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URANIUM CONCENTRATION VARIATIONS IN STREAM WATER
IN RESPONSE TO CHANGING STREAM DISCHARGE FROM
PAIRED WATERSHEDS IN WESTERN MONTANA

by

Lawrence R. Shore

B.A., University of Montana, 1975

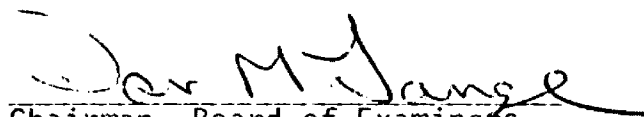
Presented in partial fulfillment of the
requirements for the degree of


Master of Science

UNIVERSITY OF MONTANA

1980

Approved by:


Chairman, Board of Examiners


Dean, Graduate School

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ABSTRACT

Shore, Lawrence R., Spring, 1980

Geology

Uranium Concentration Variations in Stream Water in Response to Changing Stream Discharge from Paired Watersheds in Western Montana

Director: Ian M. Lange

Water samples from gaged, paired, third-order watersheds draining granitic rock of the Idaho Batholith were collected approximately every two weeks during one annual hydrologic cycle to determine uranium variation. In addition, five suites of diurnal samples from each stream were collected to measure the amount of daily variation in uranium concentration.

Annually, uranium concentration varied over one order of magnitude. Diurnal variation during extreme low flow was also greater than one order of magnitude. The amount of annual and diurnal variation of uranium concentration in streams is great enough to cause errors in the interpretation of reconnaissance hydrogeochemical survey data. In effect, mineralized watersheds may appear to be unmineralized and unmineralized watersheds may appear to be mineralized.

Anomalous uranium concentrations occur in conjunction with other anomalous physical and chemical characteristics of the streams. Much of the variation is explained by dilution during the recession limb of storm events and spring runoff. However, a significant portion of the variation is not explained by dilution.

A technique is presented which attempts to identify water samples collected when streams are deviating from their long-term average chemical concentration. By plotting uranium concentration against calcium concentration, it is possible to account for the effects of dilution on uranium concentration. Anomalous high or low uranium values greater than ± 1 standardized residual are recognized in samples collected during or soon after storm events or during periods of extreme low flow. Anomalous high and low uranium values can be associated with either high or low pH values greater than ± 1 standard deviation. The change in pH is probably the result of variation in the rate that particular source areas deliver water to the stream channel. High uranium values may also be associated with high iron concentrations in stream water. This occurs only during periods of higher discharge. This appears to be the result of flushing of uranyl-ferric oxyhydroxide complexes from the stream bed during the rising limb of storm events.

ACKNOWLEDGMENTS

This work would have been impossible without the help of several people. First of all, I thank my director and teacher, Ian Lange, for his professional advice and personal concern while I was writing the manuscript. The encouragement and positive feedback I received from Arnold Silverman was never in short supply. The advice offered by Larry Gianchetta and Graham Thompson was very helpful.

My colleague Tom Bateridge and I conducted this study together. Tom's Ph.D. dissertation is distinctly different from my thesis. We used the Applebury and Steep Creek watersheds as a common testing ground for our own ideas, even though much of the raw data is shared. These days it is very difficult to find undisturbed, paired watersheds. It is perhaps more difficult to secure the permits and gain permission to install the equipment required for a long-term study such as ours. This responsibility fell on Tom, and without his special skills in diplomacy, my study would not have been possible.

Appreciation is extended to Ross Smith for permission to cross his land and his help in installing the flumes. I would like to thank Doug House for assisting us in monitoring the precipitation and discharge gages and my colleague Steve Gary for suffering through sub-zero temperatures in the quest for valuable data.

Los Alamos Scientific Laboratories provided the chemical analysis for us, and I wish to extend my thanks to Robert Sharp and Dave

Broxton of LASL for the special attention they gave us.

Lastly, I thank my beautiful and loving wife, Clare Castiglia, who acted as field assistant, cook, draftperson, and confidant. I dedicate this work to her.

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ACKNOWLEDGMENTS	iii
LIST OF FIGURES	viii
LIST OF TABLES	ix
CHAPTER	
I. INTRODUCTION	1
II. GENERAL INFORMATION	5
Local Access	5
Geology	5
Topography, Vegetation and Aspect	7
Climate and Weather	14
Soils	16
III. ROCK CHEMISTRY	17
Data	20
Discussion	20
IV. PRECIPITATION CHEMISTRY	22
Data	23
Discussion	23
V. HYDROLOGY	26
Data Collection	26
Time of Precipitation	26
Characteristics of the Hydrograph	28
Source Area Model	30

CHAPTER	Page
VI. STREAM WATER CHEMISTRY	37
Methods of Data Collection	37
Analytical Techniques	37
Data	38
Discussion of Stream Chemical Data	42
Iron in the Stream	43
pH Conditions in the Stream	44
Oxidation Potential	49
Cation Concentrations	50
VII. DISCUSSION	51
Annual and Diurnal Variation of Uranium in the Streams	51
Variability of Uranium Relative to the Other Cations	52
Solution and Adsorption Processes that Influence Uranium Solubility	57
Difference in Scatter Between Applebury-Steep Creek - Uranium Concentration Plots	63
Uranium Variation in Stream Water -- Implications for the Interpretation of Hydrogeochemical Survey Data	64
Identifying Abnormal Stream Water Samples	68
Application of Methods to Reconnaissance Data	75
VIII. CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY.	77
BIBLIOGRAPHY	80

	Page
APPENDICES	
I. Results of Chemical Analyses of Rock Samples	85
II. Summary of Standard LASL-HSSR Field and Analytical Procedures	92
III. Results of Chemical Analyses on Precipitation Data	102
IV. Listing of Discharge Data	103
V. Listing of Time and Amount of Precipitation	115
VI. Listing of Field Data and Analytical Results of Stream Water Samples	116

LIST OF FIGURES

Figure	Page
1. Study Area Location Map	6
2. Geologic Outcrop Map of Study Area	8
3. Vegetative Cover Map	12
4. Cartoon of Vegetation Distribution on Different Slopes	13
5. Histogram of Long Term Precipitation from Sula, Mt., Weather Station	15
6. Sample Site Location Map for Applebury and Steep Creek Study Area	18
7. Plot of Variation in Precipitation Chemistry With Time	24
8. Hydrograph and Uranium Chemograph of Uranium for Applebury Creek	27
9. Hydrograph and Uranium Chemograph of Uranium for Steep Creek	27
10. Channel Water, Source Area, Flow Path Diagram	34
11. Diagram of Lag Times for Applebury Creek	36
12. Chemographs for Applebury Creek Stream Water	40
13. Chemographs for Steep Creek Stream Water	41
14. Chemograph for July 2, 1978 Diurnal Sampling of Applebury Creek	48
15. Range of Eh-pH Conditions of the Streams	49
16. Log Normal Plot of Uranium on Discharge, Applebury Creek	55
17. Log Normal Plot of Uranium on Discharge, Steep Creek	56

Figure	Page
18. Distribution of Uranyl-hydroxy and Carbonate Complexes Versus pH	59
19. Adsorbtion of Uranyl Onto X-ray Amorphous Ferric Oxyhydroxide as a Function of pH	61
20. Variation in Uranium Concentration in Stream From the Boulder Batholith, Mt.	67
21. Log Normal Plot of Uranium on Calcium for Combined Water Data from Applebury and Steep Creek	71

LIST OF TABLES

Table	Page
1. Watershed Data	9
2. Uranium Concentrations in Rocks of the Study Area . .	19
3. Statistical Summary of Stream Water Data from Applebury and Steep Creek	39
4. Ratio of Mean Cation Concentrations in Applebury and Steep Creek	50
5. Correlation Coefficients for Least Squares Regression of Log Discharge on Calcium, Magnesium, Sodium, Potassium, Iron and Specific Conductivity . .	69
6. List of Outlying Samples from the Regression of Uranium on Calcium	72

CHAPTER I

INTRODUCTION

For the past five years the Department of Energy (DOE) has conducted a National Uranium Resource Evaluation (NURE) program, attempting to better define the uranium resources of the United States. One aspect of the NURE program involves a Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) program in which stream water and stream sediment samples were collected from small streams throughout the country. Using sophisticated analytical techniques the chemical concentration of uranium and a suite of other major and minor cations are determined for each stream sampled. Cation concentrations are reported on the basis of weight in parts per billion (ppb) for water and parts per million (ppm) for stream sediment, rock and soil samples. This study is concerned only with the stream water portion of the HSSR program.

A hydrogeochemical survey for uranium is an exploration technique used by geologists that relies on the dispersion of uranium away from an ore body into stream water which is relatively easy to sample. Ideally the technique allows the geologist to explore large areas of generally mountainous terrain quickly and inexpensively. By comparing the concentrations of uranium in water samples from many streams it is theoretically possible to target areas having a greater potential for containing

economic uranium deposits. This is based on the assumption that stream water containing higher concentrations of uranium comes from watersheds in which the rocks contain higher concentrations of uranium. The technique is useful only if the geologist is able to use the relative concentrations of uranium and other chemical characteristics to discriminate between stream water from mineralized and unmineralized terrain.

The usefulness of the exploration technique depends on a dispersion mechanism that continuously moves uranium from the point of origin in the rock to the stream where the water sample is collected. The dispersion mechanism should operate at nearly the same rate for all the watersheds within the area under survey even though the concentration of uranium in the rock may change between watersheds. This criterium provides a natural boundary delimiting the area within which stream water samples can reasonably be compared. The rate of the mechanism should not vary significantly from day to day within the time frame of the reconnaissance survey. If it does then two possible errors may occur in interpreting hydrogeochemical data.

The first error, designated a Type I error, occurs when a sample is taken at a time when stream water contains a significantly higher amount of uranium than it does on the long-term average. The watershed is then considered anomalous and is a potential target for more detailed exploration. This is not a critical problem because further sampling and observation will determine that the watershed is indeed unmineralized.

The second type of error, designated a Type II error, is made when a stream sample is taken at a time when concentrations are significantly lower than the long term average concentration. In this case the geologist may assume the watershed is unmineralized when, in fact, it may contain a uranium deposit. With a better understanding of uranium behavior in stream water, periods of large variation may be avoided. The large number of variables and in-field collecting experience convince the author that enormous difficulties confront the interpretation of the results of a regional hydrogeochemical survey. By studying uranium behavior in a paired hydrologic system I hope to increase our understanding of the uranium system and enhance the accuracy of interpreting hydrogeochemical results.

To the author's knowledge, a study of the long-term dynamics of uranium concentration in stream water has not been published. Several studies of limited duration, Rose et. al. (1977); Germanov et. al. (1958); Wenrich-Verbeek (1977), suggest that uranium concentrations do change as a function of discharge but the sample size of these studies are usually restricted to one or two sample periods spread out over one or more years. Thus, their usefulness for enhancing the interpretation of hydrogeochemical survey data is limited. This study suffers in several respects as well because it attempts to monitor the behavior of stream water chemistry only through one annual hydrologic cycle. One must be careful not to over-extend conclusions based on one year of stream data because as most people who work with stream data know, what occurs one year in a stream may differ quite radically from a subsequent year. I have attempted to

alleviate some of the shortcomings by studying two slightly different but adjacent watersheds. Nevertheless, it is impossible to escape the fact that weather is the driving force in every hydrologic system, and as we all know "weather can be very unpredictable".

This study deals with the behavior of uranium in stream water from two small mountain watersheds. The objectives of this study are:

1. To monitor the rate, volume and chemical nature of precipitation and discharge of two paired watersheds draining steep, partially forested, unmineralized, granitic terrain of the Idaho batholith of western Montana between September 24, 1977 and September 24, 1978.
2. To examine the relationship between uranium concentration in bedrock and stream water in the two watersheds.
3. To determine if the variations in this relationship are great enough to make conclusions based on a hydro-geochemical stream sampling program invalid.
4. If significant variation exists, to speculate on the nature of the variation, identify the variables that influence the variation and to develop a methodology for identifying stream water samples that fail to adequately predict uranium concentrations in the source rock.

CHAPTER II

GENERAL INFORMATION

Location and Access

The two watersheds studied, Applebury Creek and Steep Creek, are small tributaries to the East Fork of the Bitterroot River. They are within the Darby District of the Bitterroot National Forest in southwestern Montana, about 30 km. (18 mi.) southwest of Darby and approximately 2 km. northeast of the West Fork Ranger Station (Figure 1). The two watersheds are within sections 20, 21, 28 and 29 of T 1 N, R 21 W and are accessible from the bottom by a private bridge which crosses the West Fork below its confluence with Boulder Creek. The tops of the watersheds are accessible by the Piquett Mountain trail number 676. Flumes installed in each creek to monitor stream discharge are accessible by roads.

Geology

Three rock types outcrop within the study area. Approximately ninety percent of the combined watershed area is a pink coarse-grained, massive, equigranular, biotite-bearing granite (Figure 2, Table 1). The granite presumably belongs to the suite of Tertiary age granite plutons forming a discontinuous, concentric ring around the Bitterroot Lobe of the Idaho batholith, and are believed genetically related to the Challis volcanics (Hyndman, 1977). The rock weathers under the present climate to permeable,

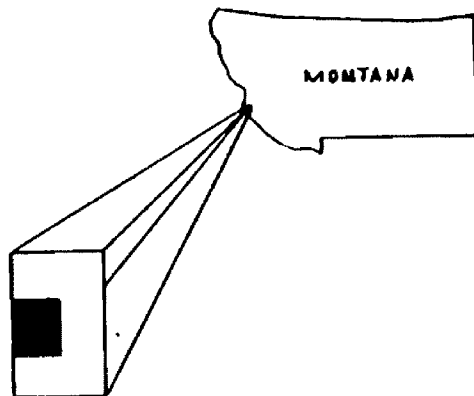
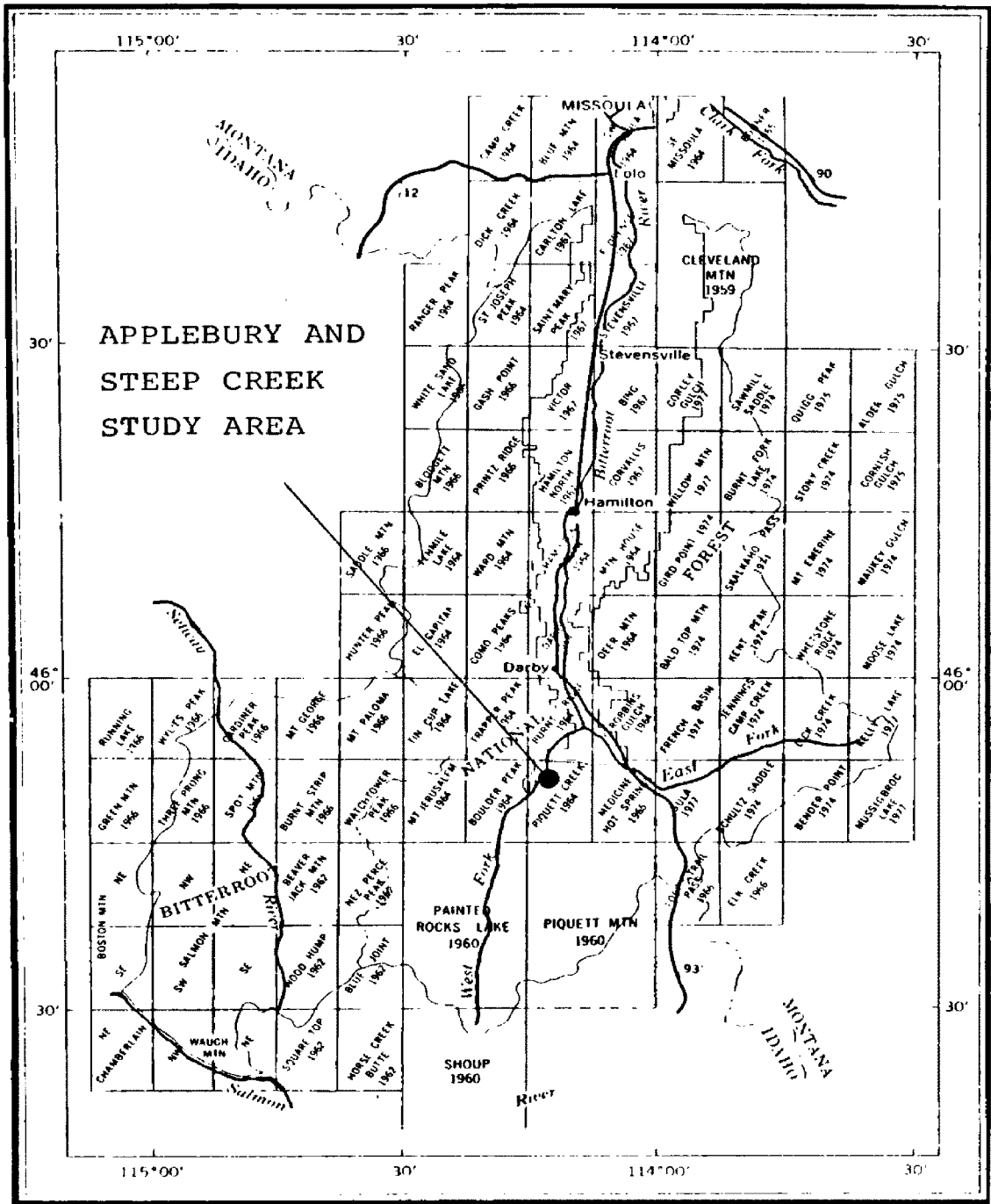


Figure 1. Location of the Applebury and Steep Creek study areas in western Montana.

coarse-grained gneiss. The second rock type, 5 to 10% of the study area, is a sequence of hypabyssal porphyritic volcanic dike rock. Angular, partially resorbed, potassium feldspar phenocrysts .4 to .8 cm in diameter typically occur in the tan to buff colored, aphanitic, crystalline groundmass. The dike rock clearly intrudes the Tertiary granite, however complex intergradation of porphyritic dike rock and medium to fine grained granite is common. The resistant dikes have a persistent north-northeast strike, following the regional northeast trend of Tertiary volcanics believed to be related to the late stages of the Challis event (Hyndman, 1977; Badley unpublished Masters Thesis, UM, 1977).

The third rock type present is a medium-grained, weakly-foliated, biotite bearing granodiorite containing conspicuous potassium feldspar megacrysts. It belongs to the suite of Cretaceous aged plutonic rock composing the interior of the Bitterroot Lobe of the Idaho batholith. This rock outcrops to a limited extent along a zone at the mouth of the two watersheds (Figure 2). The contact between the Cretaceous granodiorite and Tertiary granite is not seen in the field because of poor exposure. However, it is clear from field relationships that the hypabyssal dikes cut both granites. A moderate amount of jointing throughout the watersheds suggests some structural deformation exists.

Topography, Vegetation and Aspect

The Applebury and Steep Creek watersheds are similar topographically to most first and second order stream drainages (Horton, 1945)

GEOLOGIC OUTCROP MAP

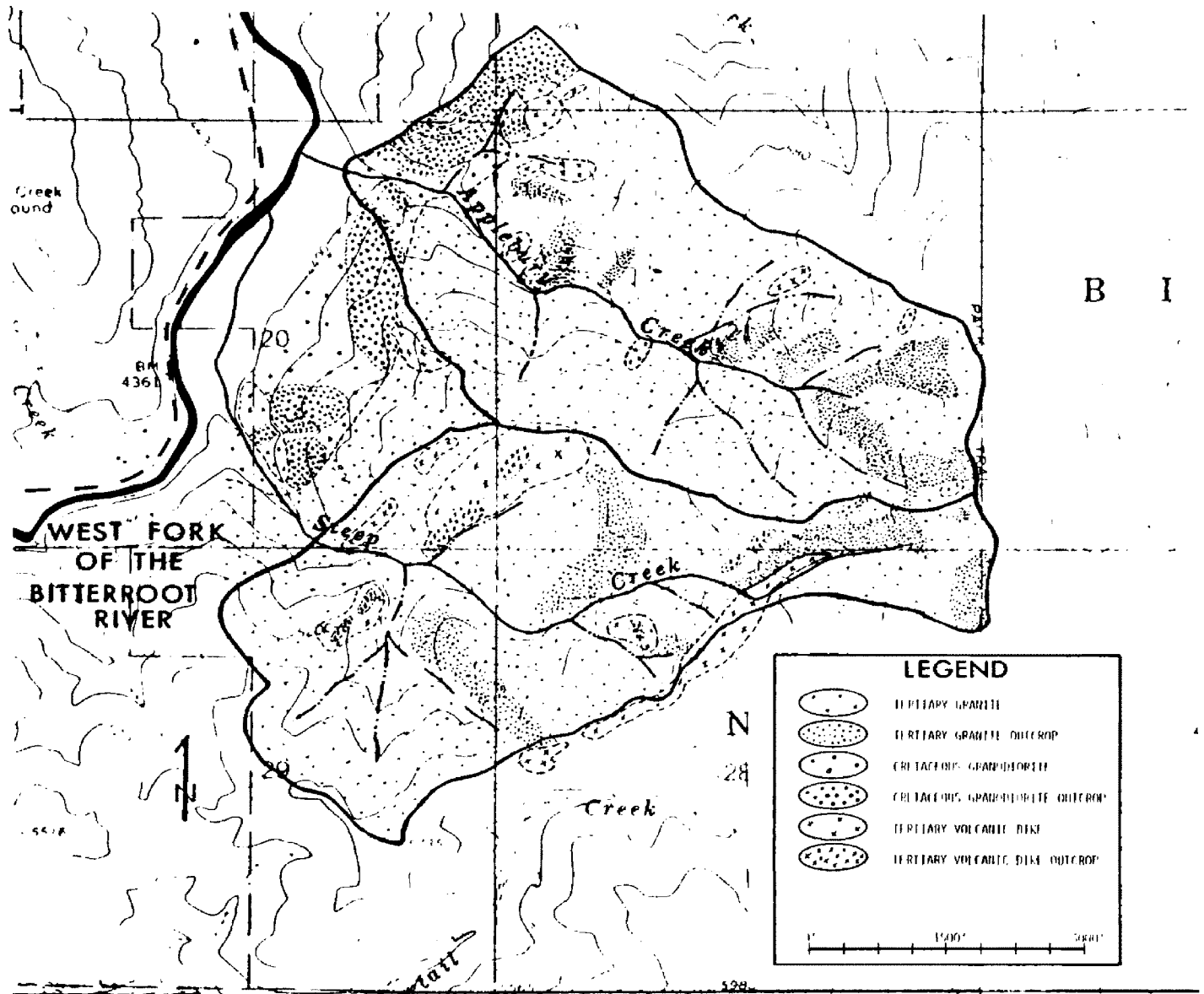


Figure 2. Geologic outcrop map of the Applebury and Steep Creek study areas.

Table 1. Watershed Data

	<u>Applebury</u>	<u>Steep</u>
Horizontal Map Area (ha)	211	197
True Area (ha)	234	211
Horizontal Map Area (ac)	520	486
True Area (ac)	577	520
Slope (ave deg)	26	20
Slope (ave %)	43	34
High Point (m)	2012	2073
Flume ele. (m)	1353	1414
Relief (m)	659	659
High Point (ft)	6600	6800
Flume ele. (ft)	4440	4640
Relief (ft)	2160	2160
Tertiary Granite	89%	91%
Tertiary Volcanics	3%	9%
Cretaceous Granite	8%	0%
Percent of watershed unforested	42%	31%
Percent of watershed forested	58%	69%
Percent of area adjacent to main channel that is unforested	33%	19%
Percent of area adjacent to main channel that is forested	67%	81%

ha = hectares

ac = acres

one might encounter in a regional reconnaissance stream sampling program in the mountains of Western Montana, Central Idaho and Northwestern Washington. The Piquett Creek 7.5 minute U.S.G.S. topographic map covers the study area and was used with air photos to derive the data in Table 1 and Figures 2 and 3.

The study area is partially covered by a mixed coniferous forest typical of the middle elevations of the region. The species present are Douglas Fir (*Pseudotsuga menziesii*), Lodgepole Pine (*Pinus contorta*), Ponderosa Pine (*Pinus ponderosa*) and Engelmann Spruce (*Picea engelmannii*). Unforested slopes are sparsely covered by brush, various herbs and grass. The bottom area along the stream margins are overgrown with deciduous trees and brush.

Applebury and Steep Creek have deeply incised stream channels forming distinct V-shaped valleys. The valley slopes are steep (21 to 30 degrees) and the slope profiles are generally straight; however, in places slopes tend to increase toward the stream margin.

The general orientation of the drainages is west-northwest. This orientation controls the water budget, and therefore the type and density of vegetation on the northeast and southwest facing slopes. Northeast facing slopes are wetter and heavily forested. Southwest facing slopes are dryer and have fewer trees. The Applebury Creek watershed is oval shaped and generally symmetrical around the trunk stream. This tends to equalize the proportion of forested versus unforested slopes.

The distribution of vegetation in a watershed can influence its hydrologic character by altering the rate that precipitation infiltrates and flows to the stream (Vorenkov, 1970; Reich, 1972; Plamondon, et al., 1972). Variation in stream water chemistry in a watershed containing various hydrologic regimes (i.e. grassland and forested land) is more complex than watersheds containing only one hydrologic regime (Vorenkov, 1970). Therefore, it is important to have a better understanding of the differences in the distribution of vegetation between Applebury and Steep Creek. In both watersheds the boundary between forested and unforested slopes is usually very distinct and results from differences in slope aspect. Most of the unforested slopes in each watershed extend down, almost to the trunk streams. They are separated from the main channel by a ravine and a zone of thick vegetation, commonly 20 to 50 feet wide. The vegetation consists of about equal proportions of deciduous brush and conifer (Figure 4). Forested slopes are usually covered completely with conifers, extending from the trunk stream to the drainage divide.

The difference in hydrologic behavior between forested and unforested slopes, during spring runoff when all soils are generally saturated, is usually small. However, during the summer months, differences in evaporation and transpiration on slopes having different aspect may cause large differences in the way each slope releases water to the stream channel (Kossovich, 1967).

Using the vegetative cover map (Figure 3) I determined the proportion of forested and unforested area on both sides and directly adjacent

VEGETATION COVER MAP

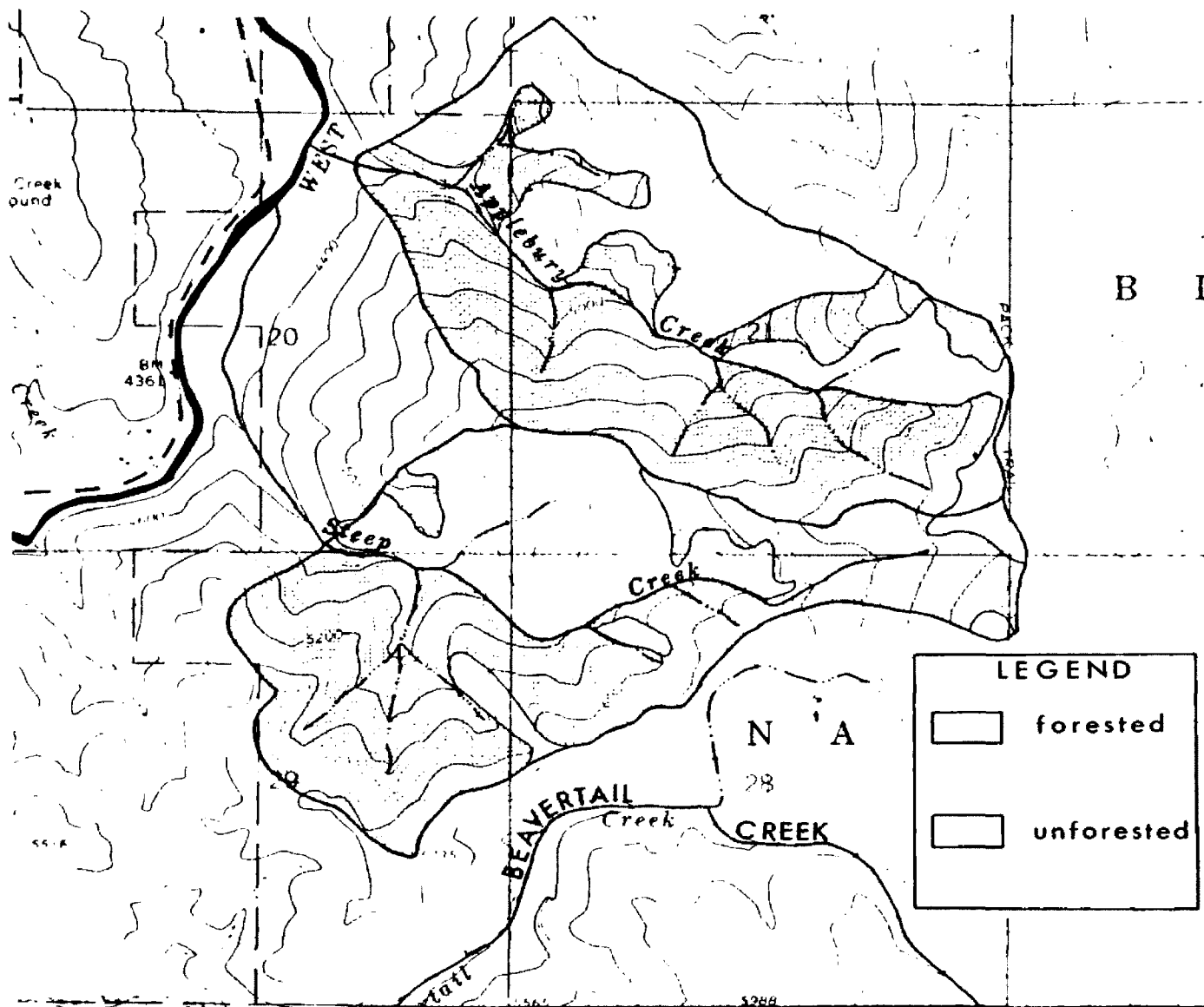


Figure 3. Vegetation cover map depicting the distribution of forested and grassland in the Applebury and Steep Creek watersheds. Shaded area depicts primarily forested area. See Table 1 for breakdown of distribution.

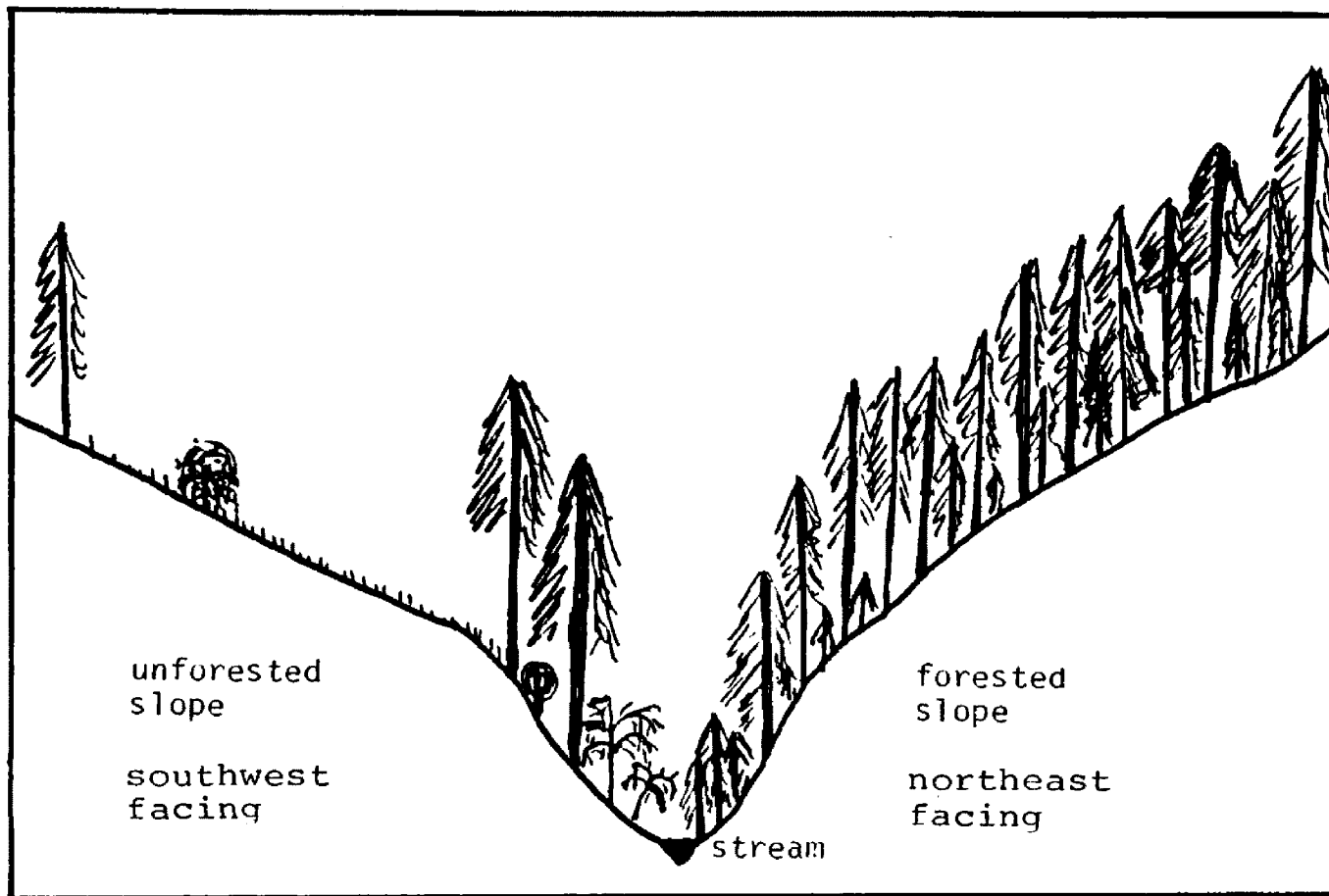


Figure 4. Cartoon depicting the distribution of vegetation on northeast and southwest facing slopes. See text for explanation.

to the perennial portions of each stream. In general, 4/5 of the Steep Creek perennial stream margin is forested compared with roughly a 2/3 forested stream margin in Applebury Creek. The differences are small but may account for the variation in stream water chemistry discussed in Chapter VI.

Climate and Weather

A large climatic gradient exists within the drainages of the study area. This is characteristic of many steep walled canyons within the region, caused by the limited incidence of sunlight in the narrow valley floors and the rapid change in elevation. Air temperatures within small watersheds in this region vary significantly. On sunny days air temperatures on the valley floor are commonly 5 - 10 degrees cooler than slopes several hundred feet higher in elevation. Data from the closest weather station of comparable elevation (Sula, Figure 1) indicate monthly mean temperatures for the study period were slightly higher than the previous 15 year average.

Data from the Sula station (Figure 5) indicate precipitation for the water year was significantly above the long term average. Precipitation in the region has a direct, positive relationship with elevation (Garn and Malmgren, 1973; Patton, et. al., 1970) therefore precipitation in the study area was greater than at the Sula station. Based upon data from the Sula station, and a isohyetal map (Garn and Malmgren, 1973), precipitation in the study area is estimated to be 700 mm (27.6 inches) per year, 50 to 70 percent falling as snow. An orographic

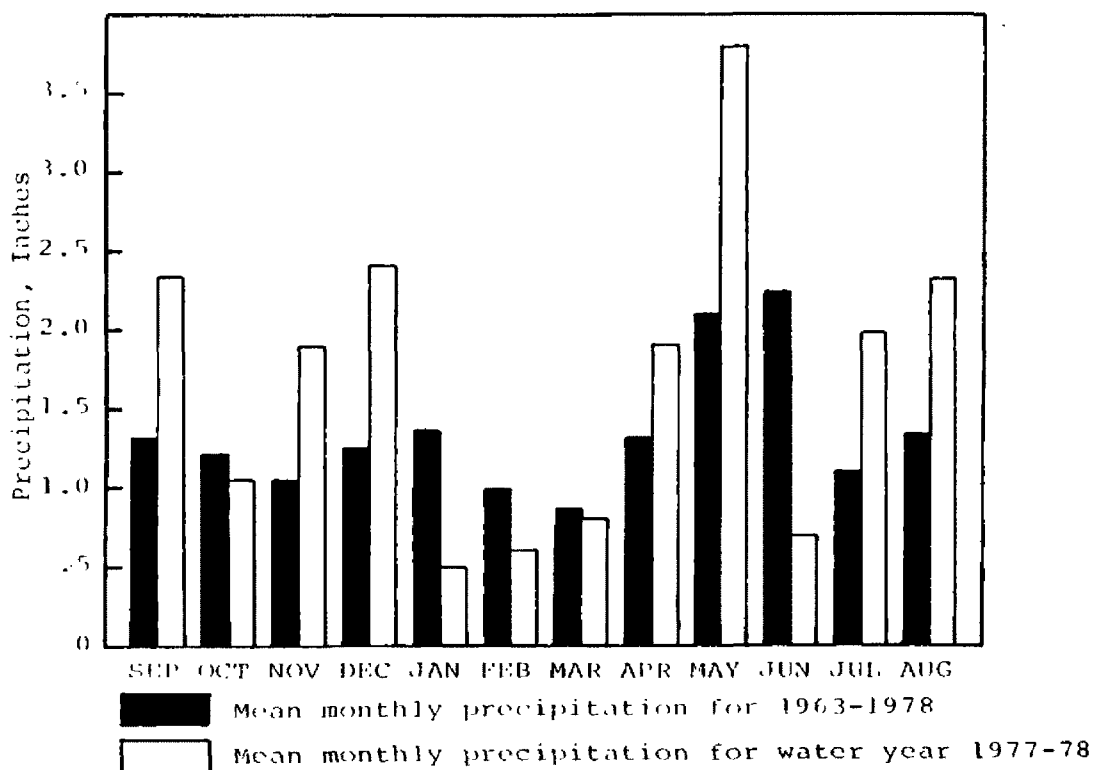


Figure 5. Precipitation data from Sula 3 ENE weather station Sula, Montana - Elevation 4440 ft. Mean annual precipitation for 1963-1978 is 16.17 inches. Total precipitation for 1977-1978 water year is 20.35 inches.

computation of total precipitation by Bateridge (personal communication) also estimates that 700 mm of precipitation fell on the watersheds during the 1978 water year. Winds in the area are predominantly southwesterly and summer evaporation is considerable due to warm drying winds. Above 6800 - 7000 feet the regional climate begins to limit vegetation growth (Garn and Malmgren, 1973), but this is not a significant factor in this study.

Soils

Soil thickness in the study area is irregular and varies primarily as a function of slope and aspect. Depth to bedrock is generally 120 to 180 cm (4 - 6 feet) on north facing slopes and 50 to 150 cm on south facing slopes. Individual horizons are not well developed and the soil is usually capped by a thin organic layer. All soils within the study area develop on granitic bedrock, contain much grass and have a sandy loam to loamy sand texture. Characteristics common to all the soils are low fertility, low water holding capacity, high infiltration and high permeability (Garn and Malmgren, 1973).

CHAPTER III

ROCK CHEMISTRY

Representative samples of each rock type in the study area were collected to determine background concentrations of uranium and differences in uranium concentration between rock types. Sample site locations are shown in Figure 6. Elemental concentrations for each sample collected are given in Appendix I. Samples were crushed to -100 mesh with a Bico disc pulverizer using porcelain plates. Analytical techniques used by LASL to determine elemental concentrations are:

1. Delayed neutron counting: uranium
2. Energy dispersive x-ray fluorescence: silver, bismuth, cadmium, copper, niobium, nickel, lead, tin, and tungsten
3. Arc source emission spectrography: beryllium and lithium
4. Neutron activation analysis: aluminum, gold, barium, calcium, cerium, chlorine, cobalt, chromium, cesium, dysprosium, erupium, iron, hafnium, potassium, lanthanum, leutetium, magnesium, manganese, sodium, ribidium, antimony, scandium, samarium, stronium, tantalum, terbium, thorium, titanium, vanadium, ytterbium, zinc.

The techniques for chemical analysis of the rocks are discussed in Appendix II.

SAMPLE SITE LOCATION MAP

FOR APPLEBURY & STEEP CREEK STUDY AREA

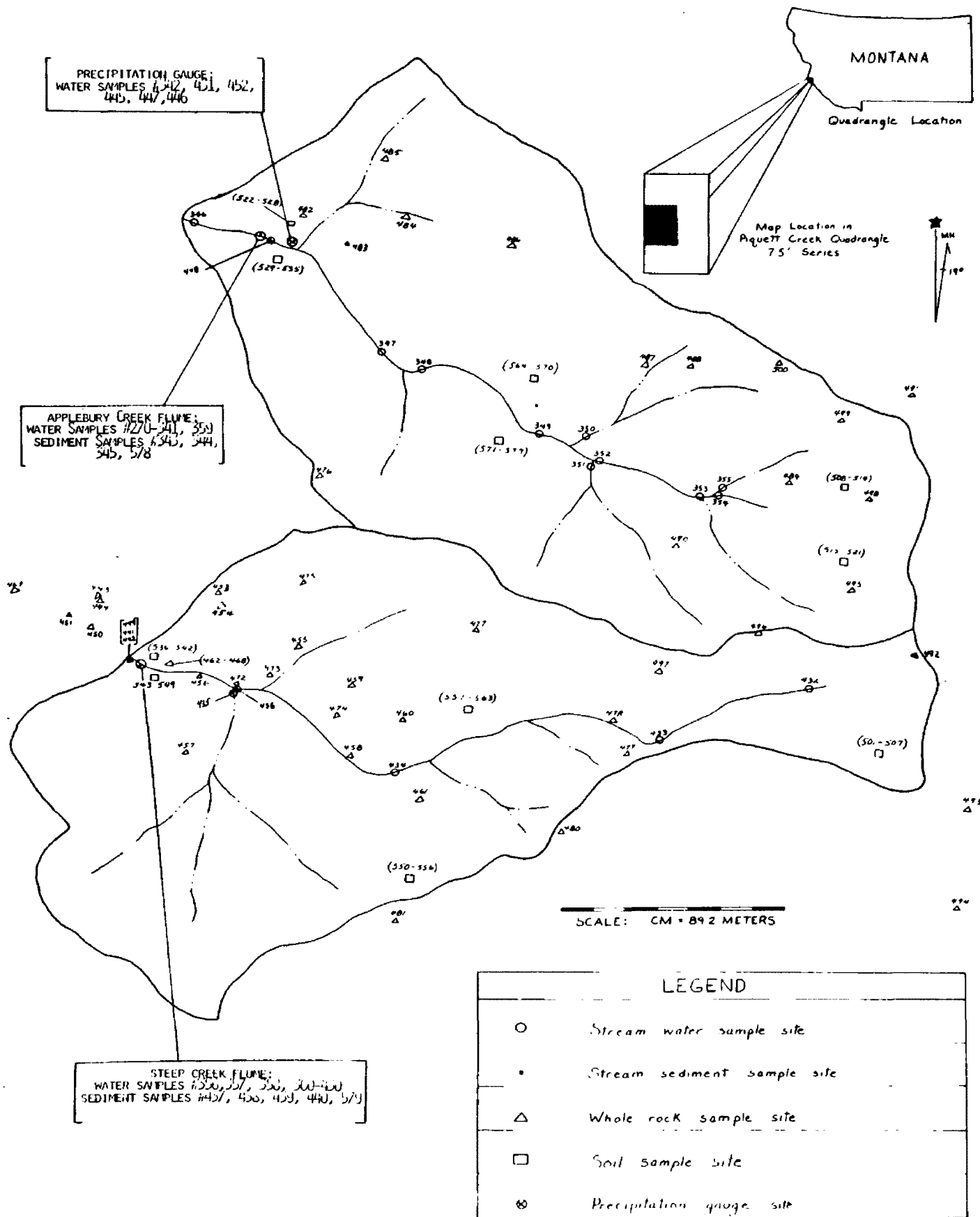


Figure 6. Sample site location map for the Steep and Applebury Creek study area.

Table 2. Uranium concentrations in rocks of the study area according to rock type, with statistics.

Applebury Creek						Steep Creek					
SN ¹	TV ²	SN ¹	TG ³	SN ¹	CG ⁴	SN ¹	TV ²	SN ¹	TG ³	SN ¹	CG ⁴
485	3.61	496	2.35	482	1.41	467	3.13	450	1.41	443	3.01
		498	3.03	483	2.47	468	2.96	451	1.70	444	2.55
		499	2.81	486	4.58	469	3.25	456	.66	$\bar{X} = 2.78$	
		500	2.35	$\bar{X} = 2.82$		480	4.37	458	2.83	$\sigma = .33$	
		476	4.16	$\sigma = 1.61$		481	1.28	460	1.94	$N = 2$	
		484	1.65	$N = 3$		494	4.18	463	1.06		
		487	1.75			497	3.30	464	1.09		
		488	4.62			453	2.42	465	1.09		
		489	2.09			454	4.27	471	.98		
		490	2.21			455	3.15	472	1.78		
		491	2.03			457	3.75	473	3.92		
		495	1.29			459	4.19	474	1.98		
		$\bar{X} = 2.528$				461	5.82	475	1.25		
		$\sigma = .995$				462	2.18	478	2.34		
		$N = 12$				466	2.94	479	3.33		
						485	3.61 ⁵	492	4.9		
						$\bar{X} = 3.42$		$\bar{X} = 2.02$			
						$\sigma = 1.05$		$\sigma = 1.19$			
						$N = 16$		$N = 16$			

¹Sample Number

²Tertiary Volcanics

³Tertiary Granite

⁴Cretaceous Granite

⁵Tertiary volcanic data combined to derive statistics

Data

The average concentration of uranium in the rocks of the study area is determined by statistical treatment of the chemical data. Table 2 gives a statistical breakdown of the uranium concentration of rock types within each of the watersheds. Cretaceous granite was not seen outcropping within the Steep Creek watershed. In Applebury Creek approximately 5% of the total rock exposed is Cretaceous granite. Its average uranium content is similar to that of the Tertiary granite. Most groundwater flow from the Cretaceous granite enters the stream below the flume. It probably does not significantly influence the stream water chemistry where the samples were collected. Therefore, the chemical values for Cretaceous granite are left from the calculations below.

Discussion

The concentration of uranium in Tertiary dikes is generally one part per million greater than in the Tertiary granite. This follows the typical trend of uranium enrichment in late stage differentiates. A T test on the difference of means between Tertiary granite from each watershed indicates there is no statistical difference at the 90%, 95% and 97.5% confidence levels. A second T test on the Tertiary dike rock from the two watersheds gives a similar result, suggesting that the uranium concentration in the dike rocks from both watersheds is statistically the same. Therefore, a weighted mean average uranium concentration, accounting for the percentage of each rock type

outcropping in both watersheds, is computed as follows:

$$U \bar{x} = \frac{(A * B + C * D) + (M * N + X * Y)}{A + C + M + X}$$

where

Applebury Creek

A = percentage of Tertiary granite

B = mean concentration of uranium in Tertiary granite

C = percentage of Tertiary volcanics

D = mean concentration of uranium in Tertiary volcanics

Steep Creek

M = percentage of Tertiary granite

N = mean concentration of uranium

X = percentage of Tertiary volcanics

Y = mean uranium concentration of Tertiary volcanics

The weighted mean uranium concentration of the rocks of both watersheds is 2.35 ppm.

CHAPTER IV
PRECIPITATION CHEMISTRY

Uranium in the streams may come from several sources other than bedrock within the watersheds. Some may be dissolved in rain or snow as it falls on the watersheds and some may deposit on vegetation as a part of airborne dust. To insure that the principal source of uranium to the streams was from bedrock, precipitation samples were collected at the lower precipitation gage throughout the study period and analyzed for their uranium content.

Six precipitation samples were collected at the lower precipitation gage. The following list gives the sample numbers and dates in which samples were collected.

Precipitation sample numbers and dates of collection

<u>Sample Number</u>	<u>Date</u>
452	10-22-77
445	12-18-77
447	1-14-78
446	1-29-78
342	7-16-78
431	9-16-78

To prevent evaporation, precipitation was collected in a polyethylene system consisting of an uncovered funnel, tubing and reservoir. The system is identical to the one described by Likens et al. (1967) and used at Hubbard Brook. Samples were filtered and acidified. Specific conductivity pH and temperature of each sample were not measured. The chemical concentration of precipitation was extremely low and concentrating by evaporation was necessary before analysis. Samples were analyzed by LASL according to procedures described in Appendix II.

Data

The results of chemical analyses for the six precipitation samples collected are given in Appendix III. Figure 7 displays the variability of uranium and other metal cations through time.

Discussion

A small amount of contamination of the precipitation samples by dust fall was expected, however the higher elemental concentrations recorded in sample numbers 452, 342, and 431 indicate that a larger amount of contamination occurred when conditions were very dry or the collection periods were sufficiently long. This allowed dust to build up on the collection apparatus which then was washed into the collection bottle.

Sample numbers 445, 447 and 446 were collected during periods when snow covered the ground. Presumably, ambient dust was at a minimum during this period and these samples probably represent the typical

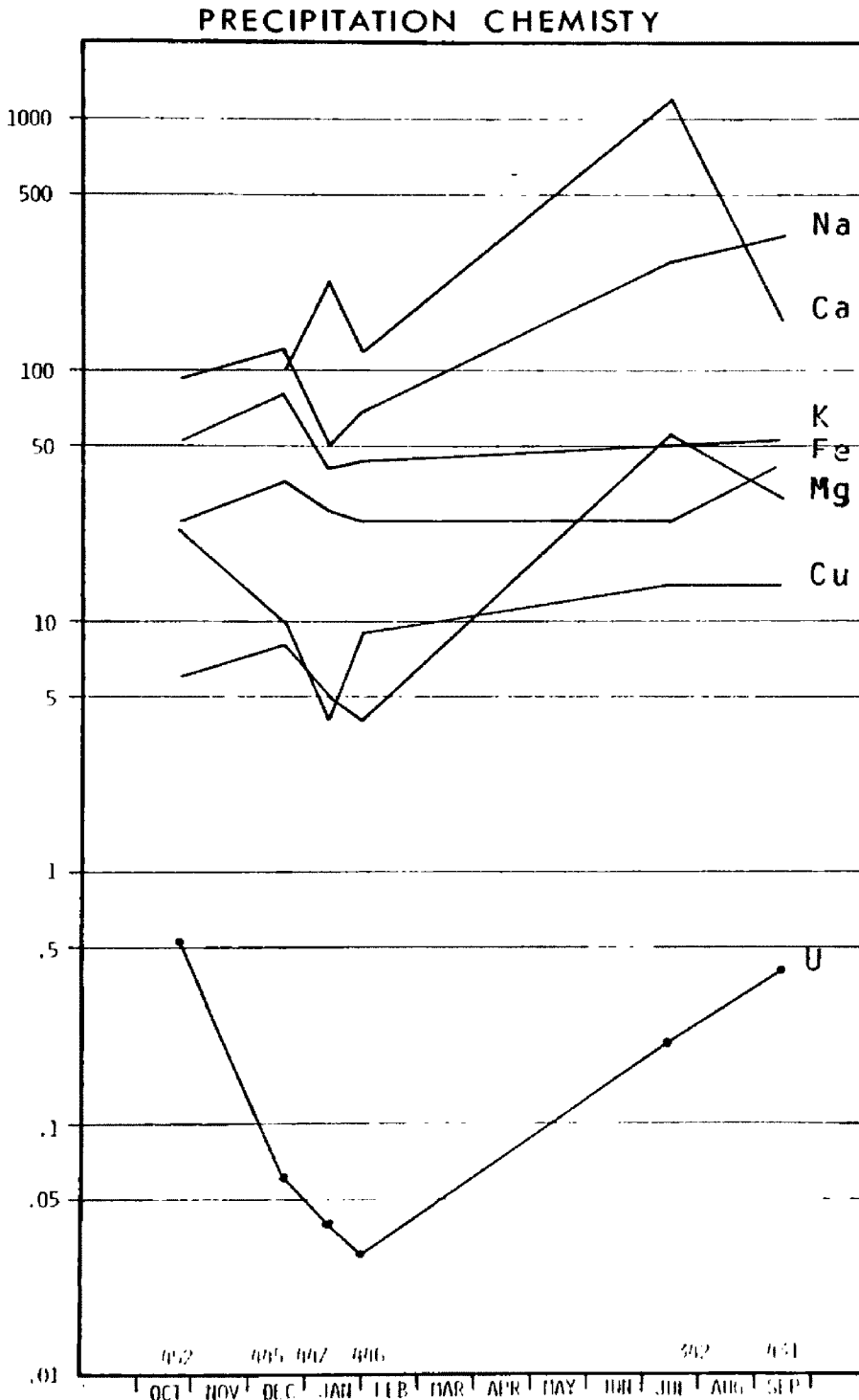


FIGURE 7. VARIATION IN PRECIPITATION CHEMISTRY OVER THE 1978 WATER YEAR. 452, 462, AND 431 ARE SAMPLES PROBABLY CONTAMINATED BY ATMOSPHERIC DUST WASHED INTO THE COLLECTION BOTTLE. LOCATION OF SAMPLE SITE SHOWN IN FIGURE 6.

chemical input into the hydrologic system. Under these conditions, uranium concentration of precipitation falls in the range of .03 to .06 ppb, with slightly higher concentrations possibly occurring in the late summer and early fall. The uranium concentration in rain water is extremely low and is at least one order of magnitude less than mean concentration in the stream water. Because of uranium's low concentration in precipitation, and its chemical activity upon entering the mineral soil, its influence on stream water is considered negligible.

CHAPTER V

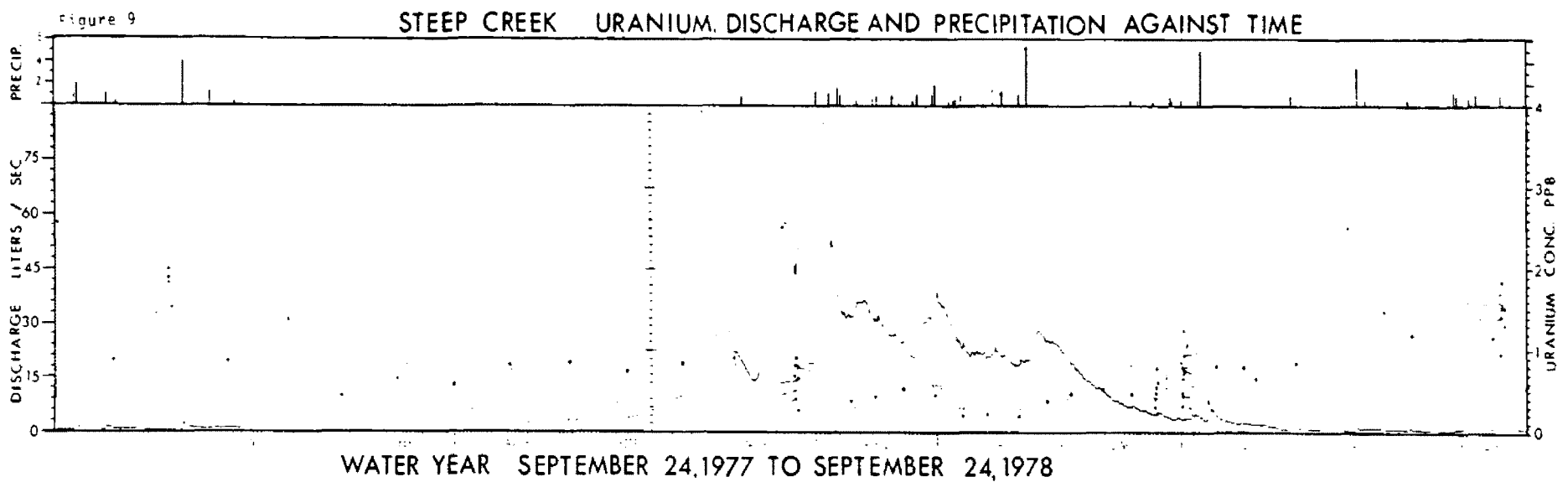
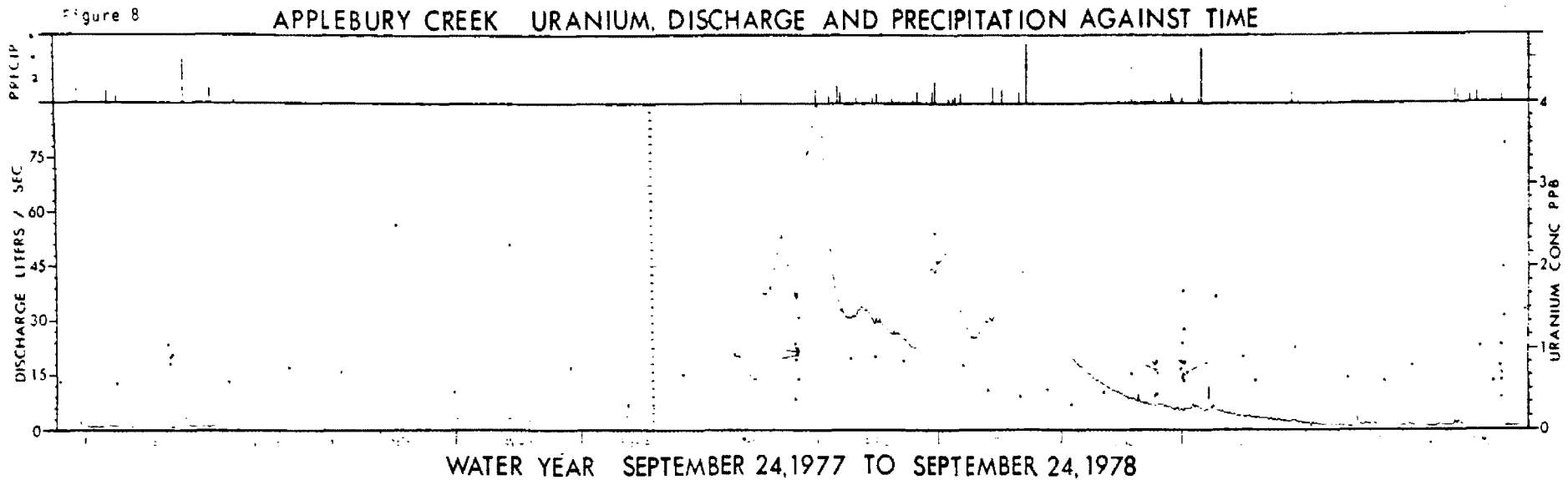
HYDROLOGY

Data Collection

Stream discharge was monitored continuously for each stream throughout the water year 24 September 1977 to 24 September 1978, except for a portion of the winter when the stream gaging devices were frozen. The discharge data for both streams is listed in Appendix IV. Discharge was monitored with strip recorders attached to v-notch flumes. The flumes were anchored securely in the stream channels, banked and sealed with bentonite to prevent leaks through the porous bank material.

Time of Precipitation

Precipitation falling into the watersheds was measured with two precipitation gages, one near the Applebury Creek flume (Figure 6) and one near the headwaters of Applebury Creek. The lower gage continuously recorded both the amount and time of precipitation of each storm. The temporal relationship between precipitation and discharge provide a better understanding of the hydrology of the watersheds, therefore the amount and period of recorded precipitation are included in both sets of hydrographs (Figures 8 and 9). The actual precipitation data is necessary for calculating lag times (discussed below) and is listed in Appendix V.



Characteristics of the Hydrographs

The annual stream hydrographs with recorded precipitation events are presented in Figures 8 and 9. Also plotted are uranium values and sample numbers of all samples collected for each stream. The sample numbers reference the data listing in Appendix VI. The streams flowed continuously throughout the study period. Several times during the year one or both discharge gages stopped recording because of freezing temperatures or mechanical failure. At those times the record is inferred by combining static discharge readings taken at water sampling times with the three day running average of the mean daily high temperatures of the Sula and Darby weather stations. Using the static discharge data, and assuming, with snow on the ground significant increases in discharge occur only when temperatures go above freezing, then it is possible to create hydrograph data for periods when the recorders were frozen.

The stream hydrographs are characterized by one distinct period of peak discharge beginning with the onset of spring runoff near the first of March, peaking on April 1 and diminishing to base flow over the next 4 months. The variation in discharge during this period spanned 2 orders of magnitude. In late November and early December several storms dropped above normal amounts of snow on the watersheds. These storm events are reflected in the precipitation histogram in Figure 5. Neither discharge gage was recording during that period, nevertheless, it is apparent that discharge response to these storms was perhaps greater than 50% bank full stage.

In addition to the overall seasonal trends, the storm hydrographs are characterized by rapid rises and falls in response to individual rainfall events. This rapid response is related to the ease with which water is transmitted through the porous and shallow soils into the streams.

A significant diurnal variation in discharge beginning in May and sustained through early September results from the uptake of soil water by trees during their daily growing cycle. In general, minimum evapotranspiration occurs in the dark, early-morning hours when air temperatures are low. Evapotranspiration increases to a maximum in mid-afternoon and then decreases again towards a minimum in the late evening, completing the diurnal cycle. There is a good correlation between maximum evapotranspiration and minimum discharge. An example of this is shown in Figure 14.

The growing cycle of trees is extremely sensitive to soil water conditions and they adjust their growing cycles accordingly (Devlin, 1969; Daubenmire, 1974). Once soil moisture conditions fall below some critical level trees stop growing and the diurnal variation in discharge ceases. Early in the summer the streams are still on the recession curve of the spring runoff peak and the percentage of the total discharge withdrawn daily by evapotranspiration is on the order of 5 - 10%. As discharge continues to decrease towards base flow the percentage change in daily discharge becomes extremely significant approaching 100%. This change in flow appears to have a some influence on the chemistry of the stream water late in the summer.

The data indicate that discharge in Steep Creek is more sensitive to this diurnal variation than Applebury Creek. For instance, on August 11, one of the lowest discharge days of the year, Steep Creek experienced an 80% reduction in flow while Applebury Creek showed a 60% reduction. This relationship is typical throughout the growing season and indicates that the greater amount of vegetation adjoining Steep Creek may be causing larger diurnal fluctuations in discharge.

Source Area Model

The water chemistry measured at the flume is influenced by the kinds of material that precipitation comes into contact with and the length of time between falling in the watershed and entering the stream. Both these factors are affected by the route precipitation takes to reach the stream. Therefore, it is necessary to consider the mechanisms that deliver precipitation to the two streams.

Overland flow (Horton, 1933), caused by surface soil saturation, occurs periodically in the early spring at times when the soil is going through daily freeze-thaw cycles. It is apparent only at places where the soil is frozen and then when the upper 2 or 3 inches melt when warmed by sunlight. In these places soil water or snowmelt, prevented from infiltrating by the frozen subsoil, percolate downslope until the unfrozen soil becomes saturated. At that point soil water flows overland. The afternoon shadows define a sharp thermal boundary during this time of year and it is common to observe overland flow

refreeze on the soil surface upon crossing the shadow interface. Hewlett (1974) stresses the point that surface flow is only that rainwater or snowmelt that fails to infiltrate the soil surface at any point along its path of travel to a gaging station in a perennial stream. Field observation and hydrograph data indicate it is unlikely that overland flow ever made a significant contribution to stream flow in either watershed during the study period.

The contribution of deep groundwater to stream discharge is also considered insignificant during most of the year for two reasons. First, deep groundwater flow in these watersheds infers movement through relatively impervious bedrock and is considered to be relatively slow. Second, during periods of low flow the large percentage change in discharge corresponding with the daily evapotranspiration cycle indicates that the source area during that period is soil water. Although deep groundwater's contribution to discharge is not usually apparent there are several instances when it appears to have a significant influence on stream water chemistry, and in particular, uranium concentration.

These instances occur when deep ground water makes up a large part of the total water flowing in the channel. One period in which this occurs is in mid-summer, before the cessation of diurnal fluctuation in discharge. During this period, usually in mid-afternoon on hot, sunny days, evapotranspiration significantly reduces the soil water contribution to the stream and deep groundwater temporarily becomes the

principal source of water. Another, longer period occurs in late summer and early fall, after the cessation of diurnal fluctuations. During this period soil moisture is very low, discharge is usually less than 1% bank full stage, and the lack of diurnal variation indicates that deep groundwater flow probably contributes the majority of water to the stream. This period continues until the first storm that adds appreciable amounts of water to the soil such that deep groundwater no longer provides the majority of water to the stream.

Subsurface flow appears to be the source of the major portion of stream flow throughout the hydrologic cycle. However, this mechanism is complex and several models have been developed to describe the path in which subsurface flow is delivered to the stream.

The variable source area model, developed by Hewlett and co-workers (Hewlett and Hibbert, 1967; Hewlett and Nutter, 1970; Nutter, 1973) has the stream channel system expanding and contracting in response to rainfall. As the channel system expands, the subsurface flow paths that join surface water systems shorten, and the effective area contributing to stormflow expands. Freeze (1972) criticizes this model on the basis that infiltration and subsurface flow rates do not transmit water fast enough to provide a significant contribution to storm runoff.

An alternative theory, the partial source area concept developed by Ragen (1968), Dunne (1970), Dunne and Black (1970, a,b) suggests that stream stormflow is caused by overland flow from partial areas near the stream channel due to surface saturation from a rising water

table. Freeze (1972) developed a complex computer program to simulate the rate and path of stormflow through a sloping soil mass which lends theoretical support to the partial source area concept. His simulation results show that in the variable source area model, subsurface flow could only contribute significantly to the storm hydrograph if saturated soil conductivities were large and steep convex slopes fed deeply incised channels.

Some hydrologists believe that storm flow to the stream channel is controlled by pipes (Hursh, 1944) formed in the soil by decay of roots and animal burrowing. During a rainfall the water passes downward through these channels much faster than water infiltrating through the soil. There is widespread evidence that piping flow exists (Aubertin, 1971; Reasley, 1976; Dixon and Peterson, 1971; Feller and Kimmins, 1979; Jones, 1971). However, measuring the actual contribution to the storm hydrograph has proven difficult.

Within the study area, especially along the lower margins of the watersheds, saturated soil conductivities are great enough and the slightly convex slopes adjacent to the streams are steep enough to meet Freeze's criteria for Hewlett's variable source area model. The fact that piping was observed within the study area along cutbanks and roadcuts suggests that subsurface flow through microchannel networks could make a significant contribution to stormflow. This study does not provide conclusive evidence supporting either the variable source area or the partial source area model. The above observations, combined with

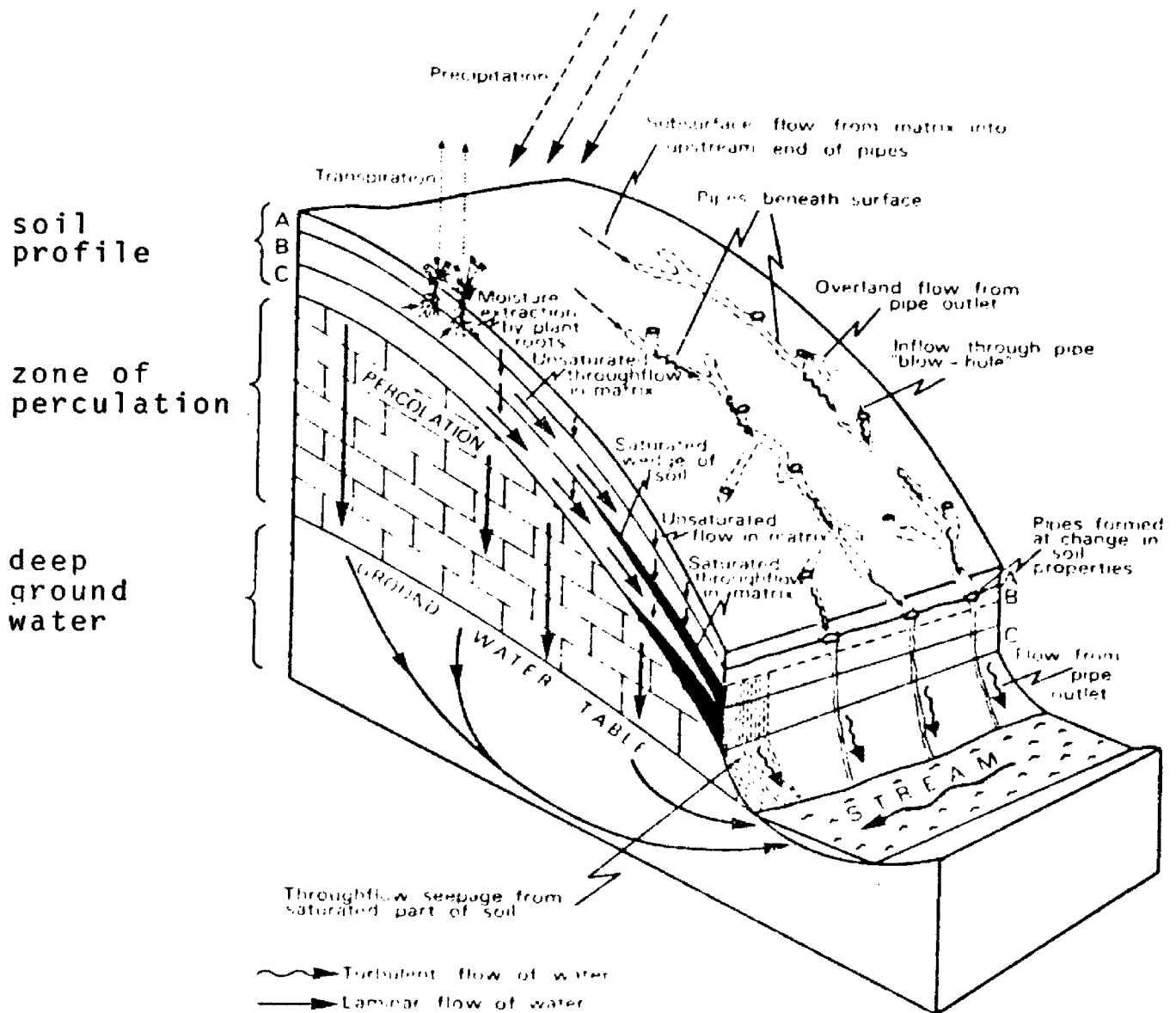


Figure 10. Flow routes followed by subsurface runoff on hillslopes (Atkinson, 1978). Water flowing from the B and C horizons of the soil profile shown above is considered the primary source of water flowing in Applebury and Steep Creek.

work published by other hydrologists, suggests that subsurface flow does make the major contribution to stream runoff according to the variable source area model. In addition, during periods of high discharge, piping flow probably delivers a significant amount of subsurface flow to the stream.

Figure 10, depicts the mechanism believed to explain the flow of soil water to the streams. A dynamic saturated soil water storage area, adjacent to the stream, is fed by unsaturated soil water that moves down slope parallel to the slope surface. This saturated area is effectively the water table in these steep watersheds and acts as a buffer between the unsaturated soil and the stream (Dunne, 1978). The activity of this buffer throughout the annual hydrologic cycle is better illustrated by observing the variation in lag times between peak rainfall events and subsequent peak discharge events.

A plot of lag times for a number of storm events throughout the study period for Applebury Creek is shown in Figure 11. This graph indicates that the buffer adjacent to the stream expands and contracts in response to both seasonal changes in soil moisture conditions and changes due to individual storm events. During spring runoff this buffer may be considered full. Rain, infiltrating the soil during this period, pushes water already in the buffer quickly into the stream resulting in short lag times. As discharge decreases during the spring and summer this buffer contracts. Presumably, during this period the buffer must expand to some extent, in response to individual storms, before it begins adding significant volumes of water to the channel.

APPLEBURY CREEK

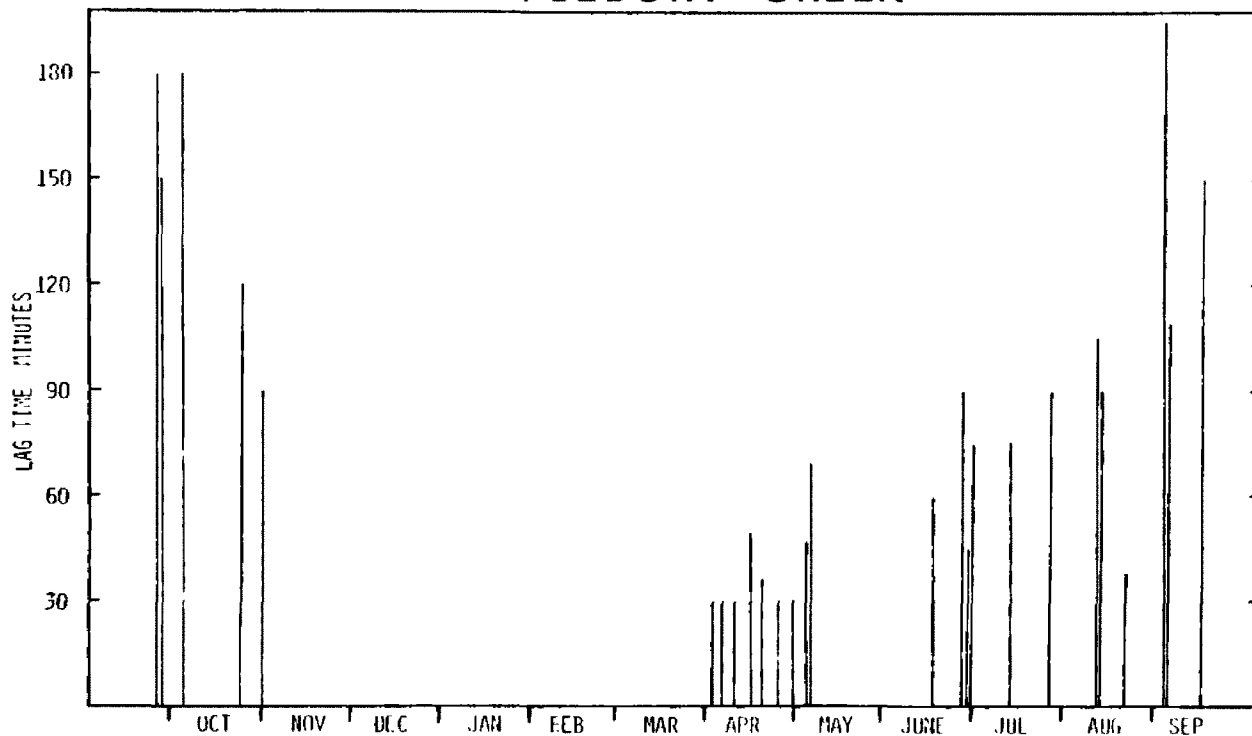


FIGURE 11. PLOT OF LAG TIME FROM MAXIMUM INTENSITY RAINFALL TO MAXIMUM DISCHARGE FOR RAINSTORMS GAGED DURING 1977 - 1978 WATER YEAR ON APPLEBURY CREEK. DISCHARGE GAGE WAS INOPERABLE BETWEEN NOVEMBER AND MARCH DUE TO FREEZING TEMPERATURES. THE LAG TIME REFLECTS THE CHANGE IN SOIL MOISTURE CONDITIONS IN THE WATERSHED DURING THE STUDY PERIOD.

As the time involved in filling the buffer increases the lag between the onset of rain and subsequent rise in stream flow also increases. This probably explains the longer lag times that occur in late summer and early fall.

CHAPTER VI

STREAM WATER CHEMISTRY

Methods of Data Collection

Water samples were collected from Applebury and Steep Creek at approximately two week intervals throughout the water year. In addition, five sets of diurnal samples were collected at random periods to test if significant daily chemical variations in stream water occurred. Samples were collected approximately 3 meters above the flume in accordance with standard LASL field procedures which are described in Appendix II. Water was filtered through a .45 u-membrane filter and acidified with nitric acid to a pH of 1.0. The sampling sites are shown in Figure 5. The following parameters were measured during each sample collection:

1. Air temperature-----to the nearest 1 degree centigrade
2. Water temperature-----to the nearest .1 degree C°
3. pH-----to the nearest .1 pH unit
4. Specific conductivity-----to the nearest 2 umho/cm
5. Stage of stream-----in centimeters

Analytical Techniques

The following analytical techniques are used by LASL for determining the stream water concentrations of the following elements:

1. Fluorometry; uranium
2. Plasma-source emission spectrography; calcium, sodium, potassium, cobalt, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, lead, titanium and zinc.

The accuracy and precision of the techniques are described in Appendix II.

Data

The chemographs for Applebury and Steep Creek are shown in Figures 12 and 13 respectively. The hydrographs for each stream are included in the plots to illustrate the relationship between discharge and various chemical parameters including uranium concentration. Uranium concentrations are also plotted on the hydrographs (Figures 8 and 9) presented in Chapter V making it easier to observe the relationship between discharge, precipitation and uranium concentrations. Appendix VI contains listings of field data and analytical results for all stream water samples.

Table 3 provides a statistical summary of the analytical results in addition to the data recorded at the time of sampling. The values for copper, nickel, titanium and zinc are not plotted on the chemographs nor considered in this study because concentrations for these elements are below the minimum detection limits of the analytical technique used.

Table 3. Statistical Summary of Stream Water Data for Applebury and Steep Creeks.

	APPLEBURY CREEK (71 samples)						STEEP CREEK (71 samples)					
	\bar{X}	σ	min	max	Range	Variability ⁴ $\frac{\sigma}{\bar{X}}$	\bar{X}	σ	min	max	Range	Variability ⁴ $\frac{\sigma}{\bar{X}}$
<u>Chemical Data</u>												
Calcium ²	15533	3571	7097	25341	18244	.23	18102	5777	8626	30158	21532	.32
Sodium ²	6716	1801	2743	10630	7887	.27	4899	1874	2493	9390	6897	.38
Magnesium ²	2233	503	1049	3419	2370	.23	1927	593	956	2979	2023	.31
Potassium ²	1308	244	818	1801	983	.19	1115	230	745	1755	1010	.21
Iron ²	50	43	25 ¹	189	164	.86	113	131	25 ¹	680	655	1.16
Uranium ²	.93	.56	.30	3.5	3.2	.60	.91	.59	.19	3.03	2.84	.65
Specific ³ Conductivity	122	21	68	174	106	.17	115	35	60	190	130	.30
pH ⁴	7.5	.3	6.9	8.1	1.2		7.5	.3	7.0	8.4	1.4	
<u>Physical Data</u>												
Discharge ⁵ L/Sec	12.25	14.4	.60	47.9	47.3	1.18	12.2	16.0	.13	50.9	50.77	1.31
Water Temp °C	6.0	3.0	0	115	115	.5	5.8	2.8	0	12	12	.48
Air Temp °C	11	10	-15	35	50	.91	9.8	9.5	-16	30	46	.97

¹Minimum detection for Fe is 25 ppb-values below this limit are reported as 25 ppb.

²All chemical concentrations in ppb.

³Specific conductivity is in $\mu\text{hos/cm}$.

⁴Variability is the relative variation associated across all parameters.

⁵Calculated only from discharge values recorded at time of sample collection.

\bar{X} = mean value for each parameter

σ = standard deviation for each element

APPLEBURY CREEK

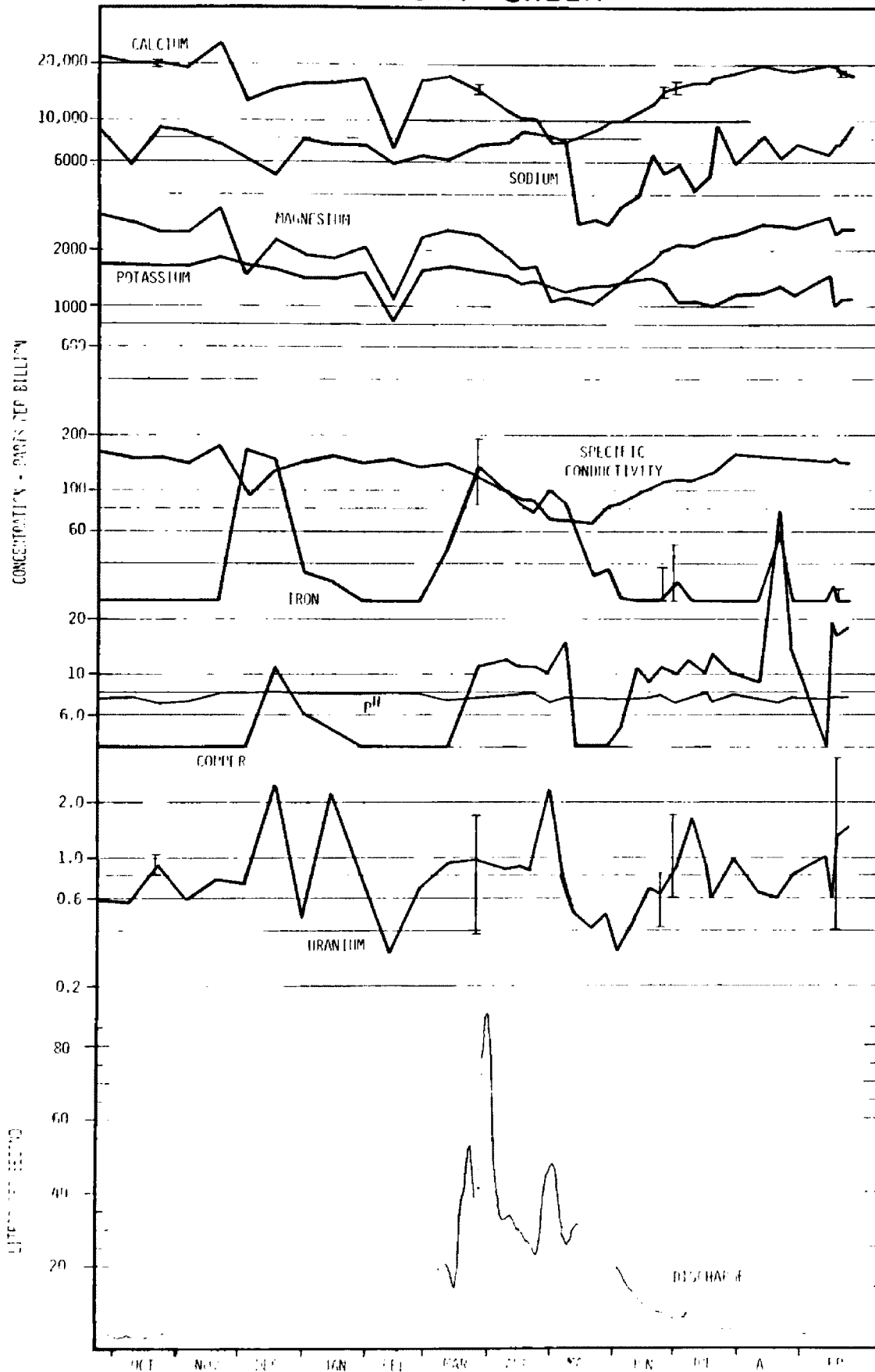


FIGURE 12. LIMITS EACH FOR APPLEBURY CREEK, UNITED STATES OF AMERICA. DATA BASED HEREON PERTAIN TO A RECENT PERIOD AND DO NOT REPRESENT THE QUALITY OF THE SITE AND SAVER HEALTH PROTECTION. FROM DATA RECEIVED FROM THE UNITED STATES OF AMERICA AS LISTED IN THE ORIGINAL REPORT.

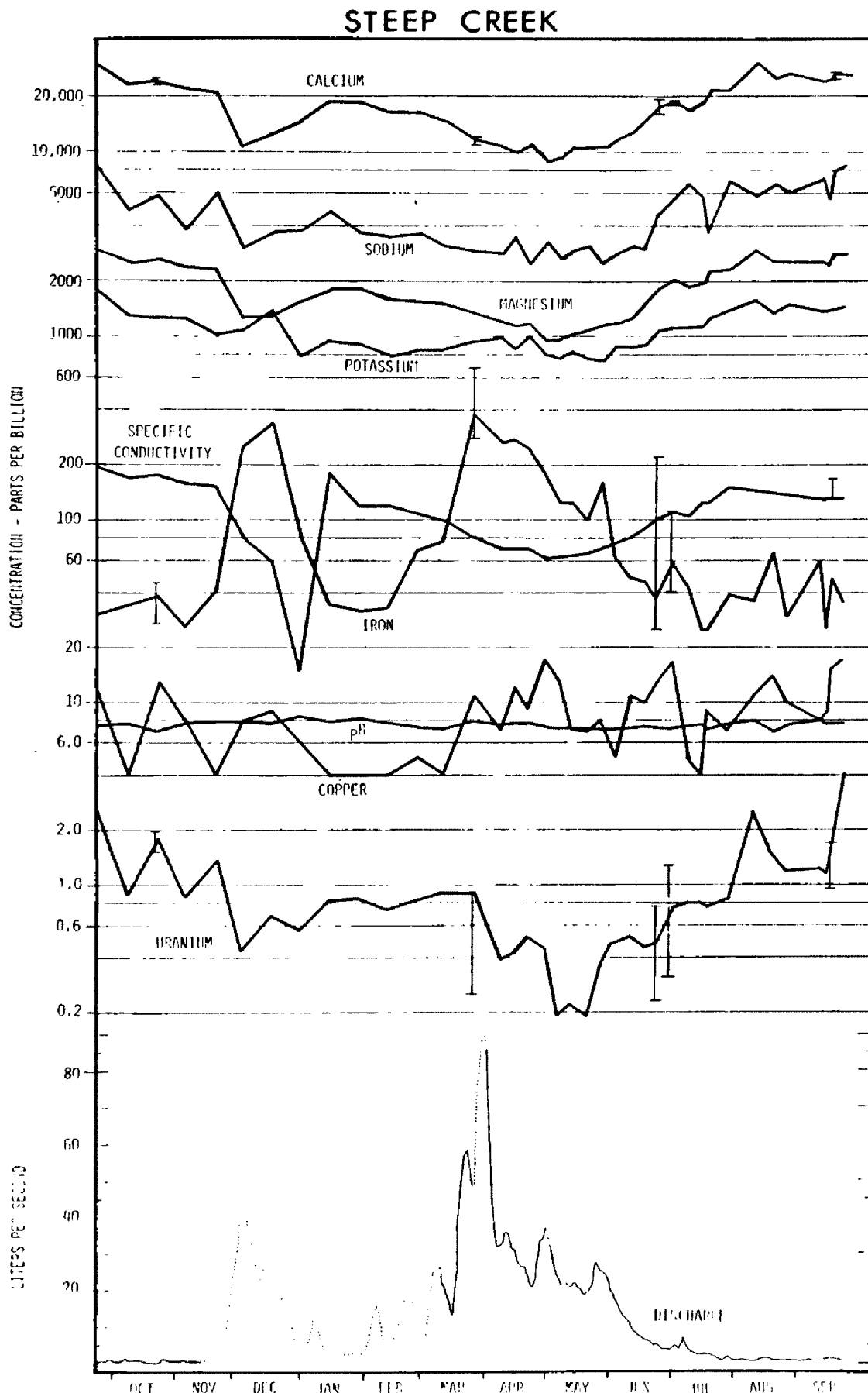


FIGURE 13. CHEMOTOGRAPH FOR STEEP CREEK. DOTTED PORTION OF HYDROGRAPH REPRESENTS INFERRED DISCHARGE DATA BASED UPON THERMOG GAGE HEIGHT READINGS AND CORRELATED TEMPERATURE INFORMATION FROM THE SULA AND DABBY WEATHER STATIONS. ERROR BARS REPRESENT THE RANGE OF VARIATION WHICH OCCURRED AT TIMES OF DIURNAL SAMPLING.

Discussion of Stream Chemical Data

The chemical characteristics of stream water results from the complex interactions between water, organic matter, soil and bedrock. Attempts to understand the fluctuations of uranium concentrations in stream water system requires more than consideration of uranium and discharge alone. This is because uranium is interacting with many other constituents in the hydrologic system. Some serve to increase uranium solubility while some interactions tend to remove uranium from solution.

The remainder of this chapter attempts to lay the groundwork for understanding why uranium concentrations vary by identifying how some of these interrelated factors behave in the hydrologic system.

The most striking feature of the chemographs is the pervasive inverse relationship between discharge and concentration of uranium and the major cations. This inverse relationship is the result of dilution, a phenomenon common to nearly all cations in solution in stream water. Dilution occurs because of the difference in the rate that concentrated and unconcentrated water enters the stream channel. When discharge is high the rate that unconcentrated water enters the stream is much greater than the rate of concentrated water, consequently the concentration of mixed waters is low. The opposite relationship exists and results in higher concentrations when discharge is low.

Several studies (O'Connor, 1976; Johnson, et. al., 1969) that deal with variation of major cations in solution use a mixing model in which the concentration of water from different source areas (ie. deep ground

water and throughflow) is constant through time, but that the rate of water flowing from these source areas change. Thus, the concentration of the waters mixed in the stream change as the rate of source area contribution to the stream changes. This allows a convenient mathematical simulation of the change in stream water chemistry. However, this model probably does not describe the actual mechanics causing stream water concentrations to change in the system, because it is unlikely that the concentration of water from individual source areas remains constant.

Presumably, some degree of mixing does occur in the Applebury and Steep Creek watersheds. The source of concentrated waters are bedrock and low horizons of deeper soils where water is in contact with rock and soils for a long period of time. These waters mix in the stream with unconcentrated water derived from zones where infiltration rates are greater and water spends less time in contact with the soil before entering the stream. Realistically, the concentrations of water from unique source areas change as some function of the source area chemistry and the rate of water flowing through the source area medium. Along the entire length of the stream many unique source areas probably exist but measuring concentrations and flow rates from individual source areas are very difficult and beyond the scope of this study.

Iron in the Stream

Iron is the only element that has a positive correlation with

discharge, thus, its behavior is different than any of the other elements studied. The apparent explanation for this is simple. The Eh-pH conditions of the streams are conducive to the oxidation of iron. Groundwater carrying reduced iron in solution is oxidized rapidly upon entering the stream. When discharge is low this oxidized iron precipitates on the bed of the stream forming a thin veneer of colloidal, ferric oxyhydroxide. During periods of low flow it is common to observe accumulations of iron precipitant forming on rocks and gravel below the stream water surface. During periods of high discharge this material is taken into suspension and flushed from the system. The colloidal particles are small and easily pass through the .4 u-millipore filters. Thus, when samples are collected during periods of high discharge iron concentrations are generally very high. However, the data indicate that not all samples collected during periods of high discharge have high concentrations of iron. This appears to indicate that over extended periods of high discharge much of the ferric iron may be flushed from the system.

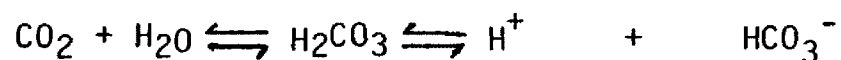
pH Conditions in the Stream

The pH of the stream waters reflects, perhaps better than any other variable, the dynamic equilibrium which exists between the physical, chemical and biological mechanisms in the watersheds. In Chapter VII I show that under certain conditions large changes in pH may accompany anomalously high uranium concentrations, thus it is important to understand the dynamics of pH in the stream waters of the study area.

The annual mean pH of both streams is 7.5 with a standard deviation of .3 pH units. Variation of pH in the streams does not correlate with changes in air temperature, specific conductivity or the concentration of the major cations. The waters of both streams appear to have lower pH during the falling limb of spring runoff which could be the result of lower water temperatures or a greater amount of water turbulence. Both conditions would increase the amount of dissolved carbon dioxide (Krauskopf, 1965) and decrease pH. However, the relationship between water temperature, discharge and pH is inconsistent and these factors do not appear to have a significant influence on the variation in pH.

The only consistent correlation that appears to exist with pH is its tendency to vary radically during or shortly after rain storms or during periods of extremely low flow. The reason for this is unclear. It appears to be related to a combination of the chemical process that controls the pH in these streams and the different response of source areas to changing hydrologic conditions.

The pH of the streams changes as a function of the partial pressure of carbon dioxide over water according to the following equations.



Thus it can be shown that a general parity exists between bicarbonate and pH (Krauskopf, 1965; Garrels and Crist, 1965). If bicarbonate is

he predominate anion in the streams then presumedly pH varies as a function of the partial pressure of carbon dioxide within the limits of the buffering capacity of the stream water.

Although no anion concentrations were measured in this study it is generally assumed that under slightly alkaline pH conditions natural stream waters flowing from granitic rock are dominated by bicarbonate anions if sulfide minerals are not abundant in the rock. The closest example of this, perhaps is Emmett's (1975) data on the concentrations of anion species in the waters of the Salmon River flowing over rocks of the Idaho batholith under similar climatic conditions (see footnote). My analysis of his data from nine streams draining only rocks of the Idaho batholith shows a mean pH of 7.6 and a ratio of HCO_3^- : $\text{SO}_4^{=}$: Cl^- : F^- : $\text{PO}_4^{=}$ to be 1: .08 : .0098 : .0043 : .0009 indicating that bicarbonate is by far the predominate anion in solution. Examination of thin sections from the three rock types in my study area showed virtually no sulfides and only trace amounts of apatite, the principal sources of $\text{SO}_4^{=}$, $\text{PO}_4^{=}$, and F^- in natural waters, respectively. Assuming Emmett's (1975) data may be extrapolated to this study area, bicarbonate is the predominate anion in solution and the pH in the streams varies as a function of the partial pressure of carbon dioxide over the waters of the study area.

The following water data station numbers from Emmett's (1975) report were used for the computation of the anion ratios given above:
 13-2924, 13-2932, 13-2934, 13-2950, 13-2956.5, 13-2960, 13-2965,
 13-2970, 13-2971.

Typical CO₂ partial pressures for soil and free atmosphere are: $P_{\text{CO}_2\text{-soil}} = 10^{-2.0}$, $P_{\text{CO}_2\text{-air}} = 10^{-3.2}$

(Devoto, 1978). However, partial pressures of CO₂ in soils are variable depending on the content and decomposition of organic material within the soil. More vegetated soils typically have high CO₂ partial pressures (Kossovich, 1967). Because the water measured at the flume is a mixture of waters from source areas with different vegetative cover and carbon dioxide partial pressures, the pH is in transition between the equilibria developed under various partial pressure conditions.

Short lived "spikes" of anomalously high or low pH values are recorded periodically in the sampling, suggesting that over short periods of time, usually on the order of hours, packages of water with unique chemical histories pass by the flume. Abnormally low pH values appear to occur most often during periods of low flow. During the period when evapotranspiration causes large variations in the daily discharge of the streams, abnormally low pH values are associated with diurnal-discharge minimums. This suggests that during this period the major source of water to the streams are springs and seeps that contain abundant decaying organic material. Spikes of high pH seem to be associated with pulses of water pushed quickly from unvegetated soils during or soon after precipitation events. One particularly good example is shown in Figure 14 which represents one suite of diurnal samples collected from Applebury Creek in early July.

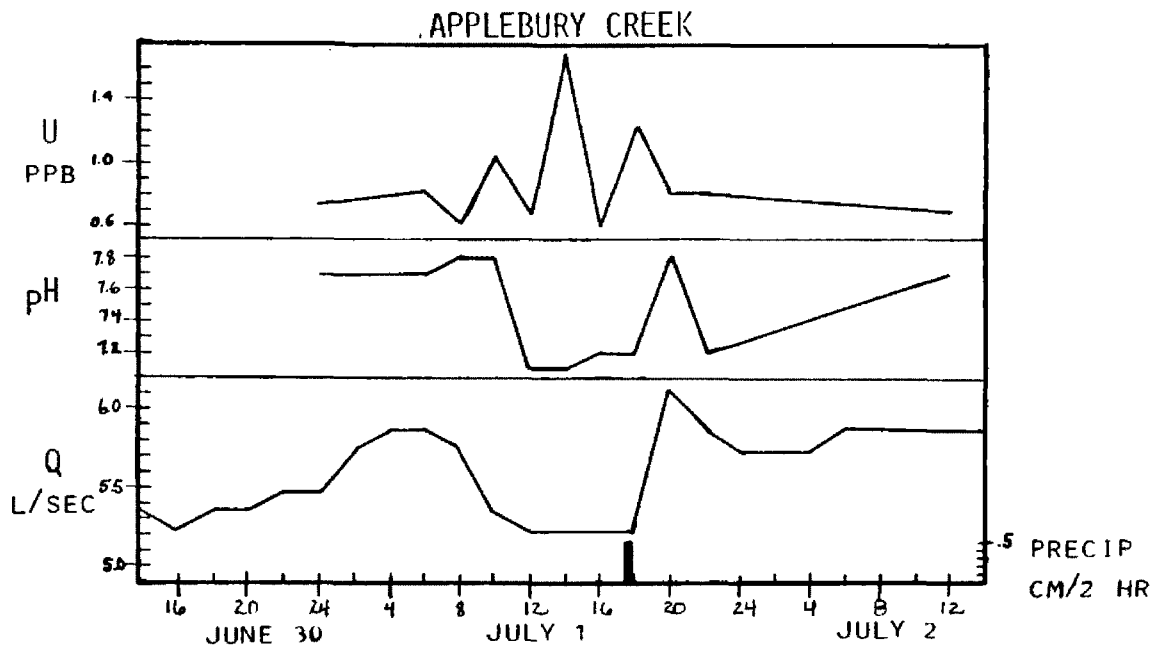


Figure 14. Chemograph for diurnal sampling of Applebury Creek in early July, 1978. By early July the diurnal variation in evapotranspiration has a significant influence on discharge and pH. Early in the morning discharge begins to decrease as evapotranspiration reduces the contribution of soil water to the stream. The pH decreases as the proportion of soil water in the stream decreases. Both discharge and pH increase rapidly in response to a small rain storm at 5:30 pm. Note the large variation in uranium concentration when discharge is at a minimum.

Although short term fluctuations in pH occur more frequently during or soon after storm events there is little reason to believe that the response is consistent throughout the year. As indicated in the discussion of hydrology, lag times vary on an annual cycle primarily as a function of soil moisture. The response of pH to a particular precipitation event is then a function not only of magnitude

and duration of an individual storm but also of the prevailing moisture conditions existing before the storm. This makes it difficult to predict the precise time and magnitude of pH change in response to storm events.

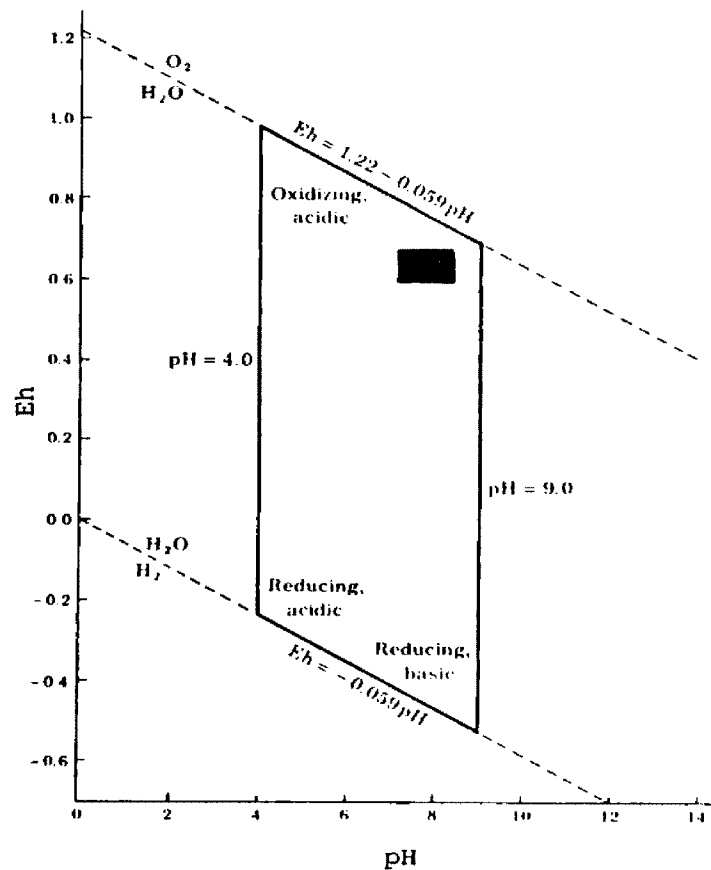


Figure 15. The dark rectangle in the diagram represents the probable range of Eh-pH conditions in the streams of the study area. (Diagram is from Krauskopf, 1965)

Oxidation Potential

The oxidation potential of the stream environment is high. Dissolved oxygen concentrations measured at the flumes at various

times throughout the year was consistently 18 mg/liter. Based on mean pH values, calculated Eh values (Krauskopf, 1965) centered around + .6 mv. Figure 15 shows the likely range of Eh-pH conditions existing in the stream channels of the study area.

Cation Concentrations

Concentrations of the major cations are not recognized as having a significant influence on uranium concentrations in stream water (Devoto, 1978). However, they provide an adequate means of measuring the influence of climate on the weathering and release of cations to the stream, including uranium. For surface waters in the common range of pH 5.0-8.5, the values for specific conductivity and total dissolved solids are determined primarily by the concentrations of major cations in solution. The ratio of mean cation concentrations of the study area are given in Table 4. Emmett's (1975) data for the nine streams mentioned previously are included for comparison.

Table 4 . Ratio of mean cation concentrations in the streams of the study area.

	Ca	:	Na	:	Mg	:	K
Applebury Creek	1		.44		.14		.09
Steep Creek	1		.26		.11		.06
Upper Salmon River (Emmett, 1975)	1		.22		.12		.04

CHAPTER VII

DISCUSSION

Annual and Diurnal Variation of Uranium in the Streams

Mean uranium concentrations and standard deviations for Applebury and Steep Creek waters are .93 ppb \pm .56 ppb and .91 ppb \pm .59 ppb respectively. (See Table 3 and Figures 12 and 13). Throughout the study period uranium concentrations for Applebury Creek ranged between .3 ppb and 3.5 ppb and Steep Creek values ranged between .19 ppb and 3.03 ppb. This is a large amount of variation and can lead to errors in the interpretation of hydrogeochemical survey data. This is discussed in greater detail later in this chapter. More significant perhaps are the results from the five sets of diurnal sampling which show that large variations in uranium concentration occur within the time span of a few short hours.

The range bars in Figures 12 and 13 represent variation in uranium concentration during the diurnal sampling periods. They indicated that on several occasions the variation in uranium concentration within a 24 hour period approached one order of magnitude. It is possible that on many days the amount of diurnal change in uranium concentration is as great as the amount of variation observed over the entire year. The number of diurnal sampling periods is small. Also, the sample population for each set is small (samples usually collected every 3-4 hours), and many periods of large variation were probably missed.

Variability of Uranium Relative to the Other Cations

Each exploration technique that a geologist may use searching for uranium involves measuring a unique parameter or set of parameters. In order to match the proper technique with the field conditions it is important for the geologist to understand the range of variability associated with the parameters he is attempting to measure. A comparison between the variability of uranium in Applebury and Steep Creek and the variability of the other chemical constituents in the streams may be useful in evaluating the hydrogeochemical technique. Variability is a useful statistic for comparing the relative amount of change associated with different chemical constituents in stream water. It is derived by dividing the standard deviation by the mean concentration of each chemical constituent for all the samples from each stream. Table 3 shows the variability for the major cations and uranium in Applebury and Steep Creeks. The table shows that variation in uranium concentration is generally 2-3 times greater than the variation in the major cations in the stream water. This suggests that uranium is generally more sensitive to the changing conditions in the watershed system. Some of the sensitivity is probably related to its much lower concentrations but probably reflects the greater chemical activity of uranium relative to the major cations.

The change in uranium concentration of the stream water tends to progress sympathetically with specific conductivity and the concentration of the major cations in solution (see Figures 12 and 13). Concentrations are generally lower between the periods of early April and mid-June because of dilution from snowmelt runoff. From mid-June on concentrations

begin to rise gradually to a maximum in late September and October. The chemograph for Steep Creek (Figure 13) shows this relationship better than the Applebury Creek chemograph (Figure 12). The months between October and April are a transition period for the streams and uranium concentration becomes less predictable. Stream discharge is low and not changing rapidly because of cold weather conditions. Precipitation falling as snow appears to have little influence on stream water concentrations. Occasional periods of above freezing temperatures do deliver short-lived pulses of rain or snowmelt water which appear to cause large perturbations in uranium concentration. Samples 279 and 281 collected from Applebury Creek (Figure 8) show this relationship. There was a heavy snowpack on the ground during this period. A three day period of above freezing temperatures preceded both of the days on which these samples were collected. A rapid flushing of uranium from the snow pack may be the cause of the higher uranium concentrations in these samples. Johannessen and Henriksen (1978), studying the chemistry of snowmelt water, found in Norway that snowpacks tend to accumulate atmospheric pollutants through the year and that 50-80% of this pollutant load is released with the first 30% of the meltwater. They suggest that the very first fractions of meltwater may contain more than 5 times the concentrations the snowpack concentrations contain. This phenomenon may explain the higher concentrations of uranium in these samples. However, it is not possible to substantiate this based upon the data collected in this study.

At the beginning of this study it was not known precisely how uranium concentrations in Applebury and Steep Creek would change through the annual

hydrologic cycle. The data indicate that uranium concentrations do vary through an annual cycle; however, the cycle is not distinct. Random perturbations do occur which appear unrelated to fluctuations in discharge. The structure of the sampling program was based on the hypothesis that the dilution effect (Walling, 1975) resulting from changes in discharge is the principal mechanism causing uranium concentrations to change in stream water. The large diurnal variations observed (Figures 8 and 9) combined with the following synthesis of chemical and discharge data suggest that other factors, in addition to the dilution effect, influence the concentration of uranium in stream water.

Log-log plots of uranium on discharge for each stream are shown in Figures 16 and 17. If uranium concentration is a function only of discharge then the data points should define a negative sloping line indicating that dilution occurs with increasing discharge. Scatter about that line should be minimal. The data from Steep Creek (Figure 17) does define a negative sloping trend and supports the dilution concept. However, there is significant scatter in the points suggesting, that for a given discharge, another variable or group of variables are acting to alter the expected uranium concentration. This is much more evident in the Applebury Creek data (Figure 16) where the scatter of points is too random to decipher a negative sloping trend. Indeed, these graphs suggest that dilution plays a less significant roll in altering uranium concentrations in Applebury Creek than in Steep Creek. In order to better understand uranium's apparent fluctuations in stream water, it is important to identify these factors and to try and understand when and how they work to alter uranium concentrations in a natural hydrologic system.

APPLEBURY CREEK LOG-LOG PLOT OF URANIUM ON DISCHARGE

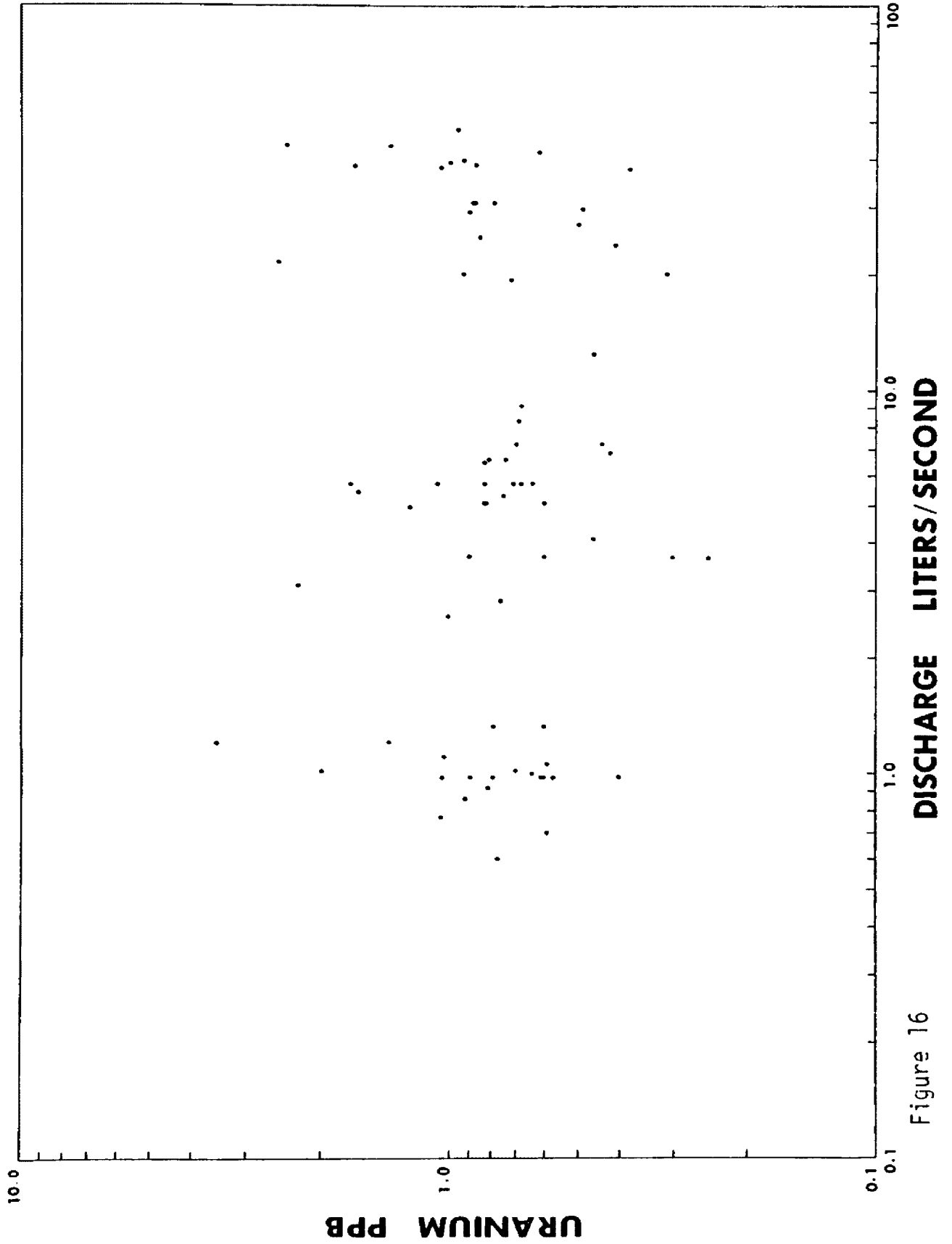


Figure 16

STEEP CREEK LOG-LOG PLOT OF URANIUM ON DISCHARGE

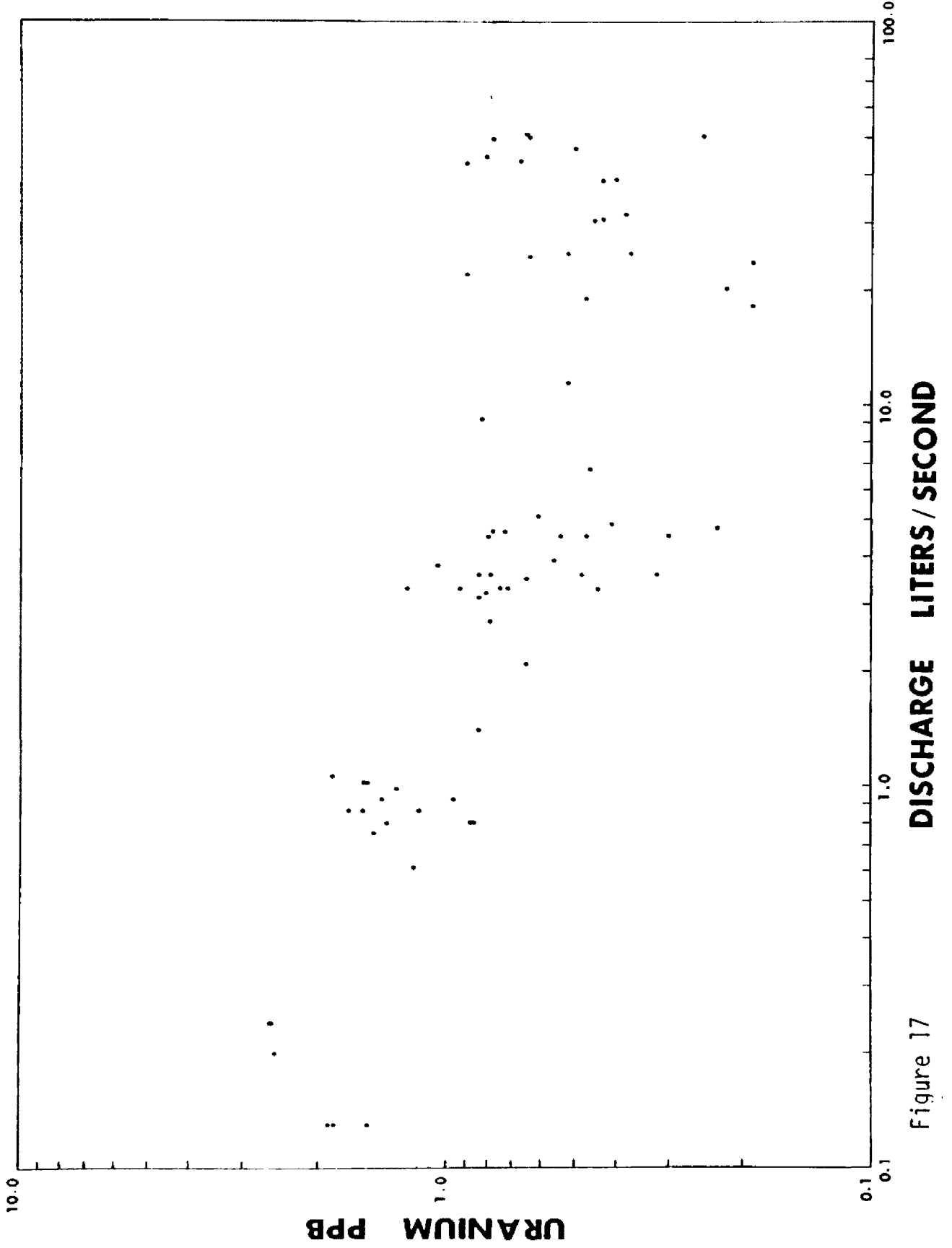


Figure 17

Solution and Absorbption Processes that Influence Uranium Solubility

Various studies on the leaching of uranium from granitic rock (Pliler and Adams, 1962; Larsen, et al., 1956; Picciotto, 1950) indicate that uranium partitions in about equal proportions into accessory minerals and common rock forming silicates, or their alteration products. In an oxidizing environment, in the presence of water, these minerals are hydrolized and the major cations go into solution. Uranium combines with oxygen to form the stable uranyl ion UO_2^{++} which is readily soluble in water. Thus, solution of uranium and the major rock forming elements proceeds concurrently. It is not surprising then that various studies find a strong correlation between uranium concentration in stream water and specific conductivity, a measure of the soluble cations in natural waters (Dall'Aglio, 1971, 1964; Dall'Aglio and Tonai, 1962; Lopatkina, 1964).

It is commonly thought that hydrolysis and solution are the principle chemical mechanisms which determine the concentrations in solution of uranium and common rock forming elements; furthermore, the longer groundwater is in contact with bedrock the greater the concentration of these constituents. However, experiments by Szalay and Samsoni (1969) on the leaching of uranium from crushed intrusive and extrusive magmatic rock of different compositions indicate that hydrolysis and solution are not the only chemical mechanisms that affect uranium equilibrium concentrations in water. A discussion of their work provides a better understanding of the varying concentrations of uranium in bicarbonate waters.

Szalay and Samsoni's (1969) results from the leaching of powdered rocks with a 2% NaHCO_3 solution show:

1. Uranium concentration in leaching solutions reached equilibrium concentrations within a few hours.
2. Equilibrium values are significantly different for different rock types of identical grainsize with the highest concentrations derived from the leaching of granite and the lowest concentrations derived from the leaching of gabbros and basalts. This is due to inherent differences in uranium concentrations for each rock type.
3. Grainsize has only a moderate effect on the uranium concentrations in solution.

The fact that equilibrium occurs so quickly led them initially to conclude that UO_4 on grain boundaries is oxidized to UO_2^{++} , complexed with $\text{CO}_3^{=}$, and taken readily into solution until all the available UO_4 is dissolved. Further experiments however, showed that in subsequent washings of the same samples, fresh leach solutions consistantly reached similar equilibrium concentrations. Thus, their final conclusion is that processes of hydrolysis and solution increase uranium in water and the process of adsorbtion of uranyl back onto grain boundaries remove it from solution. The processes act simultaneously, and independently but in opposing directions and equilibrium between the two is established within a few hours.

The concentration of various anionic ligands in water tend to increase the amount of uranium in solution by first increasing its solubility and

second by inhibiting the amount of uranium removed from solution by absorption onto particulate surfaces. Devoto (1978) and Langmuir (1978) present comprehensive reviews of these ligands and the results of their interactions with uranyl in solution. They point out that uranyl ions readily complex with any of the following anion ligands; carbonate, hydroxide, phosphate, fluoride and sulfate as a function of relative concentrations and pH. For typical ligand concentrations of stream water, the most important uranyl complexes are formed with fluoride, phosphate and carbonate under acid, near neutral and alkaline conditions, respectively (Langmuir, 1978). For the slightly alkaline waters of this study area, in which bicarbonate anions predominate, Figure 18 indicates the most probable uranyl complex is $\text{UO}_2(\text{CO}_3)_2^{-2}$.

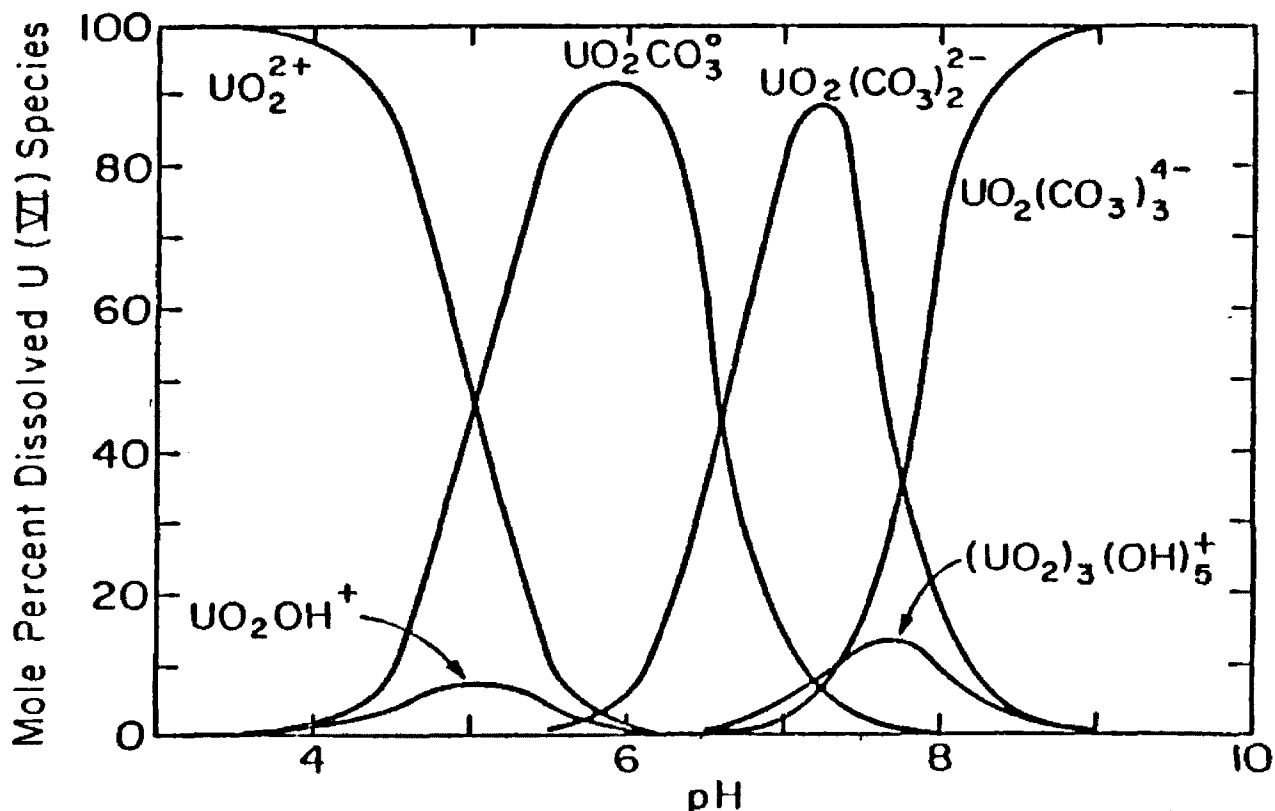


Fig. 18. Distribution of uranyl-hydroxy and carbonate complexes versus pH for $P_{\text{CO}_2} = 10^{-2}$ atm and $\Sigma\text{U} = 10^{-8}$ M (2.4 ppb) at 25°C (Langmuir, 1978).

As discussed previously, bicarbonate concentrations can be quite variable in ground water moving through a watershed, depending upon organic activity and temperature. This, combined with the ability of bicarbonate to complex with uranyl ions and effectively increasing uranium solubility, suggests that the activity of bicarbonate in the system probably is an important factor influencing the uranium concentration of Applebury and Steep Creek.

Uranyl ions may also complex with humic acids produced by biologic decay of plant material (Szalay, 1964; Jennings and Leventhal, 1976, 1977, 1978). Because humic acids are insoluble under near neutral conditions, they are relatively immobile in the biolith. Therefore, they provide a chemical sink for the uranyl ion. Humic acids complex the greatest quantity of uranyl ions in the near neutral pH region but the stability of the uranyl-humic acid complex is strongly pH dependent (Jennings and Leventhal, 1977). Deviations from neutral conditions can cause uranium to go back into solution. Because of this phenomenon changes in pH and biological decay rates probably influence the concentrations of uranium of the ground and stream waters of Applebury and Steep Creek. This interaction is probably more significant during the summer months because warmer temperatures affect the rate of biological decay and production of humic acids.

Uranyl ions not complexed with these organic or inorganic ligands are very susceptible to adsorption onto natural colloidal materials, most notably, ferric and manganese oxyhydroxides (Szalay, 1964). Sorbed uranyl ions, not chemically reduced by the sorbant, can be desorbed by increasing

the pH, or increasing alkaline ion concentrations at constant pH (Van Der Wiejen, et al., 1976; Van Der Wiejen and Langmuir, 1975). Thus, a change of PH in the stream is a potential source of uranium variation in stream water. Figure 19 illustrates that uranyl is effectively removed from solution by adsorption onto amorphous ferric oxyhydroxide in the pH range common in natural waters.

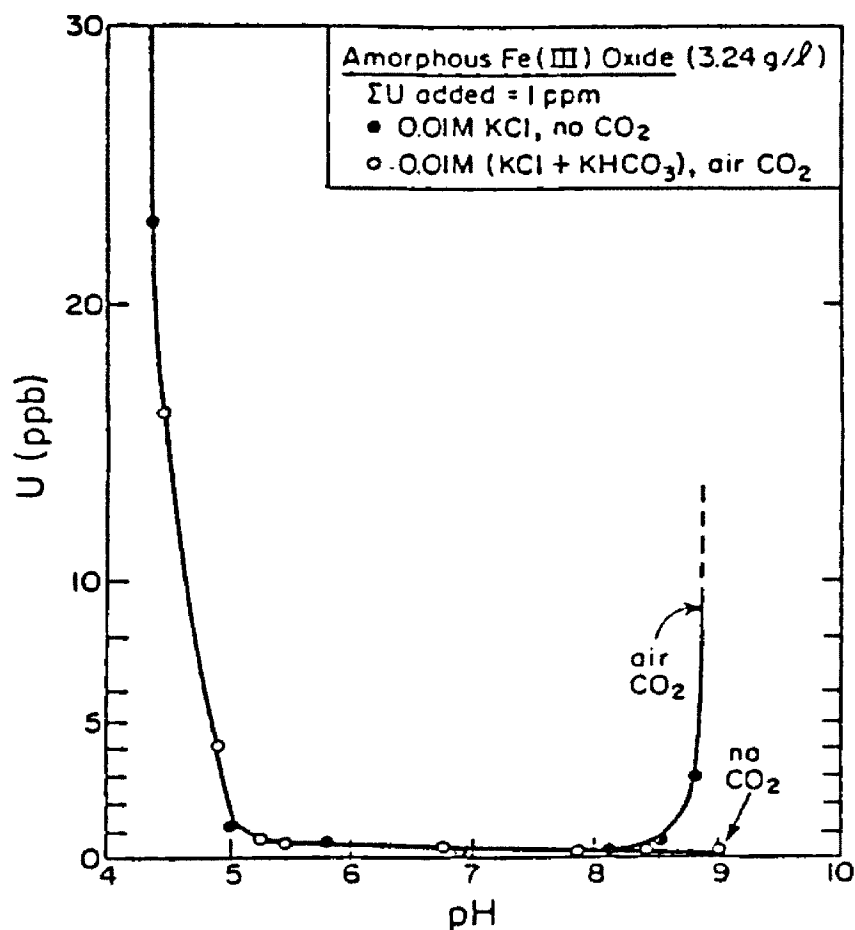


Figure 19. Adsorption of uranyl onto X-ray amorphous ferric oxyhydroxide as a function of pH (oxyhydroxide surface area 285 m²/g, H₂O/Fe₂O₃ molar = 1.38, PZC = 8.6), (Langmuir, 1978).

The large variation in uranium concentration, not explained by variation in discharge, is probably caused by the activity of the solution and adsorption processes discussed above. The following comments by Langmuir (1978) focus on the relative importance of the two processes and provide a framework for understanding the behavior of uranium in the stream waters of the study area.

Both solubility and adsorption data show uranyl to be least mobile in the pH range 5-8.5. However, whereas mineral solubilities limit only maximal uranyl concentrations, adsorption limits uranyl concentrations at all levels below saturation with the least soluble uranyl mineral in a given water. In contrast to solubility control, the highest percentage of total uranium in a sediment-water system is sorbed on the sediment at the lowest dissolved uranium levels.

Rose et al. (1977) presents evidence to indicate that, in soils surrounding a sandstone type uranium deposit, the adsorption of uranyl onto ferric oxyhydroxides has the greatest influence on the removal of uranyl dissolved in groundwater followed by the complexing of uranyl with organic material. Szalay's (1964) mechanism of resorption on to grain boundaries appears to be least important in reducing uranium concentration in natural waters. All three mechanisms are sensitive to changes in pH. Higher anion concentrations favor increased uranium mobility and higher uranium concentrations in solution by; increasing uranyl solubility; inhibiting adsorption onto ferric hydroxide particles and rock grain boundaries; and breaking uranyl-humic acid bonds. Any activity in the soil-sediment-water system that alters pH or anion concentration is a potential factor that may cause uranium concentrations to change. Several activities that may result in uranium fluctuation are changes in ground-water levels,

infiltration of unbuffered acidic rain water, or increased biological activity in the soil. It is not possible, based upon the kinds of data collected in this study, to determine how much these factors are actually acting to alter uranium concentrations. The lack of strong correlation between uranium concentration and discharge and the fact that these geochemical factors are present in the watersheds suggests that the variation of uranium concentration in the streams is caused by the interaction of mechanical and geochemical processes.

Differences in Scatter Between Applebury-Steep Creek Discharge-Uranium Concentration Plots

It is not known precisely why such a poor correlation exists between discharge and uranium concentration for Applebury Creek (Figure 16), or why the correlation differs so much between Applebury and Steep Creek. However, the differences in the amount of vegetation along the margins of each stream is seen as one possible cause. Vegetation in a watershed is an integral part of the hydrologic regime. Where trees abound evapotranspiration can greatly reduce soil moisture during the growing season and the shade from trees can prolong for many weeks the melting of snow from forested areas. Differences in slope angles, weathering, infiltration and many other hydrologic parameters are affected by vegetation. As indicated previously, the amount of vegetation may influence soil water pH which, in turn, may affect the solution and adsorption of uranyl.

In a mixed watershed, there are, in effect, at least two hydrologic systems acting, sometimes together and sometimes in opposite directions,

supplying water to the main channel. Each system delivers water to the stream with a unique chemical signature reflecting the state of the system at any point in time.

During the early stages of spring runoff, water from unforested slopes is perhaps much more dilute than waters from forested slopes where snow melt feeds runoff for longer periods into the spring. The concentration of elements in water measured at the flumes can represent an entire spectrum of water mixing from the two, or more, systems. The fact that data from Steep Creek shows a better correlation between discharge and uranium concentration than Applebury Creek suggests that the forested hydrologic system may have a dominate influence on the stream water chemistry during a greater portion of the year. This is due, perhaps, to the greater proportion of forest directly adjacent to the stream channel. In Applebury Creek the amount of forested and unforested area adjacent to the channel is nearly equal such that neither system is dominant over long periods. The data from this study however, is insufficient to resolve this problem and a much more extensive sampling program would be required to define this relationship.

Uranium Variation in Stream Water -- Implications for the Interpretation of Hydrogeochemical Survey Data

In this study, uranium concentrations in water are very low because uranium concentration in the rocks (weighted mean = 2.35 ppm) is low. However, this does not diminish the significance of the large variation recorded in the stream water samples. For instance, Germanov et. al. (1958) studied the differences in variation of uranium with discharge from

spring water draining unmineralized and mineralized terrain. His investigations showed that the character of seasonal changes is quite different between the two. In unmineralized watersheds the difference between minimum and maximum values is seldom less than twofold, much less than is observed in this study. Much more significant is his finding that for springs feeding streams in mineralized areas the variation in concentration is tenfold or more.

If Germanov's et. al. (1958) conclusions are correct, there exists a strong possibility that many mineralized watersheds could have mixed in a hydrogeochemical survey (Type II error). It is very important to establish if a type I or Type II error can occur. The author has undertaken a small study to test if uranium variation in stream water can cause errors in interpreting actual data from a large hydrogeochemical survey in a mineralized region.

During the spring and fall of 1976 the author supervised a pilot study designed to test uranium hydrogeochemical sampling techniques in a mountainous area having known hydrothermal uranium occurrences. The study (Aamodt, 1978) sponsored by Los Alamos Scientific Laboratories in support of the NURE program, was directed by Dr. Silverman and Dr. Lange at the University of Montana, Missoula. The survey area covered all of the Boulder Batholith of Western Montana comprising an area of approximately 5000 square kilometers. A total of 1046 locations were visited, and from those locations 917 water samples were collected primarily from streams. A few samples were also collected from springs and wells. Of the 917 water samples collected, 666 were collected during the spring in April,

May and June, and 251 samples were collected in fall during October and November. The samples collected in the fall were taken from identical locations that were sampled during the spring sampling which makes it possible to compare the variation in uranium concentration collected from the same source twice in one year.

In Figure 20 the concentration of uranium from 239 streams that were sampled both in the spring and the fall are plotted. The data indicate concentrations for samples collected in the spring and the lines drawn from the dots represents the variation in concentrations for each stream during the fall sampling. The mean and standard deviation of all the stream water samples collected from the Boulder batholith are $3.21 \text{ ppb} \pm 6.45 \text{ ppb}$. The mean and 1, 2 and 3 standard deviations are plotted in the upper portion of the graph.

Geologists typically will use different cutoffs for designating which streams are anomalous and deserve further investigation. The determination of a cutoff concentration usually involves a consideration of the distribution of the sample population, climate and general rock compositions. Commonly the cutoff will be 2 standard deviations above the mean concentrations of all samples collected in the survey.

This plot is important because it shows that for a number of streams the variation in concentration between the spring and fall sampling spans 2 standard deviations. For several of the streams the concentrations span 3 standard deviations. In addition, the expected trend of low concentration in spring and higher concentrations in the fall is not consistent.

EACH POINT AND LINE REPRESENT URANIUM VARIATION FOR A SINGLE STREAM

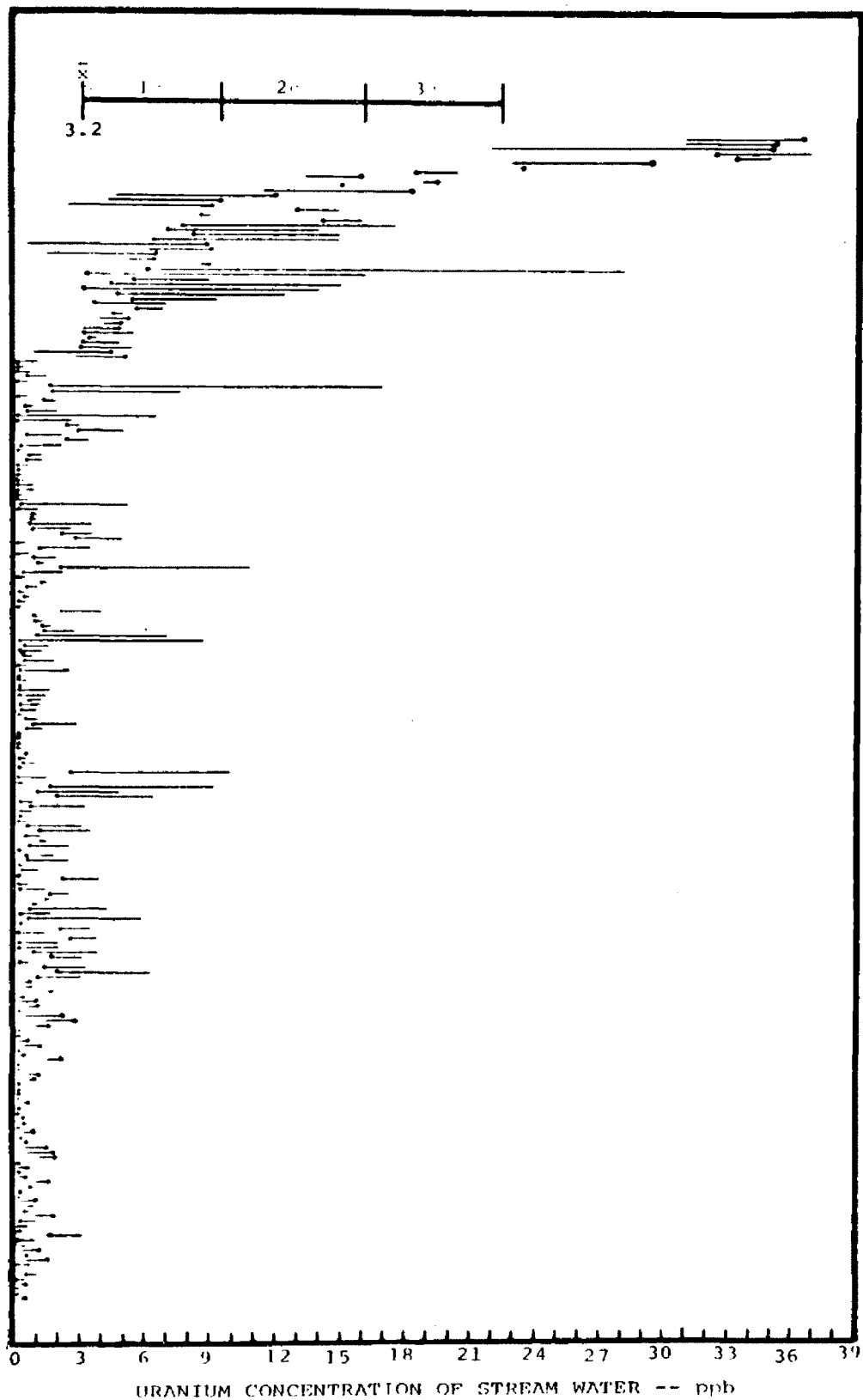


Figure 20. Range of variation in uranium concentration in water from 239 streams studied in the Boulder Batholith Pilot Study (Amodei, 1978). Streams were sampled twice in one year. The first sampling of each stream was in the spring between April and June and are represented by dots on the bar graphs. The second sampling of each stream was done in the fall between August and November. Uranium concentrations for those samples are represented by the end of the lines leading from the dots. The bar graph at the top of the figure gives the mean and range for 1, 2 and 3 standard deviations above the mean for all 851 streams sampled in the Boulder Batholith.

Some streams, particularly those with higher average concentrations, show a decrease in concentration during the fall sampling. Regardless of the designated cutoff, the data indicate that variation in uranium concentration spans a significant range and there is a strong possibility that Type I or Type II error would be made from the analysis of stream water samples collected only once in a reconnaissance survey.

Identifying Abnormal Stream Water Samples

The large amount of variation in uranium concentration raises an important question about the practicality of using stream water as an exploration tool. The fact that the HSSR program has relied heavily on stream water samples, especially during the early stages of the program and in mountainous terrain where access is limited, dictates that methods be developed for correctly interpreting stream water samples. The data from the Applebury and Steep Creek study will be of service in providing a practical methodology. The problem is how to identify samples that truly reflect high or low concentrations of uranium in the source rock from samples that appear anomalous but result from variation in uranium concentration in the stream. The method described below may provide an answer.

Variations in discharge apparently have a major influence on the variation in uranium concentration. However, in a reconnaissance sampling program it is impossible to collect samples of stream water under uniform discharge conditions. Ideally the explorationist needs an internal chemical standard to compare uranium against and that adjusts for variations in discharge. This standard must be present in both rock and water, and vary only as

a function of discharge in the stream. A series of least squares regressions were run on data from this study to identify the chemical variable that best predicts discharge for both streams over the total range of discharge.

The results of the regressions of discharge on chemical variables is shown in Table 5. Iron is shown in the table because of the strength and direction of its correlation; however, in many samples the analysis for iron is below its lower detection limit and thus it is not considered an adequate predictor of discharge in this study. When the data from both streams is considered, calcium concentration is deemed the best predictor of discharge. If calcium concentration is, as the data suggests, an

Table 5. Correlation coefficients for least squares regression of log discharge on calcium, magnesium, sodium, potassium, iron and specific conductivity.

	<u>Applebury Creek</u>		<u>Steep Creek</u>	
	R	R ²	R	R ²
Ca	-.77	.60	-.92	.85
Mg	-.61	.38	-.91	.83
Na	-.21	.05	-.77	.56
K	.25	.06	-.74	.55
Fe	.71	.50	.58	.33
Specific Conductivity	-.67	.45	-.92	.85

adequate predictor of discharge then by regressing uranium to calcium it is possible to observe the variation in uranium adjusted for the influence of discharge. The reason that calcium is used rather than discharge itself is because in a reconnaissance stream sampling program it becomes very difficult to quantitatively assess the discharge without long term flow data from individual streams.

Figure 21 is a log normal plot of uranium to calcium for Applebury and Steep Creek data combined. Included on the diagram are the statistics of a least squares regression of uranium to calcium. Also included is the best fit to the data by a least squares regression. The lines on either side represent ± 1 standardized residual and the envelope between them represents the volume within which approximately 66% of the values are expected to fall. The numbers for outlying samples shown on the diagram reference the data listings in Appendix VI and the information in Table 6

Investigating the other chemical attributes of these outlying samples greatly enhances the understanding of uranium variation in the streams. Table 6 is a listing of the outlying samples greater than one standard residual. Included is a listing of the iron concentrations and associated pH. In a reconnaissance program, where many streams are sampled, values may plot out of the standardized residual boundary either because the rocks are enriched in uranium relative to calcium, or because uranium is varying according to some internal perturbation in the stream system. However, in this study the uranium concentration in water is constant. The data in Table 6 indicate that internal variation may be identified if samples possess at least one of the following four properties:

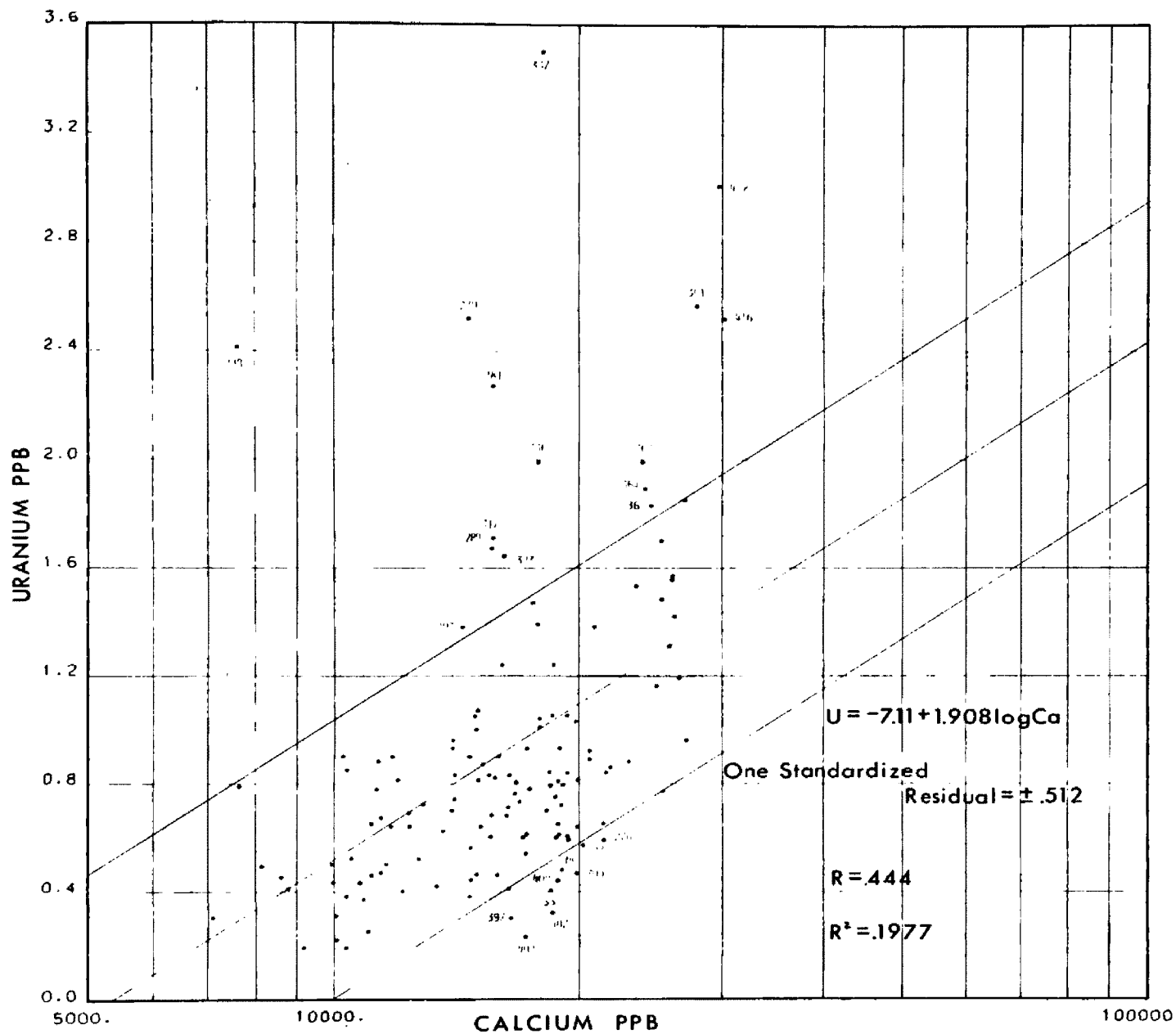


Figure 21. Log normal plot of uranium on calcium for combined water data from Applebury and Steep Creek. Computations were done by computer subprogram REGRESSION (Nie, et. al., 1975, Chapter 20). The upper and lower line represent one standardized residual on either side of the best fit line to the data (center diagonal line). Correlation coefficients for 142 samples are $R = .444$, $R^2 = .1977$.

Table 6. List of outlying samples from regression of uranium on calcium for combined water from Applebury and Steep Creek, see Figure 21. Mean pH for all samples is $7.5 \pm .28$ standard deviation. Mean iron concentration is $81.5 \text{ ppm} \pm 102 \text{ ppm}$ standard deviation.

Sample Number	pH	Q liter/sec	Fe ppb	Predictors of anomalous uranium concentrations					Explanation
				A	B	C	D	E	
279	8.1	21.7	147		X	X			
281	7.8	3.11	32					X	Sample had ten times background zinc concentration
289	7.4	38.5	121				X		
298	7.0	43.5	104		X	X			
317	7.1	5.73	-25		X	X			No explanation
323	7.5	5.46	-25						
336	7.8	1.02	28	X					
337	7.7	1.21	-25	X					
361	7.5	.24	30	X					
363	7.1	.09	45	X					
364	7.2	.13	27	X					
416	8.0	.20	36	X					
428	7.7	.71	35	X					
293	8.1	43.5	165	X			X		
332	7.5	.98	-25	X					No explanation
397	8.4	.30	33	X					
399	7.3	4.53	223		X				
402	7.3	7.76	42		X				
407	7.3	3.58	64		X				
409	7.2	3.21	50		X	X			
270	7.3	.7	-25	X					
271	7.6	.98	25	X					
406	7.6	3.58	81		X				

- A = samples that would be eliminated because of very low discharge
- B = samples that would be eliminated because of storm events
- C = samples that would be eliminated because of anomalous pH values
- D = samples with high iron
- E = contaminated samples

1. The pH of the samples are anomalously high or low. Anomalous pH values are considered to be one standard deviation above or below the mean of all pH values. Therefore, samples greater than 7.8 or less than 7.2 are anomalous.
2. Iron concentrations are greater than one standard deviation above the mean iron concentration for both streams.
3. Samples were collected in late summer and early fall after the period in which discharge ceased to be influenced by evapotranspiration by trees and when discharge is generally less than 2% of bank full stage.
4. Samples were collected during or soon after rain events.

The reason that samples appear to vary quite drastically when discharge is low is not entirely known, but it follows that these periods are a particularly poor time to sample. The potential for measuring widely varying uranium concentrations may be greater during this period for any of the following reasons:

1. The production and introduction of organic acids to the stream is greater because of higher temperatures and increase of biologic decay.
2. During periods of low flow the sources of water to the stream may be delicately balanced between deep ground water and saturated soil water. Moderate changes in the rate of contribution from these source areas may cause appreciable changes in water quality.

3. During low flow the proportion of water evaporated from the stream channel surface during the day may cause significant variation in stream water chemistry.

Whatever the reason it seems apparent that stream water sampling should be suspended during this period if reasonable results are desired in a stream water sampling program.

The data also suggests that sampling should be suspended during or within one or two days after rain events. The stream, in all physical and chemical aspects, is a system tending towards equilibrium. Rain events disrupt this equilibrium by altering the rates in which source areas deliver water to the stream. The uranyl ion, because of its affinity for bicarbonate complexes, is highly sensitive to changes in source areas that maintain different partial pressures of carbon dioxide. Thus, it is important that sampling not be conducted when the rate of water flowing from different source areas is changing rapidly.

When iron concentrations are high the chances of observing high uranium concentrations are much greater, particularly if the iron has sufficient time to scavenge uranyl ions from solution. For this reason, not all high iron concentrations correlate with high uranium. In addition, any of the three other properties above may be acting so that high uranium concentrations do not necessarily imply that iron concentrations are also high.

As the data in Table 6 indicate, anomalous pH is the property most commonly associated with high uranium concentrations. The fact that uranium

is usually high when pH is either high or low suggests that uranium concentration is changing; sometimes independently of pH as a function of dilution, and sometimes, concurrently with pH as a result of some other variable. For the streams of this study, that variable is probably a changing source area for the water making up the streams.

Application of Method to Reconnaissance Data

In regional uranium hydrogeochemical sampling programs, plotting uranium concentrations against calcium concentrations may make it possible to identify or eliminate stream water samples collected when the "chemical signature" of streams are deviating from their average chemical makeup. However, several conditions are necessary:

1. The streams compared in one survey should flow from one general rock type so that the weathering and release of uranium and calcium to the stream is generally the same throughout the survey area.
2. Climatic conditions, particularly precipitation, should not change significantly within the limits of the survey.
3. Water samples should not be collected during periods of extreme low flow (generally not less than 2% bank full stage) or during storm events.

If these assumptions are valid then anomalous pH values are those values greater or less than one standard deviation from the mean for all streams surveyed. Anomalous iron values are those greater than one standard deviation from the mean iron value for all the streams surveyed.

Mean calcium concentrations may vary between watersheds because of differences in rock type, differences in weathering rates between watersheds or differences in size of the watersheds sampled. Much of the variation in mean calcium concentration may be eliminated by comparing only samples collected within one rock type. The variation of mean calcium concentrations between various watersheds due to differences in weathering rates should not significantly affect this method because weathering of uranium and calcium proceed concurrently. Therefore, changes in uranium and calcium concentration with watershed size or aspect should be relatively similar.

When interpreting the results of plotting uranium concentrations against calcium concentrations, the geologist should suspect that values plotting outside of the one standardized residual envelope, and having anomalous pH or iron values, represent stream water chemical conditions which deviate from long run equilibrium. In this case, the stream should be sampled again before drawing any conclusions about the concentrations of uranium in the source rock.

To the authors knowledge this method has not been tested on reconnaissance hydrogeochemical data. It is not possible to apply this technique to the Boulder batholith pilot study because samples were analyzed only for uranium. The method may be especially useful if applied to distinct geologic provinces such as the major batholiths of the western United States. Many of these areas have already been sampled and sufficient data is now available from the NURE-HSSR program that this method can now be tested.

CHAPTER VIII

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

Man commonly looks within the boundaries of watersheds to find many of the natural resources that sustain his modern society. His attempt to locate and manage these natural resources is often reduced to a study of the physical and chemical properties of stream water because streams tend to integrate and reflect the chemical and physical properties of the watersheds they drain. Most studies are concerned with water quality or nutrient cycling in the biosphere and focus on the relationship between discharge and the concentration of major cations in solution. This study is different and perhaps more complex because it focuses on the behavior of uranium, a chemically unique element occurring in much lower concentrations in stream water.

This study does provide some insight into the behavior of an economically important element in a typical unmineralized watershed. Nevertheless, watersheds are extremely complex, dynamic systems and one should be careful in drawing conclusions from the limited amount of random stream water data presented in this study.

The concentration of uranium in both unmineralized watersheds is low which correlates with the low concentrations of uranium in the rocks of the study area. However, this relationship is not consistent. Uranium concentrations vary more than one order of magnitude within the period of one annual hydrologic cycle. Diurnal variation

approaches one order of magnitude and is probably greater. The amount of variation observed in Applebury and Steep Creek is consistent with the amount of variation observed in streams draining mineralized and unmineralized watersheds in the Boulder Batholith. This indicates that it is possible to overlook a mineralized watershed (Type II error) in a uranium hydrogeochemical sampling program unless a more sophisticated method is used to synthesize the water data.

Uranium concentrations in stream water is affected by changing discharge and by chemical processes involving uranium within the hydrologic system. With respect to the dilution effect, uranium behaves like the other major cations in stream water. However, its greater chemical activity and its low concentration in stream water sets its behavior apart from that of the major rock forming elements. Uranium concentration appears to vary the least during periods of moderate discharge when soil water is the primary source of water to the stream. The greatest variation in uranium concentration occurs during periods of extreme low flow when discharge is generally less than 2% bank full stage or when storm events disrupt the stream source area equilibrium.

Uranium concentrations in stream water that fail to adequately reflect the long term relationship between uranium in rock and water appear to be associated with rapid fluctuations in discharge in response to storm events, high or low pH values or high iron values. To resolve the chemical relationships between uranium, pH and iron in the stream it is necessary to filter out the variation in uranium concentration resulting from dilution. One possible way to do this

is by plotting uranium concentrations against calcium concentrations and calculating a least-squares-best-fit line to the data. If the variation in calcium concentration correlates well with variations in discharge, then the plot adjusts for variation in uranium concentration caused by changing discharge. Samples greater than one standardized residual represent anomalous streams which may or may not be mineralized. Later, with more detailed chemical analyses of water samples including anionic concentrations, the chemical state of iron in solution or suspension, and the concentration of humic acids in solution, it may be possible to accurately discriminate between streams behaving abnormally at the time of sampling and streams representing mineralized watersheds.

Further studies directed at understanding the chemical interactions of uranium in the stream should be conducted in mineralized watersheds. Watersheds containing mixed vegetation should be avoided, however, because they add an undesirable dimension to the hydrologic system that is very difficult to resolve.

BIBLIOGRAPHY

- Aamodt, Paul I., 1978, Uranium hydrogeochemical and stream sediment pilot study of the Boulder batholith: Los Alamos Scientific Laboratory, Informal Report No. LA-7176-MS, 118 pp.
- Adams, J.A.S., 1954, Uranium content of Wisconsin Rivers and their use in geochemical prospecting (abs.): Geol. Soc. Am. Bull., v. 65, p. 1225.
- Atkinson, T.C., 1978, Techniques for measuring subsurface flow on hillslopes, in Hillslope Hydrology, edited by Kirkby, J.J., John Wiley and Sons, LTD, New York.
- Aubertin, G.M., 1971, Nature and extent of macropores in forest soils and their influence on subsurface water movement: Res. Pap. NE-192, 33 pp., U.S. Dept. of Agr. Forest Serv., Washington, D.C.
- Badley, R.H., 1978, Petrology and chemistry of the East Fork Dike Swarm, Ravalli Co., Montana: Unpublished Master's Thesis, University of Montana.
- Beasley, R.S., 1976, Contribution of subsurface flow from the upper slopes of forested watersheds to channel flow: Soil Sci. Soc. Am. Jour., vol. 40, p. 955-957.
- Dall'Aglio, M., Tonani, F., 1962, Studio idrogeochemico delle acque superficiali del lazio: Notiziario CHEN 8, 28-51.
- Dall'Aglio, M., 1971, A study of the circulation of uranium in the supergene environment in the Italian Alpine Range: Geoch. et Cosmoch. Acta., v. 35, p. 47-60.
- _____, 1972, Planning and interpretation criteria in hydrogeochemical prospecting for uranium: in Uranium Prospecting Handbook, Inst. Min. Met., London, p. 121-133.
- Daubenmire, R.F., 1974, Plants and Environment: John Wiley and Sons, New York.
- Devlin, R.M., 1969, Plant Physiology: Van Nostrand Reinhold Company, New York.
- DeVoto, R.H., 1978, Uranium geology and exploration: Colorado School of Mines, Golden, Colorado.

- Dixon, R.M., Peterson, E.A., 1971, Water infiltration control; A channel system concept: Soil Sci. Soc. Am. Proc., 35, p. 968-973.
- Dunne, T., Black, R.D., 1970a, Partial area contributions to storm runoff in a small New England watershed: Water Res. Res., vol. 6, p. 1296-1311.
- _____, _____, 1970b, An experimental investigation of runoff production in permeable soils: Water. Res. Res., vol. 6, p. 478-490.
- _____, 1970, Runoff production in a humid area: Rep. ARS 41-160, 108 pp., Agr. Res. Serv., U.S. Dept. of Agr., Washington, D.C.
- Emmett, W.W., 1975, The channels and waters of the Upper Salmon River Area, Idaho: U.S. Geol. Surv. Prof. Paper, 870-A, 113 pp.
- Feller, M.C., Kimmins, J.P., 1979, Chemical characteristics of small streams near Haney in southwestern British Columbia: Water Res. Res. vol. 15, no. 2, p. 247-258.
- Freeze, R.A., 1972b, Role of subsurface flow in generating surface runoff, 2. Upstream source areas: Water Res. Res., vol. 8, p. 1272-83.
- Garn, H.S., Malmgren, R.C., 1973, Soil and water resources of the Bitterroot National Forest: United States Department of Agriculture, Bitterroot National Forest, Part 1, 107 p.
- Garrels, R.M., and Christ, C.L., 1965, Solutions Minerals and Equilibria, Harper and Row, New York, 450 pp.
- Germanov, A.I., Batulin, S.G., Volkou, G.A., Lisitsin, A.K., and Serebrennikov, V.S., 1958, Some regularities of uranium distribution of underground waters: Proc. 2nd U.N. Conf. on Peaceful Uses of Atomic Energy, vol. 2, p. 161-177.
- Hewlett, J.D. and Nutter, W.L., 1970, The varying source area of stream-flow from upland basins; Proceedings of the symposium on interdisciplinary aspects of watershed management: American Society of Civil Engineers, pp. 65-83.
- Hewlett, J.D. and Hibbert, A.R., 1967, Factors affecting the response of small watersheds to precipitation in humid areas; in Forest hydrology proceedings of a NSF advanced science seminar, W.E. Sopper and H. W. Lull (eds.), Pergamon Press, New York, p. 275-290.

- Hewlett, J.D., 1974, Comments of letters relating to role of subsurface flow in generating surface runoff, 2; Upstream source areas; by Allan Freeze: *Water Res. Res.*, vol. 10, no. 3, pp. 605-607.
- Horton, R.E., 1933, The role of infiltration in the hydrologic cycle: *EOS Trans.*, AGU, 14, p. 446-460.
- _____, 1945, Erosional development of streams and their drainage basins; Hydrophysical Approach to Quantitative Morphology: *Geol. Soc. Amer.*, Bull. 56, p. 275-370.
- Hyndman, D.W., 1977, The Bitterroot Lobe of the Idaho Batholith: *North-west Geology*, vol. 6-1, p. 1-16.
- Jennings, J.K. and Leventhal, J.S., 1977, A new structural model for humic material which shows sites for attachment of oxidized uranium species [abstr]: *U.S. Geol. Surv. Cir. No. 753*, p. 10-11.
- _____, _____, 19____, Interaction of oxidized uranium with humic acids, ion-exchange resins, and chelating resins to determine conditions of fixation: *Geol. Soc. Am.*, Abst. with Prog., p. 940.
- _____, _____, 1978, A literature review of interaction of oxidized uranium species and uranium complexes with soluble organic matter: *U.S. Geol. Surv.*, Open File Rep. No. 78-179, 21 p., illus.
- Johannessen, M. and Henriksen, A., 1978, Chemistry of snow meltwater; changes in concentration during melting: *Water Res. Res.* vol. 14, no. 4, p. 615-619.
- Johnson, N.M., Likens, G.E., 1969, A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire: *Water Res. Res.*, vol. 5, no. 6, pp. 1353-1363.
- Jones, A., 1971, Soil piping and stream channel initiation: *Water Res. Res.*, vol. 7, p. 602-610.
- Kossovich, P.S., 1967, A short course of general soil science (second edition): Israel Program for Scientific Translations.
- Krauskopf, K.B., 1967, Introduction to Geochemistry: McGraw-Hill Inc., New York, 721 pp.
- Langmuir, D., 1978, Uranium solution equilibrium at low temperatures with applications to sedimentary ore deposits: *Geochim. et. Cosmochim. Acta*, vol. 42, p. 547-559.

- Larsen, E.S., G. Phair, D. Gottfried, and W. L. Smith, 1956, Uranium in magmatic differentiation: U.S. Geol. Surv. Prof. Papers, 300, 65 p.
- Likens, G.E. F. H. Bormann, N. M. Johnson, and R. S. Pierce, 1967, The calcium, magnesium, potassium, and sodium budgets for a small forested ecosystem: Ecology 48, p. 772-85.
- Lapatkina, A.P., 1964, Characteristics of migration of uranium in the natural waters of humid regions and their use in the determination of the geochemical background for uranium: Geoch. Int., 4-6, p. 788-795.
- Nie, N.H. et. al., 1975, Statistical Package for the Social Sciences (SPSS); Second edition: K, Bowman and M. Cahill (eds.), McGraw Hill, New York.
- Nutter, W.L., 1973, The role of soil water in the hydrologic behavior of upland basins; in: R. R. Bruce, K. W. Floch, and H. M. Taylor (eds.), Field soil water regime. Spec. Publ. 5 Soil Sci. Soc. Am., Madison, Wisc., p. 181, 193.
- O'Connor, Donald J., 1975, The concentration of dissolved solids and river flow: Water Res. Res. vol. 12, no. 2, pp. 279-294.
- Plamondon, P.A., T. A. Black, B. C. Goodell, 1972, The role of hydrologic properties of the forest floor in watershed hydrology, in: Proceedings of a symposium on "Watersheds in Transition", Editors: Csallany, S.C., McLaughlin, T.G., Striffler, W.D., Proceedings Series #14. Sponsored by the American Water Resource Association and The Colorado State University.
- Piler, R. and Adams, J.A.S., 1962, The distribution of thorium and uranium in a Pennsylvania weathering profile: Geochim. et. Cosmochim. Acta, v. 26, p. 1137-1146.
- Ragan, R.M., 1968, An experimental investigation of partial-area contribution: Int. Ass. Sci. Hydrol. (Berne) Publ. 76, p. 241-249.
- Reich, B.M., 1972, The influence of percentage forest on design floods. in: Proceedings of a symposium on "Watersheds in Transition." Sponsored by the American Water Resources Association and the Colorado State University. Editors Csallany, S.C., McLaughlin, T.G., Striffler, W.D., Proceedings series #14.
- Rose, A.W., and Keith, M.L., 1976, Reconnaissance geochemical techniques for detecting uranium deposits in sandstones of northeastern Pennsylvania: J. Geoch. Expl., v. 6, p. 119-137.

- Rose, A.W., 1977, Geochemical exploration for uranium. in Symposium on hydrogeochemical and stream-sediment reconnaissance for uranium in the United States, Bendix Field Eng. Corp., Grand Junction, Colo., GJBX-77 (77), p. 303-352.
- Szalay, S., and Z. Samsoni, 1969, Investigation of the leaching of uranium from crushed magmatic rock: *Geochem. Int.*, vol. 6, no. 3, p. 613-623.
- _____, 1964, Cation exchange properties of humic acids and their importance in geochemical enrichment of UO_2^{2+} and other cations: *Geoch. et. Cosmoch. Acta*, vol. 28, p. 1605-1614.
- VanDerWeijden, C.H., R. C. Arthur, and D. Longmuir, 1976, Sorption of uranyl by hematite; Theoretical and geochemical implications [Abst.]: *Geol. Soc. Am. Abst. with Prog.*, vol. 8, p. 1152.
- Wenrich-Verbeek, 1977, Uranium and coexisting element behavior in surface waters and associated sediments with varied sampling techniques for uranium exploration: *Jour. of Geochemical Exploration*, vol. 8, no. 112, p. 337-355.
- Voronkov, P.P., 1970, Hydrochemical and hydrologic criteria of local runoff: State Hydrologic Institute, Collection of Papers on Hydrology. (GGI, Sbornik rabot po gidrologii), no. 9, pp. 3-28. Translation to English published in *Soviet Hydrology; Selected Papers: Issue no. 2, 1970.*
- Walling, D.E., I.D.L. Foster, 1975, Variations in the natural chemical concentrations of river water during flood flows and the log effect; some further comments: *Jour. of Hydro.*, vol. 26, p. 237-244.
- Walling, D.E., 1975, Solute variations in small catchment streams; some comments: *Transactions: Inst. Brit. Geog.*, no. 64, p. 141-146,

APPENDIX I

Whole Rock Chemical Analyses

Results of chemical analyses of rock samples collected from the Applebury and Steep Creek watersheds. The last three numbers of the LASL sample numbers correspond with the sample numbers given in Figure 6 . Negative values indicate concentrations that are below the lower detection limit of the analytical technique (see Appendix II).

U CONCENTRATIONS		#	ELEMENTAL CONCENTRATIONS DETERMINED BY X-RAY FLUORESCENCE														ELEMENTAL CONCENTRATIONS DETERMINED BY ARC-SOURCE EMISSION SPECTROGRAPHY						
SEDIMENT SAMPLES ANALYZED BY DELAYED NEUTRON COUNTING (DXC)	UNITS (ppm)		Ag	Bi	Cd	Cu	Nb	Ni	Pb	Sn	W	Be	Li	Concentrations in weight ppm									
327477	1.66	327477	-5	-5	-5	19	-20	-17	-5	-10	53	2	12										
327478	2.14	327478	-5	9	-5	16	-20	-15	-5	-10	28	3	26										
327479	3.33	327479	-5	7	-5	13	-20	-15	-5	-10	58	3	11										
327480	4.37	327480	-5	6	-5	11	-20	-15	7	-10	-15	3	18										
327481	1.26	327481	-5	-5	-5	-10	-20	-15	6	-10	-15	2	44										
327482	1.41	327482	-5	-5	-5	13	-20	-15	6	-10	37	2	28										
327483	2.47	327483	-5	-5	-5	41	-20	-15	-5	-10	-15	3	53										
327484	1.65	327484	-5	-5	-5	21	-20	-15	5	-10	44	1	15										
327485	3.61	327485	-5	-5	-5	-10	-20	-15	10	-10	15	3	11										
327486	4.54	327486	-5	6	-5	-10	-20	-15	5	-10	16	3	42										
327487	1.75	327487	-5	-5	-5	20	-20	-15	14	-10	49	2	10										
327488	4.62	327488	-5	6	-5	11	-20	-15	10	-10	19	3	32										
327489	2.09	327489	-5	8	-5	-10	-20	-15	5	-10	101	2	19										
327490	2.21	327490	-5	5	-5	16	-20	-15	6	-10	29	3	77										
327491	2.03	327491	-5	6	-5	19	-20	-15	-5	-10	101	2	22										
327492	4.90	327492	-5	7	-5	20	-20	-15	13	-10	70	4	4										
327493	1.92	327493	-5	7	-5	16	-20	-15	8	-10	41	2	24										
327494	4.19	327494	-5	8	-5	16	-20	-15	8	-10	56	3	27										
327495	1.29	327495	-5	5	-5	12	-20	-15	9	-10	44	1	15										
327496	2.35	327496	-5	7	-5	16	-20	-15	17	-10	65	3	21										
327497	3.30	327497	-5	5	-5	23	-20	-15	20	-10	-15	2	34										
327498	3.03	327498	-5	6	-5	13	-20	-15	7	-10	30	3	32										
327499	2.81	327499	-5	7	-5	14	-20	-15	11	-10	31	2	30										
327500	2.35	327500	-5	6	-5	10	-20	-15	8	-10	55	2	13										

ELEMENTAL CONCENTRATIONS DETERMINED BY NEUTRON ACTIVATION ANALYSIS

Concentrations reported in weight parts per million (ppm)

ISOTOP NUMBER	Al	Au	Ba	Ca	Ce	Cl	Co	Cr	Cs	Dy	Eu	Fe	Hf	K	La	Lu
327477	55150	-0.04	479	5040	62	-111	4.7	-6	-0.8	3	0.4	7095	9.0	25530	39	0.2
327478	71810	-0.05	497	5881	155	-110	3.8	-8	1.5	4	0.8	11950	9.1	35440	99	0.4
327479	71490	-0.04	604	-1142	179	-95	6.1	-6	1.5	3	0.6	11720	11.7	36530	49	0.3
327480	72520	-0.03	409	-873	77	-73	3.1	-5	1.7	5	0.4	6812	5.8	38530	57	0.3
327481	76550	-0.04	1402	15270	49	-102	5.8	23	1.4	1	0.7	7679	2.7	35530	30	-0.1
327482	75170	-0.05	1289	15670	58	-120	5.5	16	-1.0	-1	0.9	7194	2.6	31210	35	-0.1
327483	82700	-0.04	488	33760	42	-109	15.4	146	1.7	2	1.0	27420	2.5	9442	24	0.2
327484	83520	-0.05	2040	11970	41	-100	3.4	-7	2.2	2	1.6	17460	8.7	49580	29	0.2
327485	67740	-0.03	207	-1127	116	-90	2.8	-5	1.3	5	0.3	6431	6.3	37740	63	0.4
327486	71440	-0.04	703	3949	61	-99	3.7	-7	1.6	1	0.6	9092	4.7	36500	29	0.2
327487	80720	-0.03	379	3283	32	-96	5.8	-5	2.4	2	0.5	9338	7.8	48260	16	0.2
327488	74250	-0.03	817	4963	62	-80	5.7	-5	2.6	2	0.7	8513	4.6	36560	41	0.2
327489	66350	-0.04	-134	4231	156	-103	7.8	9	2.1	3	-0.2	6473	7.4	35800	103	0.2
327490	64310	-0.05	204	-1165	204	-100	2.9	-8	1.6	2	-0.2	10100	10.2	38620	84	0.2
327491	54030	-0.03	259	2630	177	-84	5.8	-5	2.0	3	0.4	7942	8.2	37590	106	0.2
327492	61710	-0.03	-100	-927	19	-84	5.3	-4	1.9	4	0.3	4043	4.6	30270	9	0.3
327493	57750	-0.03	639	5134	115	-96	3.6	-5	2.2	4	0.6	8846	6.7	38370	76	0.2
327494	74280	-0.05	428	-1246	122	-113	8.6	-8	2.0	5	-0.2	9862	8.7	41540	46	0.5
327495	70760	-0.03	566	-993	125	-84	5.9	-5	1.4	2	0.3	8154	7.7	43500	17	0.2
327496	63300	-0.03	344	4711	19	-83	4.9	-4	1.3	1	0.4	4903	2.8	32820	11	0.2
327497	70740	-0.05	904	2961	62	-109	6.5	-7	1.0	4	0.7	14080	5.0	45010	30	0.2
327498	72040	-0.05	448	1483	177	-102	3.3	-7	1.7	3	0.7	12800	11.1	41000	86	0.3
327499	64850	-0.03	-102	1401	141	-82	3.4	-5	0.9	3	0.4	12950	10.0	39110	32	0.3
327500	77470	-0.04	-114	2599	87	-94	4.9	-5	2.4	3	0.6	11540	13.6	45360	40	0.2

ELEMENTAL CONCENTRATIONS DETERMINED BY NEUTRON ACTIVATION ANALYSIS																U/Th RATIO
Concentrations reported in weight parts per million (ppm)																
	Mg	Mn	Na	Rb	Sb	Sc	Sm	Sr	Ta	Tb	Th	Ti	V	Yb	Zn	
327477	-4412	247	29200	36	-1	1.8	3.5	-304		-1	7.5	2015	-7	1.8	52	0.221
327478	-4472	247	27120	94	-2	2.7	7.2	-294	2	-1	15.1	2129	11	2.9	100	0.155
327479	-3055	204	25990	86	-1	3.5	5.7	-263	1	-1	20.3	1926	14	3.2	70	0.164
327480	-3132	28	21030	119	-1	1.7	6.0	-184	2	1	25.4	783	-5	3.2	51	0.172
327481	11430	202	26550	84	-1	2.4	2.3	331		-1	9.9	1777	17	-0.9	-46	0.129
327482	5573	161	31590	56	-1	2.5	2.0	-310	-1	-1	11.4	1131	19	-1.1	30	0.124
327483	30670	596	26720	46	-2	15.5	3.3	-329	-1	-1	5.1	3043	109	-1.2	47	0.484
327484	-3027	555	27460	47	-2	14.9	3.0	-299	1	-1	7.3	2639	-7	1.6	-22	0.226
327485	-3533	176	23670	63	-1	1.4	6.5	-245	1	-1	16.4	911	-6	3.3	63	0.270
327486	-4027	224	25480	84	-1	2.9	3.5	-266	1	-1	21.1	1502	18	1.4	51	0.217
327487	-3709	199	29610	68	-1	2.0	2.5	-250	1		5.9	1329	-6	1.5	51	0.302
327488	7722	194	22460	106	-1	2.9	4.7	-213	1		21.7	1978	14	2.1	-37	0.213
327489	-4135	197	24050	59	-1	1.7	6.9	-281	2	-1	12.9	1380	-7	2.9	-23	0.162
327490	-4123	191	24220	65	-1	1.9	4.9	-269	-1	-1	15.7	1258	-7	2.7	57	0.141
327491	-3549	210	23680	66	-1	1.9	7.9	-232	2		13.2	1200	-6	1.9	37	0.154
327492	-3543	40	25330	126	-1	0.7	2.5	-208	3		24.2	-506	-5	3.4	46	0.202
327493	-3753	262	25050	55	-1	2.3	6.2	-266	-1	1	10.2	1614	-6	2.2	63	0.183
327494	-4807	124	25340	87	-2	2.1	3.8	-294	2	-1	21.5	-714	-8	4.7	95	0.194
327495	-3555	243	22630	80	-1	2.0	1.7	-244	1		10.3	1149	-6	1.8	49	0.125
327496	-3487	105	24290	60	-1	0.4	0.8	-216	1		7.7	-519	-5	-0.5	41	0.305
327497	5448	524	22090	67	-1	4.3	6.0	-340		-1	5.2	4035	37	1.7	72	0.635
327498	-4127	248	25200	70	-1	3.2	6.2	-275	1	-1	18.0	1127	-7	3.1	-52	0.168
327499	-3327	300	22090	65	-1	2.2	4.3	-232	1		14.3	1493	-6	2.7	55	0.197
327500	-3206	213	28370	75	-1	2.8	4.3	-250	1	-1	10.2	1760	-6	2.0	64	0.270

LAB SAMPLE LOCATION NUMBER	U CONCENTRATION SEDIMENT SAMPLES ANALYZED BY DELAYED NEUTRON COUNTING (DNC) UNITS IN ppm	ELEMENTAL CONCENTRATIONS DETERMINED BY X-RAY FLUORESCENCE									ELEMENTAL CONCENTRATIONS DETERMINED BY ARC-SOURCE EMISSION SPECTROGRAPHY	
		Concentrations reported in weight parts per million (ppm)									Concentrations in weight ppm	
		Ag	Bi	Cd	Cu	Nb	Ni	Pb	Sn	W	Be	Li
327443	3.71	-5	9	-5	14	-20	-15	-5	-10	39	2	16
327444	2.55	-5	5	-5	-10	-20	-15	18	-10	-15	2	21
327450	1.41	-5	-5	-5	16	-20	-15	-5	-10	-15	2	27
327451	1.70	-5	-5	-5	22	-20	-15	6	-10	24	1	14
327453	2.42	-5	6	-5	-10	-20	-15	-5	-10	20	2	23
327454	4.27	-5	8	-5	10	-20	-15	9	-10	31	4	14
327455	3.15	-5	-5	-5	13	-20	-15	-5	-10	-15	3	35
327456	0.56	-5	-5	-5	12	-20	-15	-5	-10	22	1	17
327457	3.75	-5	7	-5	10	-20	-15	7	-10	52	2	21
327458	2.43	-5	-5	-5	21	-20	-15	16	-10	26	2	22
327459	4.19	-5	-5	-5	16	-20	-15	16	-10	-15	5	14
327460	1.34	-5	-5	-5	11	-20	-15	8	-10	27	1	16
327461	5.42	-5	8	-5	10	-20	-15	-5	-10	19	2	16
327462	2.18	-5	-5	-5	15	-20	-15	18	-10	-15	2	27
327463	1.06	-5	-5	-5	16	-20	-15	13	-10	18	-1	24
327464	1.09	-5	-5	-5	13	-20	-15	-5	-10	19	-1	13
327465	1.39	-5	-5	-5	-10	-20	-15	-5	-10	29	1	13
327466	2.24	-5	-5	-5	11	-20	-15	11	-10	16	3	31
327467	3.13	-5	7	-5	24	-20	-15	6	-10	23	3	31
327468	2.26	-5	-5	-5	16	36	-15	-5	-10	25	3	25
327469	3.25	-5	-5	-5	-10	57	-15	-5	-10	-15	3	9
327470	2.95	-5	-5	-5	33	-20	-15	-5	-10	19	3	10
327471	0.98	-5	-5	7	23	-20	-15	-5	-10	55	-1	9
327472	1.78	-5	-5	-5	21	-20	-15	-5	-10	123	2	10
327473	3.92	-5	-5	-5	16	-20	-15	7	-10	28	3	16
327474	1.98	-5	5	-5	11	-20	-15	13	-10	-15	2	8
327475	1.25	-5	-5	-5	18	-20	-15	-5	-10	54	1	12
327476	4.16	-5	-5	-5	17	-20	-15	6	-10	25	3	6

ELEMENTAL CONCENTRATIONS DETERMINED BY NEUTRON ACTIVATION ANALYSIS

Concentrations reported in weight parts per million (ppm)

ISOTOPE NUMBER	Al	Au	Ba	Ca	Ce	Cl	Co	Cr	Cs	Dy	Eu	Fe	Hf	K	La	Lu
327453	37547	-0.08	2191	12640	26	-108	5.0	-8	2.7	1	1.8	19800	10.7	47710	18	0.2
327454	110177	-0.07	1598	11400	22	424	4.2	-7	2.0	-1	1.7	20150	12.8	47530	11	0.1
327450	105307	-0.09	2061	2048	26	498	3.4	-9	-1.3	1	1.2	7709	9.3	48140	-7	0.1
327451	97430	-0.11	1326	3509	30	-128	4.3	-12	-1.9	-1	1.5	19160	10.2	44870	-8	-0.2
327453	45970	-0.04	156	-334	61	44	3.6	-4	-0.5	4	0.4	1830	5.1	8525	33	0.3
327454	71320	-0.05	300	4242	90	146	4.2	-5	-0.7	4	0.4	6841	5.8	33920	61	0.2
327452	72257	-0.07	1154	7623	105	-103	4.4	-7	-0.9	6	1.2	16450	11.5	32770	72	0.4
327455	96420	-0.10	-153	18130	63	-129	1.7	-9	-1.4	-1	0.9	14340	4.0	33160	50	-0.1
327457	67117	-0.04	151	-770	123	-78	4.8	-4	1.1	5	0.3	2665	6.6	37600	50	0.4
327458	92350	-0.08	757	4478	61	-106	4.0	-7	1.8	4	1.0	16560	13.7	44200	42	0.3
327459	68170	-0.05	245	2103	58	-90	3.5	-5	1.3	3	0.3	5219	4.9	32770	25	0.2
327460	73920	-0.10	-165	7394	22	-127	2.5	-10	3.4	3	1.0	18000	15.4	40470	-8	0.4
327461	61240	-0.04	165	-674	57	-62	2.8	-4	2.0	5	0.2	4684	4.2	36910	24	0.4
327462	92710	-0.07	1630	5512	83	-94	4.6	-7	1.1	4	1.5	17710	9.1	45570	48	0.4
327463	81107	-0.09	1080	-1910	61	-119	3.0	-9	-1.3	2	1.2	15480	8.7	34930	36	0.1
327464	94127	-0.11	1156	6644	56	-124	1.9	-12	-1.8	1	1.8	22390	13.3	44220	34	0.2
327465	87620	-0.10	1359	11070	71	-116	4.5	-9	1.9	2	1.5	19990	12.5	48040	44	0.3
327466	78107	-0.04	1521	9910	127	-116	5.3	-10	-1.4	4	1.7	20550	13.0	41160	70	0.4
327467	74707	-0.04	1127	4581	129	-96	5.3	-6	-0.9	5	1.3	19130	13.1	32940	65	0.5
327468	72270	-0.05	1435	-1234	120	-102	6.1	-7	-1.0	5	1.1	19270	12.3	34790	44	0.4
327469	64850	-0.03	308	-968	76	-81	3.4	-5	1.4	4	0.3	5623	5.3	36890	22	0.4
327470	66370	-0.04	-123	-1068	132	-91	3.0	-6	1.2	5	0.4	7069	7.7	39630	92	0.4
327471	92750	-0.07	1514	11300	35	-122	5.2	-11	-1.7	2	1.3	25660	16.8	44610	20	0.2
327472	93620	-0.04	548	8967	67	-120	7.3	-9	2.6	2	1.2	22760	20.3	43410	43	0.3
327473	69060	-0.03	323	2108	83	-89	4.2	-5	1.0	3	0.4	7003	5.0	34120	42	0.2
327474	79060	-0.06	535	7205	62	-121	3.7	-9	2.5	2	1.3	16370	20.7	46810	40	0.4
327475	81140	-0.05	1716	10370	91	-112	5.5	-8	1.8	2	1.6	17610	6.9	44530	56	0.2
327476	62650	-0.03	-87	2748	104	-76	2.4	-4	1.0	3	0.3	5729	5.7	32140	51	0.2

Sample No.		Concentrations reported in weight parts per million (ppm)															U/Th RATIO
		Mg	Mn	Na	Rb	Sb	Sc	Sm	Sr	Ta	Tb	Th	Ti	V	Yb	Zn	
327443	9509	532	26920	84	-2	8.1	2.7	-315	1	-1	6.4	4081	-8	-1.4	69	0.479	
327444	6117	570	30090	91	-2	6.3	2.0	-325			2.8	3195	-8	1.9	64	0.911	
327450	3084	118	2125	39	-3	12.6	1.0	-170	-1	-1	3.4	3801	-5	-1.8	72	0.415	
327451	-5799	550	27430	54	-4	17.0	-1.2	-370	-1	-1	5.2	3015	-9	-2.6	-46	0.327	
327452	-1151	70	281	-9	-1	1.4	4.2	-104	1		13.5	673	-3	3.0	-13	0.179	
327454	-3534	142	24600	96	-2	1.7	7.3	-227	2	1	23.8	1163	-6	4.2	42	0.179	
327455	8519	374	25290	51	-2	4.4	7.3	-294	1	-1	14.3	2726	-7	3.4	79	0.220	
327456	-5051	477	35380	31	-3	12.8	1.9	-342	-1	-1	4.4	-813	-9	-1.9	-32	0.150	
327457	-3751	10	22020	94	-1	1.2	5.8	-193	2	1	18.4	556	-5	3.5	-14	0.199	
327458	-4238	309	30400	91	-2	7.4	4.6	-293	-1	-1	10.4	2597	-7	3.8	73	0.272	
327459	-3465	115	25060	84	-1	1.2	2.6	-237	1		21.1	-578	-6	3.8	34	0.199	
327460	-5001	536	29690	70	-3	8.7	2.0	-359	-1	-1	4.9	2428	-9	3.6	-34	0.396	
327461	-2635	55	15400	119	-1	0.9	4.9	-162	2	1	25.8	-395	-4	3.7	31	0.226	
327462	-3715	462	23440	70	-2	9.1	5.6	-274	1	-1	10.5	1992	-7	3.2	75	0.204	
327463	-4611	550	30200	49	-3	13.3	2.3	-346	-1	-1	5.3	2151	-6	-1.8	79	0.200	
327464	-4072	545	28550	76	-4	19.1	1.8	-361	-1	-1	4.0	2640	-9	-2.6	-41	0.273	
327465	-4633	704	27950	45	-3	17.8	3.5	-352	-1	-1	6.1	2977	-9	-2.1	91	0.173	
327466	-4403	506	24060	69	-2	5.9	9.0	-358	2	-1	14.6	2236	-9	3.6	100	0.201	
327467	-3845	402	27950	60	-1	5.1	7.9	-273	2	-1	16.5	2978	-7	3.5	98	0.197	
327468	-4000	307	27550	83	-1	5.6	6.4	-290	2	-1	15.0	2653	-7	3.0	88	0.197	
327469	-3318	119	19510	74	-1	1.1	3.6	-227	2		16.4	814	-5	2.9	58	0.194	
327470	-3911	140	21290	73	-1	1.5	9.9	-246	2	-1	18.4	-601	-6	4.6	47	0.160	
327471	-4406	719	27530	52	-2	26.3	2.3	-380	-1	-1	2.4	4197	-9	-1.6	49	0.403	
327472	-4730	662	31100	-18	-2	14.2	3.3	-354	2	-1	6.0	4046	-8	1.7	-27	0.297	
327473	-3502	158	24280	94	-1	1.4	5.6	-236	1	1	17.3	1167	-6	1.9	101	0.227	
327474	-4885	397	30020	81	-2	5.6	4.3	-336	-1	-1	7.7	2855	-8	2.3	77	0.257	
327475	-4444	597	28480	52	-2	10.9	3.9	-333	1	-1	7.2	3238	-8	2.3	57	0.174	
327476	-3190	71	25810	74	-1	1.7	6.2	-189	1		17.0	806	-5	3.1	46	0.245	

APPENDIX II

SUMMARY OF STANDARD LASL HSSR FIELD AND ANALYTICAL PROCEDURES

I. Field Procedures

Water Sampling

Water samples are collected from the fast flowing current away from the stream bank, filtered through a 0.45- μ m membrane filter directly into one each, prewashed and sealed, 41-ml reactor "rabbit" and 25-ml vial (both polyethylene). Water samples in both the rabbit and vial are then acidified to a pH ≤ 1 with 8N reagent-grade HNO_3 . All sample containers are doubly labeled with preprinted, adhesive labels carrying the same sample location number as that preprinted on the field data form.

Field Measurements

The air temperature, read in the shade at the time of sampling, is recorded to the nearest whole degree Celsius. The water temperature is measured in the source water and recorded to the nearest one-half degree Celsius. The pH of the source water is measured with a calibrated, portable pH meter and recorded to the nearest one-tenth of a pH unit. The conductivity (in mho/cm) of the source water is measured with a calibrated, temperature-compensated (25°C), portable meter.

II. Analytical Procedures

Uranium Determination in Water Samples by Fluorometry

Under normal procedures, the 25-ml water vial is vigorously shaken

and duplicate 0.20-ml aliquots of water are transferred to platinum dishes. The aliquots are evaporated under heat lamps and a 0.4-g pellet of 2% LiF-98% NaF flux is added to each dish. The pellets are first preheated under lamps, then fused over special propane burners. After each pellet/sample cools, it is excited with ultraviolet radiation in the fluorometer and the fluorescence is read and recorded. The uranium concentrations are determined by using a computer routine which compares the fluorescence from each pellet with those from other pellets, run at the same time, containing uranium-standard solutions and blanks. The uranium concentration of the sample, as given in the appropriate data listing, is then the average obtained from the duplicate aliquots. The lower limit of detection for each aliquot by the normal procedure is 0.2 ppb; however, in some areas many samples have uranium concentrations below this. Consequently, when a sample run by the normal procedure is determined to have 0.2 ppb uranium, it is routinely reanalyzed using new duplicate aliquots that have been put through an additional evaporative concentration step that provides a 10X concentration factor. This additional procedure, using the same basic fluorometric method, reduces the lower limit of detection of uranium in natural waters to 0.02 ppb. When a uranium concentration lower than 0.02 ppb is found in an aliquot, it is arbitrarily assigned a value of 0.01 ppb. If the uranium value given in the data listing is 0.01 ppb, both aliquots had uranium concentrations below the detection limit. Whether concentrated or not (which can be determined from the uranium level in the listing), the fluorometric analytical precision is 30%

at the lower detection limit, 20% at one order of magnitude above this, and 10% at two or more orders of magnitude above the lower detection limit.

Uranium Determination in Water Samples by Delayed-Neutron Counting (DNC)

Only waters with 40ppb uranium (as determined by fluorometry at the LASL, where this is the upper limit of detection without recalibration) or those with impurities that cause interference with uranium-induced fluorescence are analyzed using DNC. Samples are received in 41-ml or 25-ml vials (used exclusively in some of the early work) and are transferred to clean, labeled, 41-ml rabbits before being analyzed. Each water sample is weighed, and its weight (less that of the rabbit) and location number are recorded. The rabbits are then loaded into a 25-sample transfer clip. The reactor pneumatic transfer system and background radiation levels are checked and four standards are run for calibration. The transfer clip is installed on the pneumatic feed line and the samples are cycled through the system (typically, a 60-s irradiation, 30-s delay, and 60-s count cycle is used). The uranium concentration is automatically measured, converted to ppb, and entered into a computer data base. The lower detection limit for uranium in water by DNC as used at the LASL is 0.2 ppb. The statistical error of this method is 20% at a uranium concentration of 1 ppb, 6% at 10 ppb, and 4% at 40 ppb or greater. Statistical treatments of uranium concentrations obtained from the same suites of samples analyzed both by fluorometry and DNC have shown that there is no significant difference

between the results of the two analytical methods as used at the LASL. This analytical comparability is rechecked periodically.

Elemental Determinations in Water Samples by Plasma-Source Emission Spectrography

The concentrations of Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ti, and Zn in water samples are determined at the LASL by inductively coupled plasma-source emission spectrography. To allow complete system equilibration, the inductively coupled plasma and photomultiplier tubes are powered for at least 1 h prior to making any analyses. Argon coolant and sample carrier gas lines are adjusted and calibrated using a zinc standard. The sample solution is taken up from its container, nebulized, and injected into the plasma source at a rate of $9.2 \times 10^{-9} \text{ m}^3/\text{s}$. After the computer determines that the photomultiplier tubes have stabilized, a 15-s exposure of the resultant spectrum is made on a direct-reading spectrograph. The resulting signals are read directly into a computer, and converted automatically to give the elemental concentrations. Corrections for interfering elements are made simultaneously by computer. When high (off-scale) results are obtained, the computer calls for the insertion of a filter between the plasma source and the spectrograph, repeats the readings, and then converts and stores the corrected elemental concentrations. The lower analytical detection limits generally achieved are (in ppb): Ca (20), Co (55), Cr (25), Cu (4), Fe (25), Mg (2), Mn (3), Mo (25), Ni (25), Pb (200), Ti (4), and Zn (50). When an analysis results in an elemental concentration that is below the detection limit, a minus sign preceding the value of

the detection limit for that element is inserted in the data listings. Analytical precision for the elements as determined in water by this method is 50% at the lower detection limit, improving to 10% one order of magnitude above the lower detection limit and to 5% two orders of magnitude above the detection limit.

Uranium Determination in Sediment Samples by DNC

All sediment samples are analyzed for total uranium by DNC. A split of each sample (dried and sieved as described) is transferred to a clean 4-ml vial, weighed (less the tare), and its weight recorded along with the appropriate location number. These vials are then loaded into a 50-sample transfer clip. The reactor pneumatic transfer system and background radiation levels are checked, and standards are run for calibration. The transfer clip is installed and the samples are cycled through the system (typically, a 20-s irradiation, 10-s delay, and 30-s count cycle is used). The uranium concentration is automatically measured, converted to ppm, and entered into the data base. The lower limit of detection of this method is 20 ppb (not ppm) uranium, below the range of uranium concentrations in natural sediment samples. Above the 1 ppm level, the uranium values in sediment measured by DNC at the LASL have a one-sigma error of less than 4%.

Elemental Determinations in Sediment Samples by Energy Dispersive X-Ray Fluorescence

A computer-controlled, energy-dispersive x-ray fluorescence system is used to determine Ag, Bi, Cd, Cu, Nb, Ni, Pb, Sn, and W in sediments.

The system consists of an automatic 20-position sample changer, a lithium-drifted silicon detector, a pulsed molybdenum transmission-target x-ray tube, a multi-channel analyzer, and a minicomputer. The sediment samples are prepared for analysis by grinding 6 g of each minus 100-mesh sample to a minus 325-mesh powder. A computer program positions the 6-g samples in the x-ray beam, unfolds overlapping peaks, determines peak intensities for each element, and calculates the ratio of the intensity of each peak to that of the molybdenum K Compton peak. Concentrations of each element are then calculated using equations obtained by analyzing prepared standards. Detection limits are: 5 ppm for Ag, Bi, Cd, and Pb; 10 ppm for Cu and Sn; 15 ppm for Ni and W; and 20 ppm for Nb. When an analysis results in an elemental concentration that is below the detection limit, a minus sign preceding the value of the detection limit for that element is inserted in the data listings. The relative standard deviation is 10% or less at the 100-ppm level and 20% or less at the 20-ppm level.

Beryllium and Lithium Determinations in Sediment Samples by Arc-Source Emission Spectrography

A 7.5-mg portion of the minus 325-mesh sample that has already been analyzed by x-ray fluorescence is mixed with 7.5 mg of a buffer consisting of one part graphite and one part SiO_2 . The sample/buffer mixture is placed into a graphite electrode that is used as the anode of a dc arc having a short circuit current of 17A. A 60-s exposure of the resulting spectrum is made on a direct-reading spectrograph. Photomultiplier tubes are used to measure the second order 313.0-nm line of

Be, the first order 670.7- and 610.3-nm lines of Li, the background spectra near these lines, and the 327.6-nm line of V. The 670.7-nm Li line is used for Li concentrations up to 30 ppm and the 610.3-nm line of Li is used for concentrations above 30 ppm. The V line is used to correct the Be value when V is above 1000 ppm. The signals from the photomultiplier tubes are read by a digital voltmeter and are processed by a desk-top calculator. The results are simultaneously printed on paper and written on cassette tape for later transmission to a computer data file. The elemental concentrations of Be and Li are determined from the spectra, based on the results of previously run calibration standards. The lower detection limit for both elements is 1 ppm. When an analysis results in an elemental concentration that is below the detection limit, a minus sign preceding the value of the detection limit for that element is inserted in the data listings. Precision at the lower detection limit is 50% for both and improves to 25% at one order of magnitude above the lower limit.

Elemental Determinations in Sediment Samples by Neutron Activation Analysis (NAA)

Immediately upon completion of the uranium analysis of sediment samples by DNC, the same 4-ml sediment splits are entered into the NAA sequence. The concentrations of 31 additional elements are determined by this procedure. The full DNC/NAA timing sequence used at the LASL for each sediment sample is: 20-s irradiation, 10-s delay, 30-s, DNC analysis, 20-min delay, 500-s γ -ray count for short-lived radionuclides, 96-s re-irradiation, 14-day delay, and finally a 1000-s γ -ray count for

long-lived radionuclides. The γ -ray counting is done by lead-shielded Ge(Li) detectors; the 4096-channel γ -ray data are recorded and subsequently analyzed for each individual element by computer. The analytical data for each sample are automatically printed out along with the associated statistical errors. The lower detection limits for the various elements as reflected by the "less than" values (denoted by a minus sign in front of a concentration) in the data listings are the values for the individual elements at which the statistical counting error approaches 50%. Current "typical" lower detection limits for the elements determined by NAA are reported in Nunes and Weaver (1978); however, the actual detection limit for an element depends upon the composition of the sample and this limit may be higher or lower than the "typical" value. At concentration values one order of magnitude above the lower detection limits, the relative errors are generally less than 10%.

No.	MEDIA	ELEMENTS		METHOD
1.	H ₂ O	U (initial run)		Fluorometry
2.	H ₂ O	Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Ti, Zn		Emission Spectroscopy
3.	Rock	Al, Ba, Ca, Cl, Dy, K, Mg, Mn, Na, Sr, Ti, V		Neutron Activation Analysis (short counts)
4.	Rock	Au, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, Rb, Sb, Sc, Ta, Tb, Th, Yb, Zn		Neutron Activation Analysis (long counts)
5.	Rock	Be, Li		Arc-Source Emission Spectroscopy
6.	Rock	Ag, Bi, Cd, Cu, Nb, Ni, Pb, Sn, W		X Ray Fluorescence
7.	Rock	U		Delayed Neutron Counting

LOS ALAMOS SCIENTIFIC LABORATORY
LIMITES OF DETECTION IN MULTIELEMENT ANALYSES IN SEDIMENTS

<u>Element</u>	<u>* Minimum Detection (ppm)</u>	<u>Analytical Method</u>	<u>Element</u>	<u>Minimum Detection (ppm)</u>	<u>Analytical Method</u>
<u>NEUTRON ACTIVATION ANALYSIS</u>			<u>X-RAY FLUORESCENCE</u>		
Al	200	NAA	Ag	5	XRF
Au	0.01	NAA	Bi	5	XRF
Ba	300	NAA	Cu	10	XRF
Ca	4000	NAA	Nb	20	XRF
Ce	10	NAA	Ni	15	XRF
Cl	200	NAA	Pb	5	XRF
Co	2	NAA	Sn	10	XRF
Cr	20	NAA	W	15	XRF
Cs	2	NAA	Cd	5	XRF
Dy	2	NAA			
Eu	0.8	NAA	<u>EMISSION SPECTROSCOPY</u>		
Fe	2000	NAA	Be	1	ES
Hf	1	NAA	Li	1	ES
K	2000	NAA			
La	6	NAA			
Lu	0.3	NAA			
Mg	3000	NAA			
Mn	10	NAA			
Na	150	NAA			
Rb	30	NAA			
Sb	1	NAA			
Sc	0.1	NAA			
Sm	0.5	NAA			
Sr	300	NAA			
Ta	1	NAA			
Tb	1	NAA			
Th	0.8	NAA			
Ti	200	NAA			
V	5	NAA			
Yb	3	NAA			
Zn	20	NAA			

* Because of elemental interference, the detection limits for those elements determined by NAA will shift as a function of the composition of the sediment.

APPENDIX III

Results of Chemical Analyses for Precipitation Samples

Concentrations reported in weight parts per billion (ppb).

Sample Number	342	431	446	447	445	452
Element						
U	.21	.40	.03	.04	.06	.54
Ca	274	342	69	51	121	93
Co	-55	-55	-55	-55	-55	-55
Cr	50	52	43	40	30	52
Cu	14	14	9	-4	10	23
Fe	-25	41	-25	27	36	-25
K	173	119	-100	-100	-100	-100
Mg	55	31	4	5	8	6
Mn	7	13	4	8	8	11
Mo	43	-25	-25	-25	-25	55
Na	1202	160	120	230	-100	-100
Ni	168	-25	-25	-25	-25	39
Pb	-200	-200	-200	-200	-200	321
Ti	-4	16	12	9	8	18
Zn	104	-50	-50	-50	-50	-50

Minus sign indicates concentrations below low detection limit (see Appendix II)

Listing of Discharge Data

The data listings that follow record the amount of water flowing through the flume at two-hour intervals on each day of the study period. Columns 6-17 are the two-hour readings given in liters per second. Values in column 5 are the daily average in liters per second. Columns 2-4 are the date of record, and values in column 1 are a sequence number for reference. The days in which a -1.00 appears in the last six columns represent periods when the flumes were not working and stream discharge is inferred from weather data as described in the text. Where a -1.00 occurs in columns 6-11, the daily record is incomplete.

S E Q U E N C E N U M	M O N T H	D A Y	Y E A R	A V E R A G E D A I L Y	Applebury Creek													
					TIME OF DISCHARGE READING													
					2	4	6	8	10	12	14	16	18	20	22	24		
1	9	24	77	0.65	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.70	0.64	0.64	0.64	0.64	0.64
2	9	25	77	0.76	0.64	0.64	0.64	0.70	0.70	0.74	0.77	0.80	0.80	0.92	0.92	0.92	0.92	0.92
3	9	26	77	0.74	0.80	0.80	0.80	0.80	0.80	0.74	0.74	0.74	0.74	0.64	0.64	0.64	0.64	0.64
4	9	27	77	0.65	0.64	0.64	0.64	0.64	0.74	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
5	9	28	77	0.91	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.70	0.70	0.80	0.92	1.15	1.45
6	9	29	77	1.57	1.50	1.46	1.71	1.11	1.02	1.11	1.11	1.11	1.11	1.21	2.66	3.11	2.17	
7	9	30	77	1.11	1.53	1.46	1.71	1.11	1.11	1.02	1.02	1.02	1.02	0.92	0.92	0.92	0.92	
8	10	1	77	0.86	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
9	10	2	77	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
10	10	3	77	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
11	10	4	77	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
12	10	5	77	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
13	10	6	77	0.95	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
14	10	7	77	1.18	1.50	1.53	1.71	1.11	1.11	1.11	1.02	1.02	1.02	1.21	1.21	1.11	1.11	1.11
15	10	8	77	0.99	1.11	1.02	1.72	1.02	1.02	1.02	1.02	1.02	0.92	0.92	0.92	0.92	0.92	0.92
16	10	9	77	0.84	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	1.02	1.02	1.02
17	10	10	77	0.84	1.02	1.02	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
18	10	11	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
19	10	12	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
20	10	13	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
21	10	14	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
22	10	15	77	0.89	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.80	0.80	0.80	0.80
23	10	16	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
24	10	17	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
25	10	18	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
26	10	19	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
27	10	20	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
28	10	21	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
29	10	22	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
30	10	23	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
31	10	24	77	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
32	10	25	77	2.10	0.80	0.80	0.80	0.92	0.92	1.11	2.02	3.79	3.79	3.58	2.58	3.11	3.11	3.11
33	10	26	77	1.53	2.33	2.02	1.37	1.59	1.46	1.46	1.33	1.33	1.33	1.33	1.21	1.21	1.21	1.21
34	10	27	77	1.16	1.71	1.71	1.71	1.71	1.21	1.15	1.15	1.15	1.15	1.11	1.11	1.11	1.11	1.11
35	10	28	77	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11
36	10	29	77	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.11
37	10	30	77	1.03	1.11	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
38	10	31	77	1.01	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	0.98	0.98	0.98	0.98	0.98
39	11	1	77	1.27	1.02	1.46	1.33	1.21	1.21	1.21	1.21	1.33	1.33	1.33	1.33	1.33	1.33	1.21
40	11	2	77	1.08	1.21	1.15	1.11	1.11	1.11	1.11	1.11	1.06	1.02	1.02	1.02	1.02	1.02	1.02
41	11	3	77	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
42	11	4	77	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02

Applebury Creek

TIME OF DISCHARGE READING

S E Q	M O N T H	D A Y	Y E A R	A V E R A G E	TIME OF DISCHARGE READING											
					2	4	6	8	10	12	14	16	18	20	22	24
331	H	20	78	1.25	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	1.33	1.27	1.21	1.21	1.21	1.27
332	H	21	78	1.33	1.33	1.33	1.33	1.33	1.46	1.39	1.33	1.27	1.21	1.15	1.15	1.21
333	H	22	78	1.44	1.27	1.27	1.33	1.33	1.39	1.33	1.59	1.66	1.59	1.46	1.46	1.46
334	H	23	78	1.37	1.46	1.46	1.46	1.46	1.52	1.46	1.33	1.27	1.27	1.21	1.21	1.27
335	H	24	78	1.24	1.33	1.33	1.39	1.39	1.39	1.37	1.21	1.11	1.06	1.11	1.11	1.15
336	H	25	78	1.14	1.21	1.21	1.27	1.27	1.27	1.15	1.06	1.07	1.02	1.02	1.06	1.11
337	H	26	78	1.27	1.11	1.15	1.15	1.21	1.21	1.11	1.11	1.52	2.09	1.87	1.59	1.39
338	H	27	78	1.24	1.39	1.33	1.33	1.33	1.33	1.33	1.21	1.15	1.11	1.11	1.11	1.11
339	H	28	78	1.14	1.15	1.21	1.21	1.21	1.27	1.21	1.15	1.11	1.06	1.02	1.06	1.06
340	H	29	78	1.19	1.11	1.15	1.15	1.15	1.21	1.15	1.11	1.07	1.02	1.07	1.07	1.07
341	H	30	78	1.11	1.06	1.11	1.11	1.15	1.15	1.11	1.06	1.15	1.11	1.11	1.11	1.11
342	H	31	78	1.05	1.21	1.21	1.21	1.21	1.21	1.15	0.98	0.92	0.85	0.86	0.96	0.98
343	9	1	78	1.00	1.06	1.11	1.11	1.11	1.11	1.06	0.98	0.92	0.86	0.86	0.96	0.98
344	9	2	78	1.14	1.02	1.06	1.06	1.06	1.06	0.92	1.11	1.33	1.27	1.27	1.27	1.27
345	9	3	78	1.36	1.33	1.39	1.46	1.52	1.52	1.52	1.33	1.27	1.21	1.15	1.15	1.15
346	9	4	78	1.24	1.21	1.27	1.33	1.33	1.39	1.39	1.33	1.21	1.11	1.11	1.11	1.11
347	9	5	78	1.23	1.15	1.21	1.27	1.27	1.33	1.33	1.27	1.15	1.11	1.15	1.21	1.27
348	9	6	78	1.40	1.33	1.39	1.46	1.46	1.46	1.46	1.39	1.33	1.27	1.21	1.21	1.27
349	9	7	78	2.00	2.66	2.53	1.94	1.73	1.73	1.73	1.80	1.73	1.66	1.66	2.33	2.49
350	9	8	78	1.71	2.25	2.02	1.87	1.80	1.80	1.80	1.59	1.52	1.46	1.46	1.46	1.46
351	9	9	78	1.57	1.52	1.52	1.59	1.59	1.59	1.59	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
352	9	10	78	1.20	1.20	1.20	1.20	1.20	1.20	1.20	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
353	9	11	78	1.40	1.40	1.40	1.40	1.40	1.40	1.40	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
354	9	12	78	0.80	0.80	0.80	0.80	0.80	0.80	0.80	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
355	9	13	78	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
356	9	14	78	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
357	9	15	78	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00
358	9	16	78	0.80	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	0.80	0.80	0.80	0.80
359	9	17	78	0.94	0.86	0.86	0.86	0.92	0.92	0.98	0.98	0.98	0.98	0.98	0.98	0.98
360	9	18	78	1.12	0.94	0.94	1.11	1.11	1.15	1.15	1.15	1.15	1.15	1.21	1.15	1.15
361	9	19	78	1.12	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.21	0.80	1.11
362	9	20	78	1.11	1.11	1.11	1.11	1.11	1.15	1.15	1.15	1.11	1.11	1.06	1.06	1.06
363	9	21	78	1.04	1.11	1.11	1.11	1.11	1.11	1.11	1.11	1.06	1.02	1.02	1.02	1.02
364	9	22	78	1.01	1.06	1.06	1.06	1.06	1.11	1.06	1.07	0.98	0.92	0.92	0.92	0.98
365	9	23	78	0.95	0.94	0.98	0.98	1.02	1.02	1.02	0.98	0.92	0.86	0.86	0.86	0.92
366	9	24	78	0.84	0.92	0.92	0.98	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00

S E Q N U M	M O N T H	D A Y	Y E A R	A V E R A G E	Steep Creek											
					TIME OF DISCHARGE READING											
					2	4	6	8	10	12	14	16	18	20	22	24
360	9	18	78	1.06	0.85	0.92	1.02	1.06	1.06	1.06	1.11	1.15	1.15	1.11	1.11	1.11
361	9	19	78	1.14	1.11	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.11	1.15	1.15
362	9	20	78	1.14	1.15	1.15	1.15	1.15	1.27	1.27	1.27	1.15	1.15	1.15	1.15	1.15
363	9	21	78	1.13	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.11	1.06	1.06	1.11	1.11
364	9	22	78	1.04	1.11	1.11	1.11	1.11	1.11	1.11	1.06	1.02	0.92	0.92	0.92	1.02
365	9	23	78	0.96	1.02	1.02	1.02	1.06	1.06	1.02	1.02	0.96	0.86	0.96	0.86	0.86
366	9	24	78	0.86	0.86	0.86	0.86	0.86	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00	-1.00

Appendix V

Precipitation Data

The following data is taken from the precipitation gage strip chart records. The data indicate the beginning and end of storm events in which the recorder was working properly (columns 2 and 4). In addition, the time of maximum precipitation and total precipitation for each storm event in cm. of water are shown (columns 3 and 5).

<u>Date</u>	<u>Beginning of storm event</u>	<u>Time of maximum precipitation</u>	<u>Time at end of storm event</u>	<u>Total precipitation in cm. of water</u>
9/28/77	21:00	1:00	4:00*	1.4
9/29/77	19:30	20:30	24:00	1.9
10/6/77	21:00	23:00	2:00*	1.0
10/25/77	12:00	16:00	24:00	4.0
11/1/77	14:00	15:30	16:30	.8
11/2/77	4:00	4:20	6:00	.5
3/14/78	18:00	22:00	1:00*	.8
4/4/78	15:00	15:15	15:45	.6
4/7/78	14:00	16:00	18:00	1.0
4/11/78	2:30	2:45	3:15	.3
4/15/78	19:45	20:00	20:30	.6
4/16/78	12:45	13:00	14:00	.9
4/20/78	1:40	2:00	2:30	.2
4/20/78	19:00	19:30	20:40	.8
4/26/78	11:30	12:15	13:00	1.0
4/30/78	17:00	18:00	6:00*	1.8
5/6/78	14:30	15:15	16:00	.6
5/7/78	20:00	20:45	21:00	.9
5/12/78	0:15	0:30	0:45	.3
6/18/78	23:30	24:00	1:00*	.4
6/29/78	19:00	19:30	20:00	.3
6/30/78	11:00	11:15	11:20	.3
7/1/78	22:00	22:15	22:30	.5
7/15/78	19:30	19:45	20:00	.4
7/28/78	13:00	14:15	15:30	.2
8/13/78	13:00	13:30	14:00	.4
8/13/78	20:45	21:00	21:30	1.8
8/15/78	23:20	24:00	1:30*	.4
8/22/78	15:00	15:15	15:30	.3
9/6/78	22:45	23:00	1:00*	1.2
9/7/78	20:00	21:15	23:00	.8
9/18/78	4:00	7:00	12:00	.8

* indicates that storm continued into following day

Appendix VI

Stream Water Data

The data that follows is a listing of the pertinent physical and chemical information associated with each water sample collected from Applebury and Steep Creek. The hour of collection is rounded to the nearest even whole hour. Air and water temperatures are in degrees Celsius. Discharge is that observed at the time of sampling and is given in liters per second. Specific conductivity is reported in $\mu\text{mho/cm}$. All element concentrations for water samples are reported in parts per billion (ppb).

