prior to and at the start of the diurnal temperature measurements there was a stiff wind blowing from the northwest. As the wind died down between 6 and 8 p.m., the water temperature increased steadily. As the air temperature increased the next day, the water temperature increased due to the decreased temperature differential between water and air. During the night both the air and water temperatures were steady.

Using the Na-K-Ca geothermometer for natural waters presented by Fournier and Truesdell (1973), the temperature of last interaction of water with rock occurred at 150°C. Presumably this is the temperature of the aquifer.

Table II presents a summary of the chemical constituents of one of the springs within the source pool, Station 1, collected May, 1976. The data of Piper et al. (1939) are also included.

South Harney Lake Hot Spring can be classified as a volcanic Na, Cl-HCO_3 spring (Castenholz, 1969). The source is high in sodium (655

TABLE I

SEASONAL TEMPERATURES (°C)

Distance (M) from source	3/7/75	5/18/75	9/4/75	5/1/76	$\bar{T}$ (sd)
0	59.0	59.0	62.2	60.5	60.1 (1.8)
10	-	-	-	50.6	-
30	-	-	-	50.6	-
60	47.0	50.0	54.0	49.2	50.3 (3.5)
72	-	-	-	49.2	-
102	-	48.8	53.0	48.0	-
132	43.0	-	-	46.0	-
162	42.0	44.2	48.0	44.5	44.7 (3.0)
212	41.0	43.5	47.0	43.0	43.8 (3.0)
262	40.0	41.0	46.0	41.0	42.3 (3.2)
292	39.2	-	-	40.0	-
322	38.8	39.5	44.5	39.5	40.9 (3.1)
352	38.0	39.5	44.5	39.5	40.9 (3.1)
382	37.0	38.0	43.0	37.5	39.3 (3.2)
407	35.5	-	-	36.0	-
427	35.0	37.0	42.0	36.0	38.1 (3.6)

TABLE II

SUMMARY OF CHEMICAL DATA FOR STATION 1

All concentrations in mg/l except Alk (meq/l), conductivity (umho/cm^2), and pH

	This Study (May, 1976)	Piper, et al (1939)*
pH	6.99	-
Alk	9.51	-
P	0.10	-
NO_3-N	0.14	0.50
NO_2-N	0.01	-
O_2	0.0	-
Ca	13.8	13.
Mg	1.5	3.0
Na	655.	622.
K	21.5	12.
Si	40.2	43.
Fe	-	0.03
HCO_3	578.	601.
CO_3	1.2	0.
Cl	593.	562.
SO_4	170.	140.
F	1.9	-
TDS	1841.	1782.
Hardness**	41.4	45.
Conductivity	4033.	-

IONIC BALANCE

(Concentrations in meq/l)

Cations:		Anions:	
Na^+	28.49	HCO_3^-	9.48
Ca^{+2}	0.69	$CO_3^=$	0.04
K^+	0.55	$SO_4^=$	3.52
Mg^{+2}	0.12	Cl^-	16.73
		F^-	0.10
	29.85		29.87

Ionic Strength: 0.034 M

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* Sample collected 21 August, 1931

** As $CaCO_3$

mg/l), chloride (575 mg/l), bicarbonate (516 mg/l) and silicon (40.2 mg/l).

Table III presents the stream length distribution of some of the chemical constituents of the effluent stream. Station 1 is a spring within the source pool, Station 2 is the start of the effluent channel and Station 16 is the point where the stream enters a marshy area. A simple analysis of variance was performed to detect any gradients.

The streamlength variation in pH and alkalinity is presented in Figure 3. pH increases steadily downstream from the source spring, due mainly to the elolution of CO_2. The CO_2 concentration (Figure 4) drops from a value of 98.1 mg/l at Station 1 to 8.5 mg/l at Station 16. This loss in CO_2 is reflected in the loss of total inorganic carbon (C_t), from 141 mg/l to 126 mg/l at Station 16. After an initial increase both alkalinity and bicarbonate ion concentrations remain constant. The downstream upturn in alkalinity, and hence bicarbonate ion, and to some extent carbonate ion concentrations, is due to disturbances at this end of the stream. Several times during the sampling period cattle used the lower portion of the stream as a watering hole. Along the lower portion of the stream where C_t and HCO_3^- remain constant, decreasing CO_2 is flected in increasing $CO_3^=$. This redistribution of carbon is brought about by the effect of decreasing water temperature upon the equilibrium constants. The same effect is seen in the initial increase in HCO_3^- and $CO_3^=$ between Stations 1 and 2.

Dissolved oxygen (Figure 5) increases rapidly within the first 60 meters, from 0 mg/l to 5.3 mg/l. Thereafter dissolved oxygen remains essentially constant despite decreasing temperature. In Figure 5, the dissolved oxygen value at Station 1 was taken as zero. This is the

TABLE III

SUMMARY OF STREAMLENGTH CONCENTRATION OF VARIOUS CHEMICAL PARAMETERS

All concentrations in mg/l
except Alk (meq/l), pH

Station	Distance	pH	Alk	PO_4-P	NO_3-N	NO_2-N	DO	Hard-ness	Cl^1
1	0	6.99	9.51	.10	.14	.01	1.7	41.4	593
2	10	7.25	9.82	.21	.15	.01	4.3	39.2	597
3	30	7.43	-	.19	.15	.01	-	-	-
4	60	7.50	-	.21	.10	.01	5.3	-	-
5	72	7.50	-	.19	.10	.01	-	-	-
6	102	7.57	9.78	.18	.15	.01	5.6	40.4	597
7	132	7.60	9.79	.17	.12	.01	-	39.4	608
8	162	7.69	9.87	.17	.14	.01	5.8	38.8	606
9	212	7.75	9.87	.16	.19	.01	5.6	39.0	606
10	262	7.80	9.94	.14	.30	0	-	38.4	615
11	292	7.84	9.78	.14	.39	.03	-	39.4	611
12	322	7.90	9.89	.14	.36	.03	5.3	39.4	613
13	352	7.95	9.78	.11	.38	.02	-	38.4	611
14	382	8.00	9.90	.12	.34	.03	-	39.4	615
15	407	8.10	10.1	.11	.34	.02	6.0	38.8	615
16	427	8.10	-	.15	.32	.01	5.9	-	-

Station	Na	K	Ca	Mg	Si	F^-	Cond. (umho/cm^2)
1	655	21.5	13.8	1.5	40.2	1.9	4033
2	-	-	12.1	2.2	42.4	1.9	4103
3	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-
6	-	-	12.1	2.5	38.8	1.9	4138
7	-	-	12.1	2.3	37.3	1.9	4175
8	560	24.0	12.1	2.1	38.8	1.9	4179
9	-	-	13.0	1.6	39.5	1.9	4172
10	-	-	11.3	2.6	42.4	1.9	4176
11	-	-	12.1	2.3	40.2	1.9	4189
12	-	-	12.6	1.7	40.2	1.9	4204
13	-	-	12.5	2.0	38.0	1.9	4189
14	-	-	12.1	2.3	41.0	1.9	4201
15	690	23.0	12.1	2.0	41.7	1.9	4195
16	-	-	-	-	-	-	-

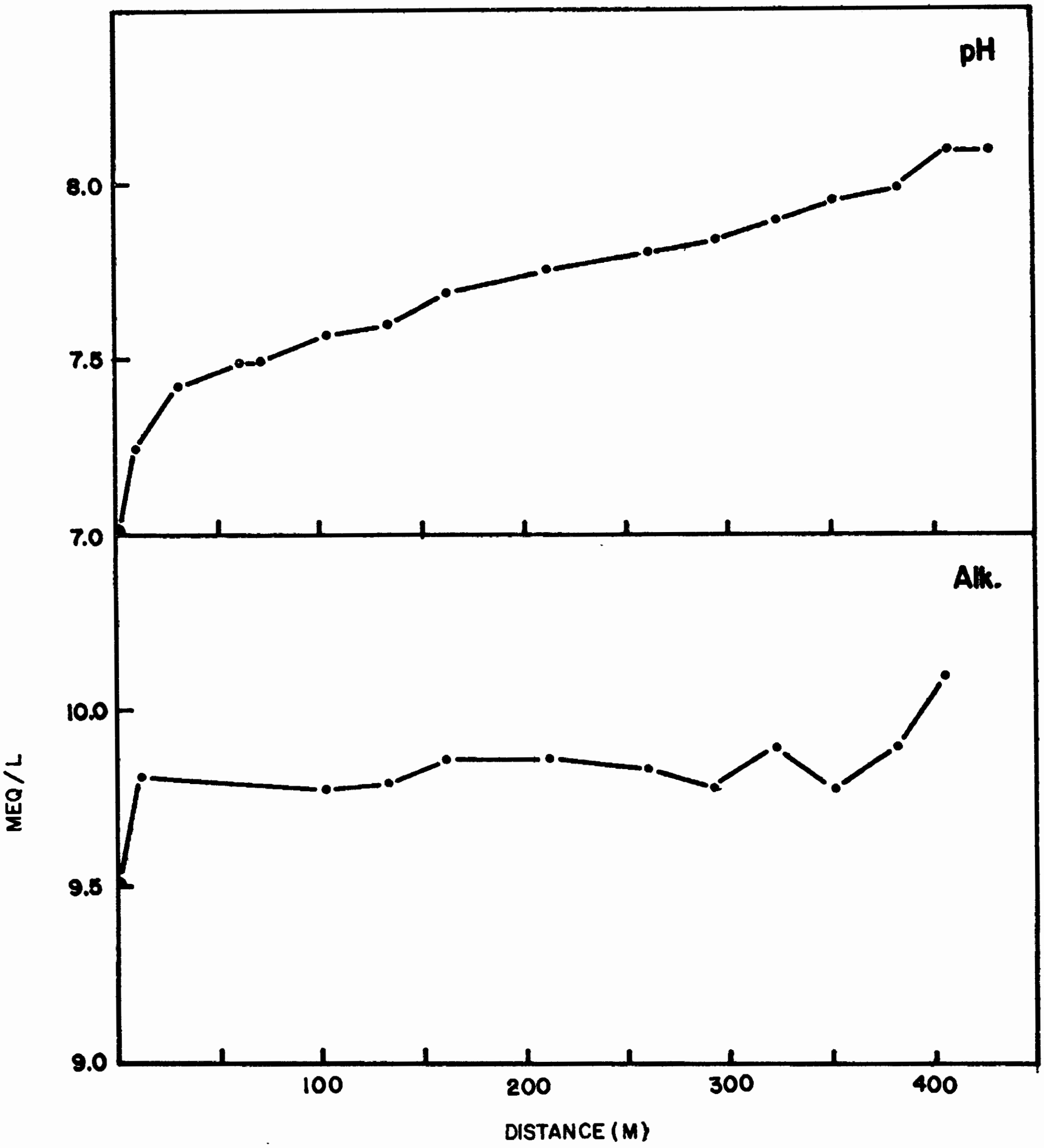

Figure 3. Streamlength alkalinity and pH measurements

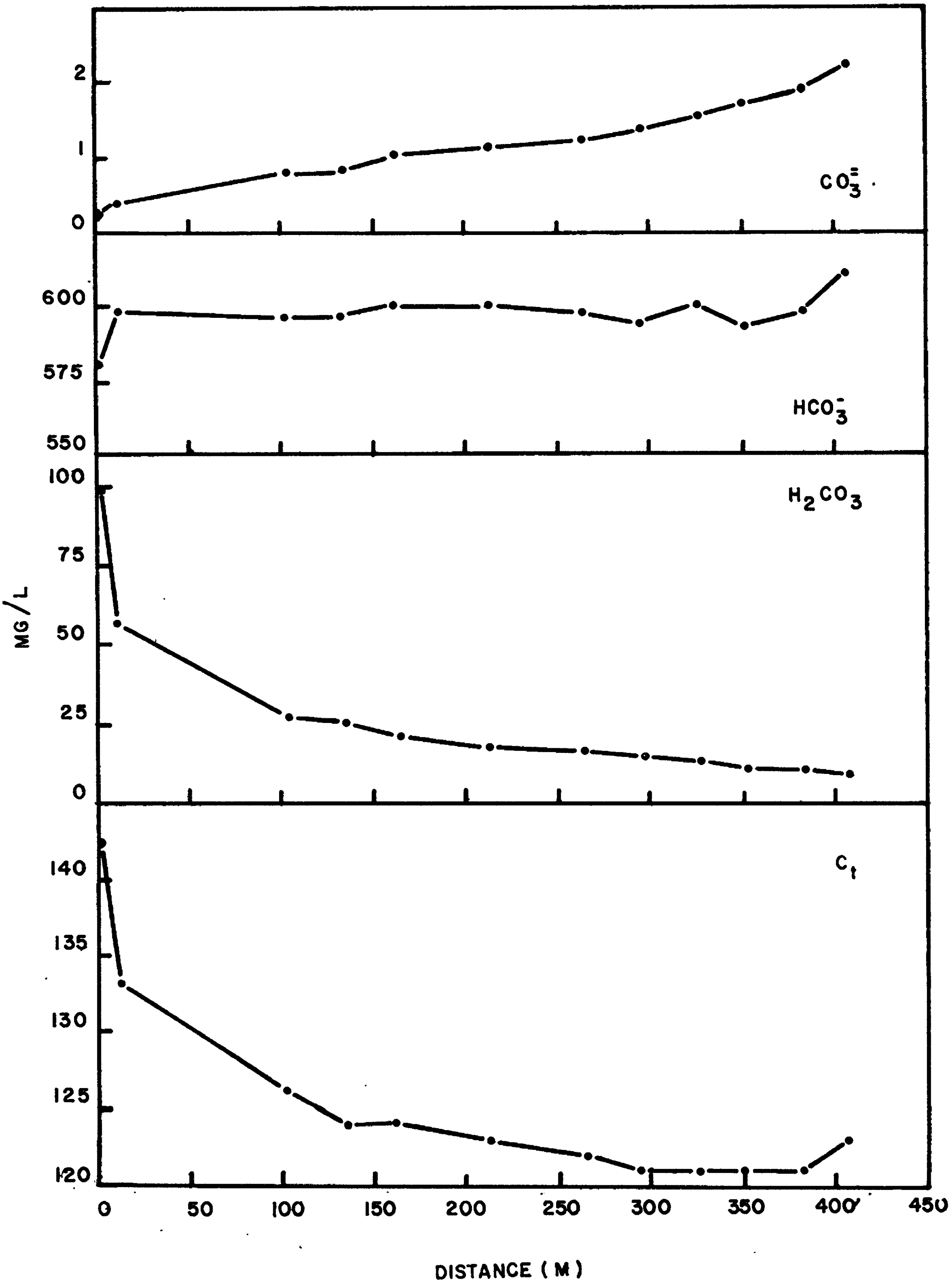

Figure 4. Streamlength carbon species distribution

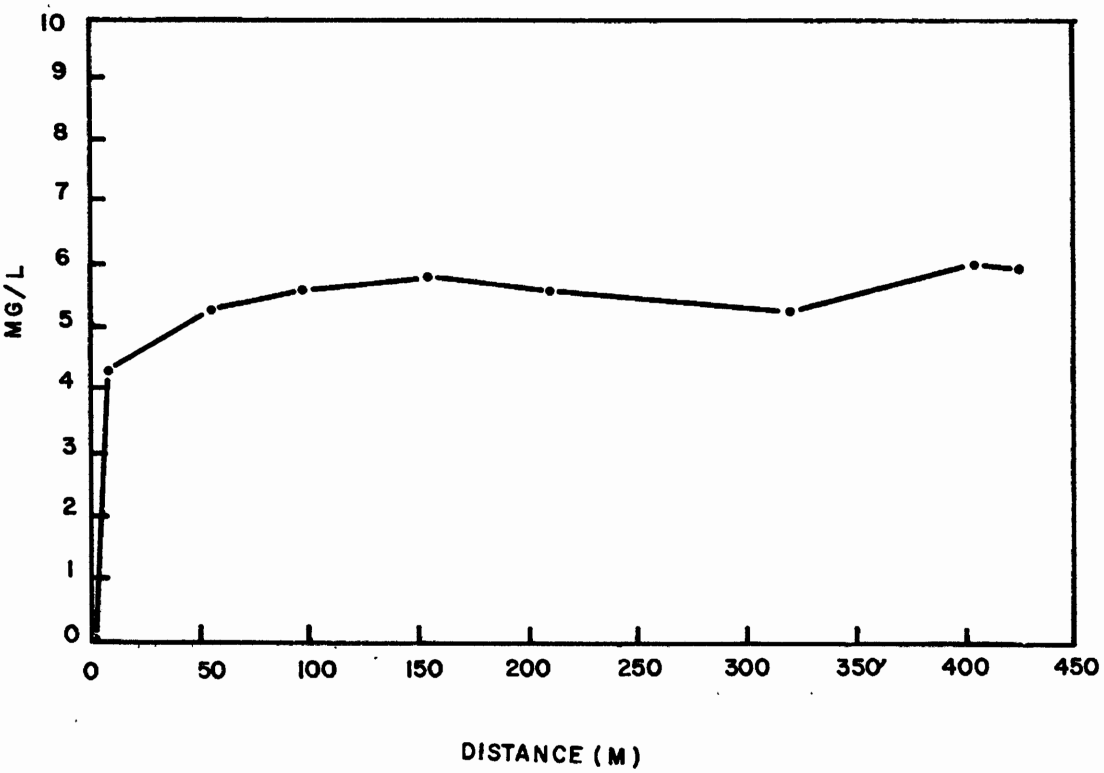

Figure 5. Streamlength dissolved oxygen measurements

value measured from a sample taken within the throat of the spring. The value of 1.7 mg/l reported in Table III is from a sample taken near the surface. The relatively large increase in dissolved oxygen is probably indicative of a large residence time within the pool. The percent saturation increases from zero within the throat to 38% near the surface to 76% at Station 2. After Station 2 the percent saturation reaches 95% at Station 6 and steadily decreases from thereon. This decrease is due to slower oxygen infusion into the stream as the equilibrium value is reached and to the lag time between temperature decrease and O_2 increase.

The increase in chloride ion and specific conductivity go hand in hand and can be accounted for by evaporation. The loss of only 36 ml water per liter results in the observed increase in Cl^-.

The data for nitrate-nitrogen and orthophosphate-phosphorous is presented in Figure 6.

At approximately 130 meters downstream from Station 1 (Station 7) nitrate-nitrogen starts to increase dramatically, from 0.12 mg/l to 0.39 mg/l 160 meters further on, Station 11. The increase can be attributed to nitrogen fixation. Stewart (1970), investigating nitrogen fixation in Yellowstone National Park, found the peak of fixation activity at a temperature of 37°C with a broad range from 28° to 45°C. Above 60°C there was a rapid decrease in the fixation rate. The upper temperature limit found by Stewart coincides nicely with the temperature of 46°C at Station 7 and as the temperature decreases further downstream the nitrate-nitrogen concentration increases.

Although biological assimilation can contribute to the downstream decrease in dissolved orthophosphate-phosphorous, the major process is

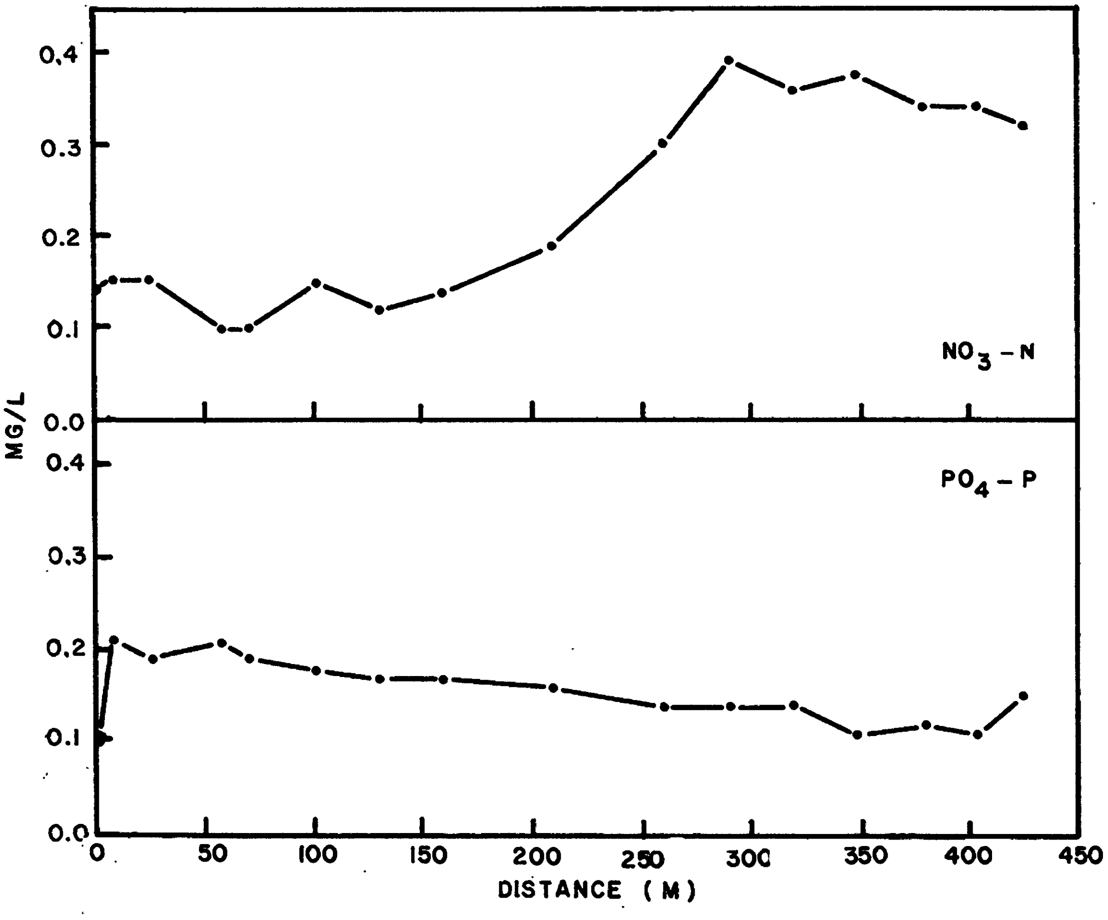

Figure 6. Streamlength nitrogen and phosphorous measurements

probably precipitation of hydroxyapatite. Using the average value of 0.27 mg/l for total phosphorous obtained from the diurnal phosphorous data (Table IV) and 13.8 mg/l for total calcium from Table II and the equilibrium constant of $10^{2.7}$ for calcium orthophosphate from Stumm and Morgan (1970), the source starts out saturated with calcium orthophosphate, $CaHPO_{4(aq)}$, with approximately 15% of the total phosphorous complexed with calcium. Calcium hydroxyapitite precipitates by the reaction

$$Ca_5OH(PO_4)_{3(s)} + 4H^+ \rightleftharpoons 2Ca^{+2} + 3CaHPO_{4(aq)} + H_2O.$$

Thus with an adequate supply of calcium orthophosphate and the downstream increase in pH (decreasing H^+ concentration) the precipitation reaction is pushed to the left.

The analysis of sediment samples collected on 2 April, 1977 presents evidence for the precipitation of phosphorous. Carbonate, measured as the loss of CO_2 upon acidification, comprises 39% of the sediment as $CaCO_3$ on a dry weight basis. Acid extractable phosphorous comprises about 0.03% of the sediment or 0.357 mg/gm on a dry weight basis.

Table IV presents the diurnal measurements collected during 2 to 3 April, 1976.

Once the water leaves the ground it is subject to atmospheric conditions (Figure 7). As noted earlier, atmospheric wind and air temperature influence the stream temperature.

The diurnal oxygen concentration behaves as one would expect (Figure 8). During the evening hours O_2 concentration decreases then remains low throughout the night due to respiration. At sunrise the O_2

TABLE IV

STATION 2 DIURNAL MEASUREMENTS

(Temperature, °C; Alk, meq/l; all else, mg/l)

Time	Air Temp.	Water Temp.	DO	pH	Alk	PO_4-P	Pt	NO_3-N
6 pm	6.0	47.5	3.10	7.67	11.40	0.058	0.275	0.20
7	-	48.0	2.70	7.66	11.33	0.058	-	0.18
8	-	51.3	2.45	7.70	11.34	0.046	0.278	0.20
9	-	50.0	2.50	7.71	11.37	0.043	-	0.20
10	-2.0	50.2	2.25	7.75	11.28	0.038	0.275	0.19
11	-4.0	50.0	2.50	7.75	11.29	0.045	-	0.16
12 am	-4.0	49.5	2.40	7.75	11.26	0.043	0.257	0.22
1	-4.0	50.0	2.40	7.75	11.30	0.039	-	0.18
2	-4.0	50.0	2.50	7.75	11.29	0.035	0.267	0.15
3	-4.0	50.0	2.40	7.75	11.32	0.030	-	0.15
4	-4.0	50.0	2.40	7.75	11.21	0.033	0.251	0.14
5	-3.5	50.0	2.30	7.70	11.26	0.028	-	0.15
6	-2.5	50.0	2.45	7.70	11.27	0.033	0.257	0.11
7	2.0	50.0	2.90	7.51	11.25	0.060	-	0.15
8	6.0	51.5	3.35	7.40	11.19	0.082	0.263	0.25
9	6.0	51.5	3.40	7.65	11.21	0.078	-	0.23
10	9.0	52.0	3.60	7.60	11.19	0.064	0.263	0.23
11	13.0	52.7	3.50	7.50	11.15	0.067	-	0.22
12 pm	18.0	52.7	3.40	7.45	11.24	0.088	0.244	0.23
1	18.0	52.2	3.40	7.45	11.21	0.067	-	0.25
2	19.0	51.9	3.40	7.41	11.23	0.103	0.257	0.23
3	15.5	51.0	3.25	7.40	11.31	0.066	-	0.23
4	16.0	50.5	3.10	7.40	11.27	0.085	0.239	0.25
5	15.5	49.7	3.00	7.45	11.28	0.057	-	0.20

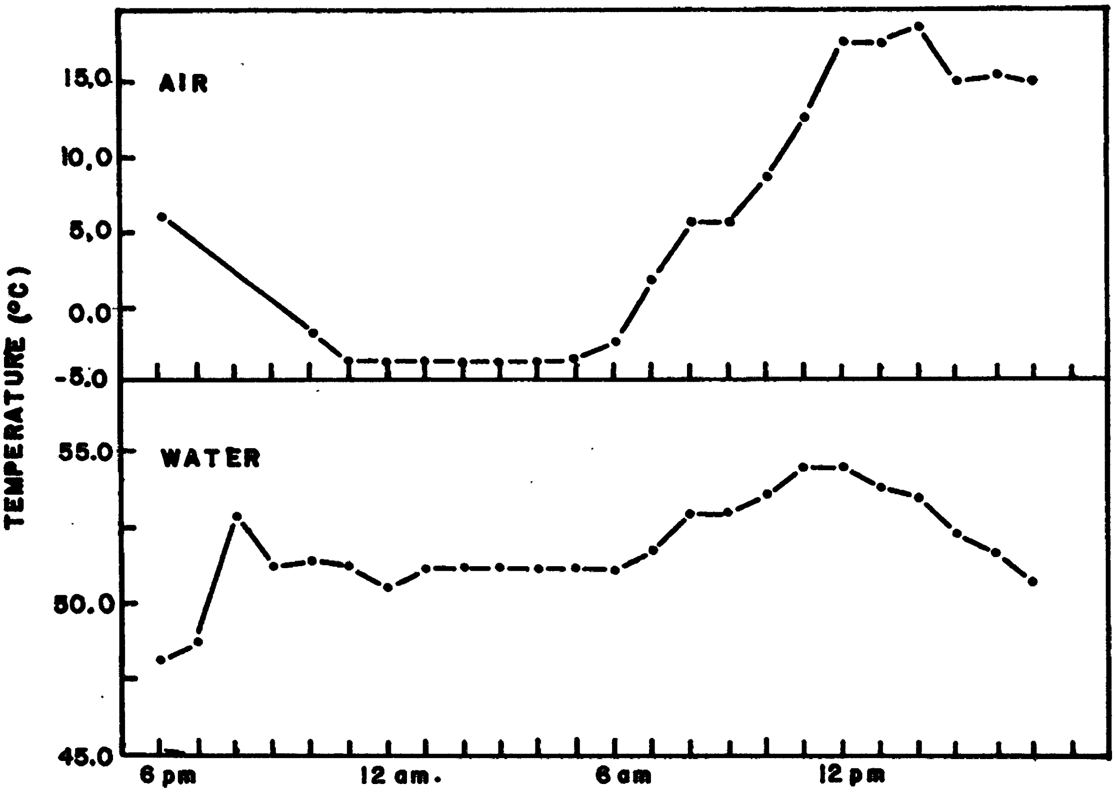

Figure 7. Diurnal water and air temperature measurements

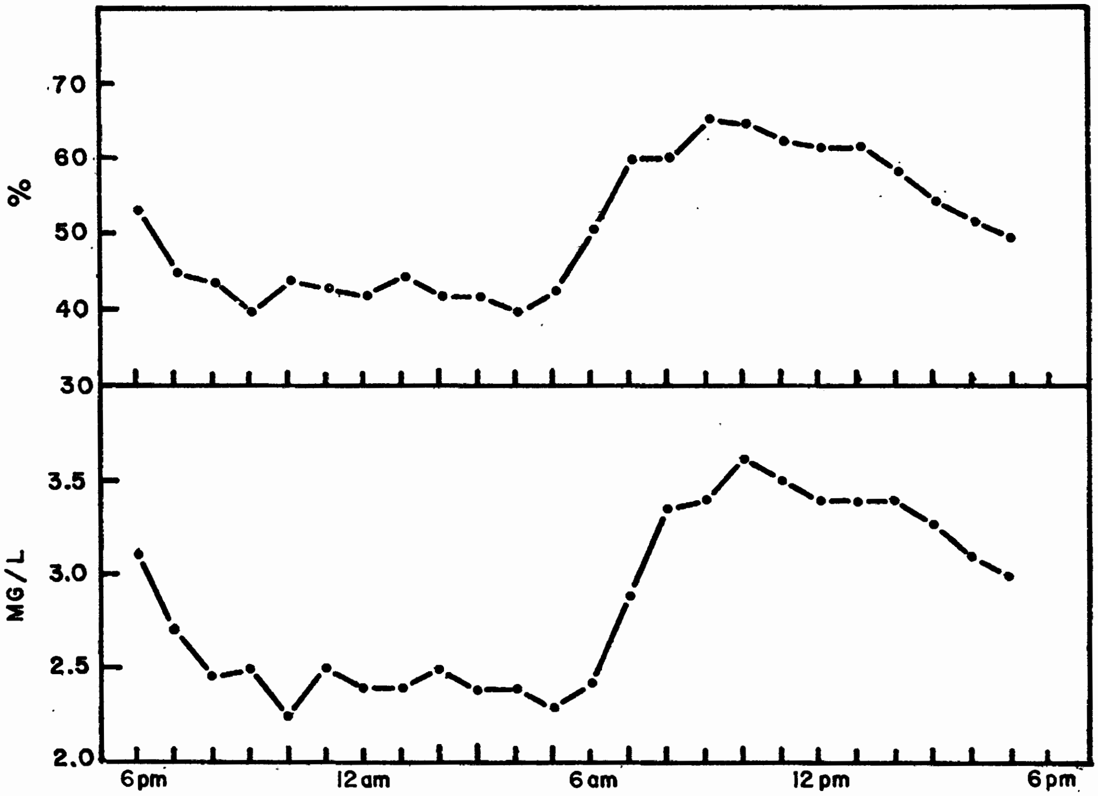

Figure 8. Diurnal dissolved oxygen measurements

concentration begins to increase, reaching a peak at around 10 am. This increase is attributable to photosynthesis.

The diurnal pH curve (Figure 9) does not behave as one would expect. Due to respiration during the dark hours pH should decrease due to a net increase in CO_2 and during the daylight hours pH should increase due to the net removal of CO_2 by photosynthesis (Verduin, 1956). The pH curve in Figure 10 displays just the opposite behavior; there is an increase in pH during the dark hours and a decrease during the light hours. (The sudden pH change between 6 and 9 am appears to be real as the pH meter was correctly calibrated.)

Alkalinity similarly decreases during the daylight hours (Figure 9). In an otherwise unperturbed system, alkalinity is independent of changes in CO_2 due to photosynthesis (Stumm and Morgan, 1970). The partitioning of the carbon species is presented in Figure 10. Of special interest is the increase in total inorganic carbon during the daylight hours, presumably due to the dissolution of precipitated carbonates by the increased H^+ concentration.

Figure 11 presents the diurnal changes in dissolved orthophosphate phosphorous, total phosphorous and nitrate-nitrogen. Dissolved orthophosphate-phosphorous increases during the daylight while total phosphorous decreases slightly. In two previous partial measurements of diurnal total phosphorous there was no detectable change. The increase in phosphate-phosphorous can also be accounted for by the increase in H^+ concentration causing the dissolution of hydroxyapatite:

$$Ca_5OH(PO_4)_{3(s)} + 4H^+ \rightleftharpoons 2Ca^{+2} + 3CaHPO_{4(aq)} + H_2O$$

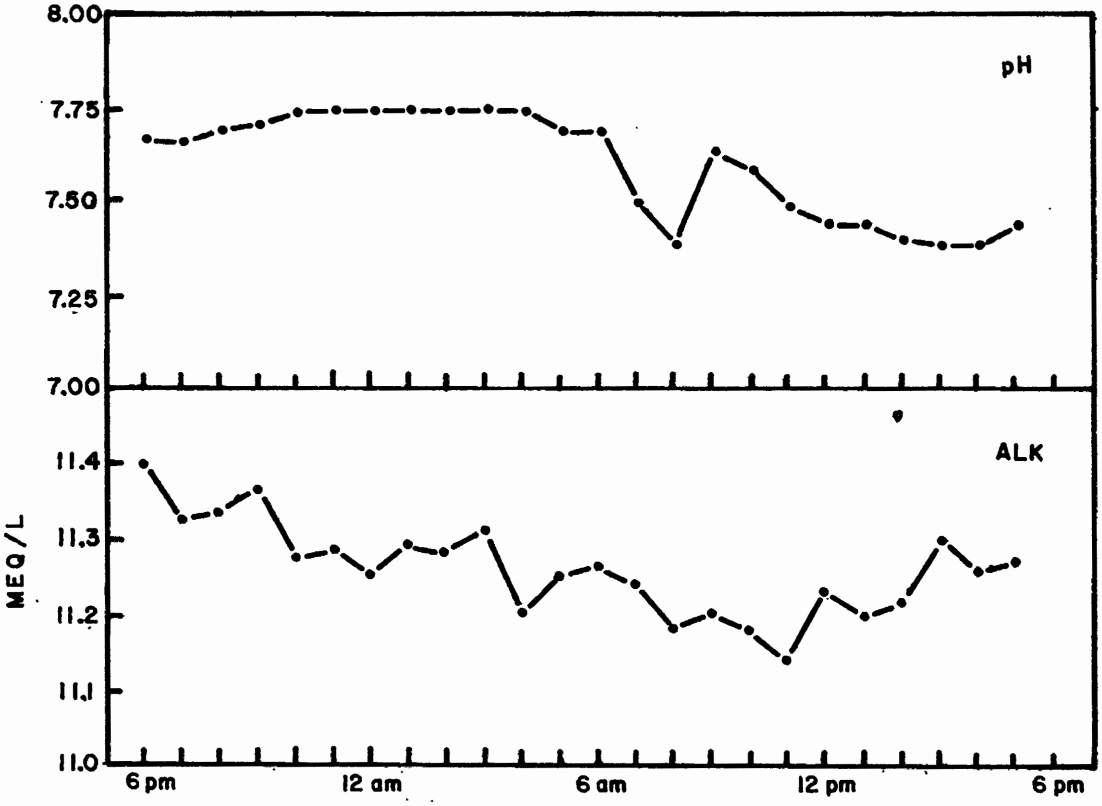

Figure 9. Diurnal pH and alkalinity measurements

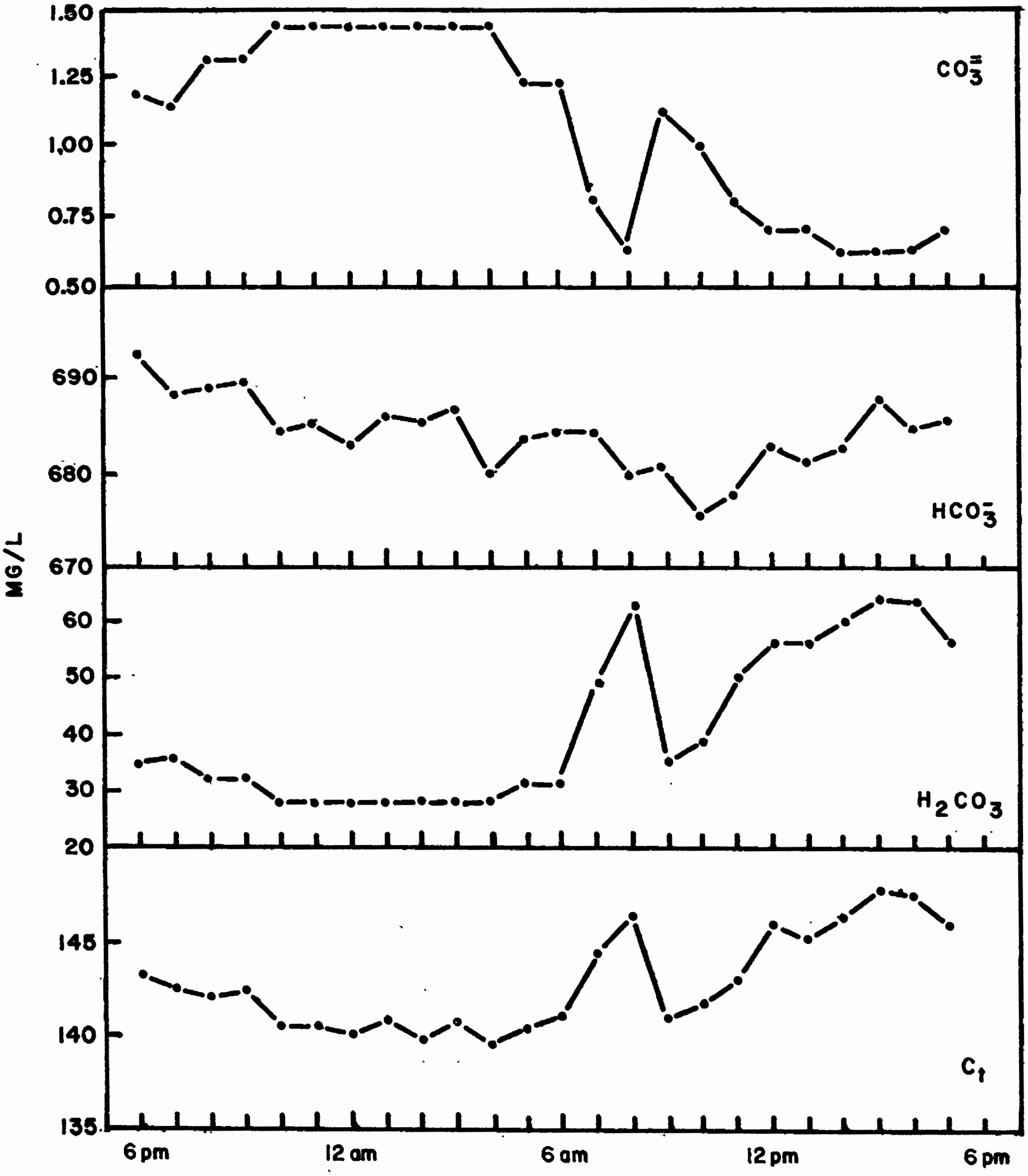

Figure 10. Diurnal carbon distribution

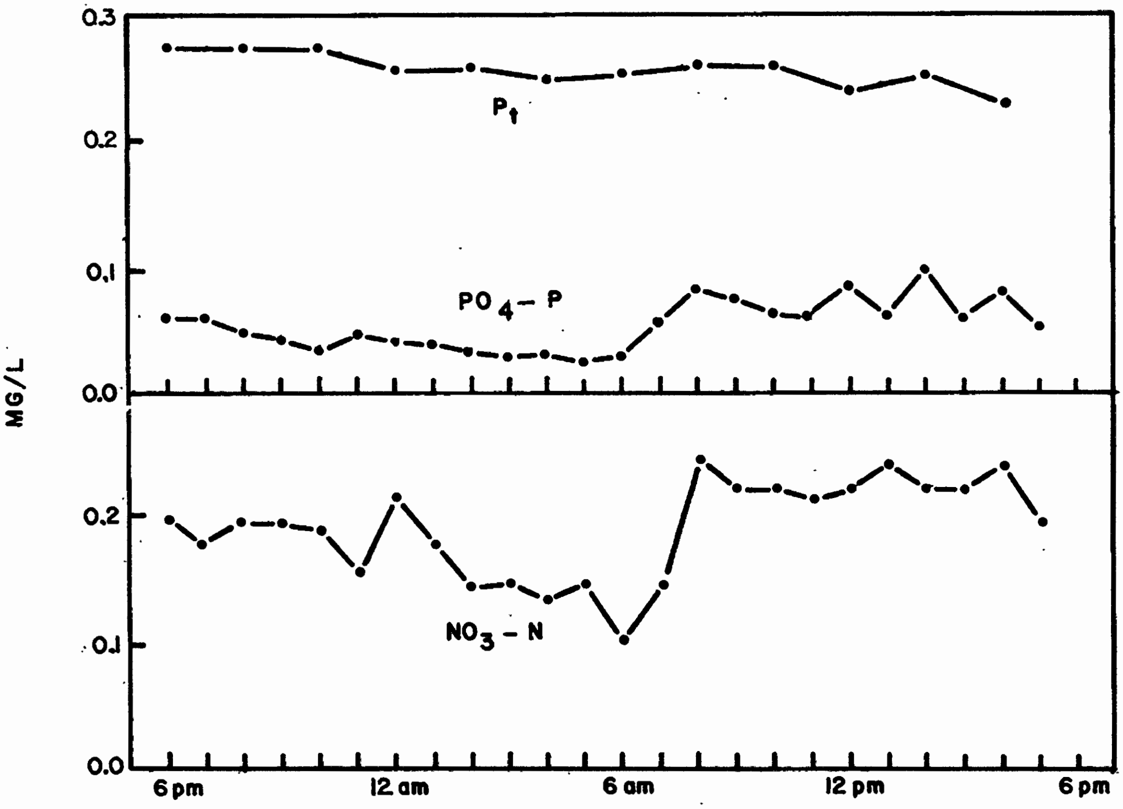

Figure 11. Diurnal phosphorous and nitrogen measurements

The increased H^+ concentration will push the reaction to the right and by

$$CaHPO_{4(aq)} \rightleftharpoons Ca^{+2} + HPO_4^=$$

the phosphate ion concentration is increased.

Nitrate-nitrogen also increases during the daylight hours as one would expect if nitrogen fixation were taking place (Peterson, et al, 1977; Stewart, 1977).

It appears that varying hydrogen ion concentration is the main process that affects the diurnal variation in PO_4^{-3}, alkalinity and total inorganic carbon concentration.

There are several processes that can account for the observed increase in H^+ concentration, two of which are suggested by Brewer and Goldman (1973). Although nitrogen fixation does not affect alkalinity, the subsequent biological use of NH_4^+ can. The assimilation of NH_4^+

$$NH_4^+ \longrightarrow \text{organic-N} + H^+$$

results in an incease in H^+ concentration. Bacterial nitrafication can also result in proton production;

$$NH_4^+ \longrightarrow NO_3^- + 2H^+$$

Although the water temperature above Station 2 is above 50°C the temperature inside the mat material is about 45°C for those portions that are at or above the water surface. This temperature is at the upper end of the temperature range found by Stewart (1970) for nitrogen fixation.

A third process, the oxidation of NH_4^+ by dissolved oxygen (nitrafication), could potentially be the most important process. The overall reaction may be written (Wetzel, 1975 p. 199) as

$$NH_4^+ \longrightarrow NO_3^- + 2H^+ + H_2O.$$

Depending upon the relative rates of nitrogen fixation and photosynthesis, the oxidation of NH_4^+ could produce more hydrogen ions than is lost through photosynthesis;

$$CO_2 + H_2O \xrightarrow[photo]{} CH_2O + O_2$$

$$H^+ + CO_3^= \rightleftharpoons HCO_3^-$$

$$H^+ + HCO_3^- \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2$$

SUMMARY

Southeast Harney Lake Hot Spring exhibits marked downstream increases in some of the chemical parameters studied. pH and alkalinity increases are mainly due to loss of CO_2 to the atmosphere and the redistribution of the remaining carbon between $CO_3^=$ and HCO_3^-. This redistribution is brought about by the effect of the lower downstream temperatures upon the equilbria constants of the carbonate buffering system. The lower temperatures push the equilibria toward HCO_3^- and $CO_3^=$ formation.

The downstream decrease in phosphorous is likely due to the effect of increased pH upon the equilibrium between calcium orthophosphate and calcium hydroxyapatite. Increased pH favors the precipitation of hydroxyapatite.

The increased nitrate concentration is probably biological in origin, resulting from nitrogen fixation. The fixing organisms are likely to be bacterial, as no blue green algae that are known to fix nitrogen were observed in any appreciable numbers.

The diurnal pH curve is unusual. It is the usual case in nonthermal waters that pH increases during the day due to the net depletion of CO_2 by photosynthesis (Verduin, 1956). Just the opposite was observed in this study. pH and alkalinity both decreased during the day. The likely cause is the oxidation of ammonia to nitrate within the algal-bacterial mat.

Nitrate-nitrogen increases also during the day, as one would expect if biological nitrogen fixation were taking place.

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APPENDIX I

STREAMLENGTH DISTRIBUTION OF ALGAE SPECIES
(* = abundant)

Station	Temperature (C)	Species
1	60	_Chloroflexus aurantiacus_ * _Synechococcus lividus_ * _S. minerva_ _Spirulina labyrinthiformis_
2	50.6	_Synechococcus lividus_
4	49.2	_Chloroflexus aurantiacus_ * _Pseudanabaena_ sp.
5	49	_Oscillatoria terebriformis_ * _Spirulina labyrinthiformis_ _Synechococcus lividus_
6	48	_Pseudanabaena_ sp * _Ocillatoria jenneri_ * _Spirulina labyrinthiformis_ _Synechococcus minerva_ _Synechococcus lividus_
9	43	_Spirulina labyrinthiformis_ _Synechococcus lividus_ _Oscillatoria limnetica_
10	41	_Gomphonema_ sp. * _Achnanthes gibberula_ * _Denticula elegans_ * _Philodina_ sp. Nematodes
11	40	_Achnanthes gibberula_ * _Spirulina labyrinthiformis_ _Chroococcus giganteus_
12	39.5	_Oscillatoria princeps_ * _Gomphospheria alponina_ _Chroococcus giganteus_
13	38.9	_Oscillatoria princeps_ *
14	37.5	_Oscillatoria princeps_ * _Achnanthes gibberula_ * _Denticula elgans_ *

STREAMLENGTH DISTRIBUTION OF ALGAE SPECIES (cont.)
(* = abundant)

Station	Temperature (C)	Species
15	36	Achnanthes gibberula * Denticula elegans * Oscillatoria princeps Gomphospheria alponina Chroococcus giganteus Nematodes