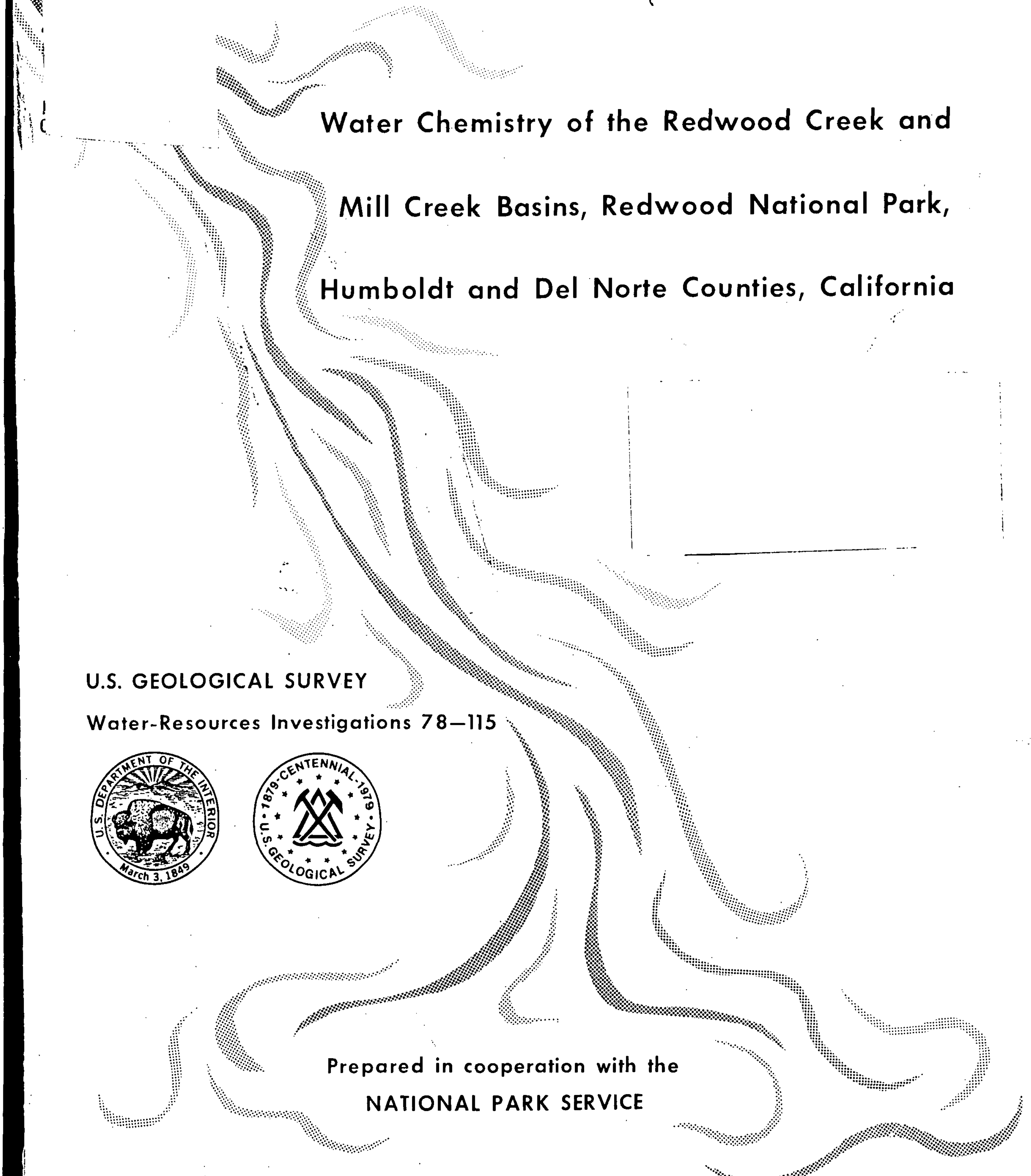

Water Chemistry of the Redwood Creek and Mill Creek Basins, Redwood National Park, Humboldt and Del Norte Counties, California

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations 78—115

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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A two-year study made in Redwood National Park (September 1973-September 1975) determined existing chemical water-quality conditions and identified possible effects of logging on water quality in streams. Water quality was generally good, with dissolved-solids concentrations ranging from 25 to 139 milligrams per liter in the Redwood Creek basin and 21 to 49 milligrams per liter in the Mill Creek basin. Water type and pH tended to shift seasonally. Exposure of soils to the elements in areas logged or having naturally sparse vegetation accelerated chemical weathering and increased dissolved-solids concentrations. Nitrogen and phosphorus concentrations were generally too low to support nuisance algae, but were higher in logged areas. Higher nitrogen concentrations in areas well exposed to sunlight could support modest algae populations. Trace-metal concentrations were low, typical of clean streams.

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UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY

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CONVERSION FACTORS

Metric units are used in this report. For those readers who prefer to use inch-pound units rather than metric units the conversion factors for units used in this report are given below.

Metric	Multiply by	Inch-pound
m (meters)	3.281	ft (feet)
m/km (meters per kilometer)	5.279	ft/mi (feet per mile)
m^3/s (cubic meters per second)	3.531×10^1	ft^3/s (cubic feet per second)
$(m^3/s)/km^2$ (cubic meters per second per square kilometer)	9.149×10^1	$(ft^3/s)/mi^2$ (cubic feet per second per square mile)
mm (millimeters)	3.937×10^{-2}	in (inches)
km (kilometers)	6.214×10^{-1}	mi (miles)
km^2 (square kilometers)	3.861×10^{-1}	mi^2 (square miles)

Additional Abbreviations

°C (degrees Celsius)
mg/L (milligrams per liter)
μg/L (micrograms per liter)
μm (micrometers)
μmho (micromhos per centimeter)

WATER CHEMISTRY OF THE REDWOOD CREEK AND MILL CREEK BASINS, REDWOOD NATIONAL PARK, HUMBOLDT AND DEL NORTE COUNTIES, CALIFORNIA

By Wesley L. Bradford and Rick T. Iwatsubo

ABSTRACT

A 2-year study was made in the Redwood Creek and Mill Creek drainage basins of Redwood National Park to determine existing chemical water-quality conditions and to identify the effects of logging on water quality in the main stems and tributaries of the two basins.

Overall, the chemical water quality of the main stems and the tributaries is excellent, suitable for most beneficial uses. Dissolved-solids concentrations range from 25 milligrams per liter in the Redwood Creek basin and 21 milligrams per liter in the Mill Creek basin during the rainy season to 139 and 49 during the dry season. Water shifts from a mixed calcium-sodium bicarbonate-chloride type toward a calcium bicarbonate type from the end of the wet season to the end of the dry season. It shifts back toward a mixed calcium-sodium bicarbonate-chloride type from the end of the dry season to the end of the wet season. The pH shifts with the water type from a median value of 6.80 in the rainy season to 7.37 in the dry season. Nitrogen and phosphorus concentrations are generally too low to support nuisance algae but are high enough, in some streams, to support modest populations, particularly in the main stem where light levels are high. Trace-metal concentrations are low, typical of clean streams.

Evidence suggests that dissolved calcium and bicarbonate in stream water is produced by weathering of the Franciscan assemblage underlying the basins but that chlorides are transported inland from the ocean as dry fallout and spray and in rain. Exposure of the surface soils to the elements, either by logging or by natural causes such as sparse vegetation, seems to accelerate weathering, which leads to a calcium bicarbonate water type. Logging accelerates weathering most in the tributary watersheds with regoliths derived from sandstone and least in those with regoliths derived from schist; however, the data suggest that the rate of weathering in a schistose watershed can increase dramatically if soil disruption is extensive.

Studies during storms indicated that specific conductance and alkalinity were two to three times as likely to decrease at the discharge peak in logged watersheds as in forested ones. This suggests that overland flow containing lower concentrations of soil-derived dissolved solids than flow from other sources is a larger component of peak flow in logged watersheds than in forested watersheds.

Comparing a storm in November 1974 to one in February 1975, nitrate concentration increased significantly from November to February in a stream draining a logged watershed and decreased significantly in a stream draining a forested watershed. Then from the rainy season to the dry season, nitrate decreased in both logged and forested watersheds. This pattern suggests that soil nitrate produced by fixation and organic decomposition early in the rainy season tends to wash out of logged watersheds but be taken up in tree growth in forested watersheds. As the dry season progresses, base flow containing little nitrate enters the streams, causing a decrease in nitrate concentration. By contrast, the other plant nutrients--phosphorus, Kjeldahl nitrogen, ammonium, and dissolved organic carbon--all decreased in streams from the November 1974 storm to the February 1975 storm and changed little from the rainy season through the dry season. This pattern suggests that these materials tend to accumulate in the soil during the dry season and be washed out and diluted as the rainy season progresses. Very little reaches the water table due to soil absorption so that little appears in the base flow during the dry season.

INTRODUCTION

Purpose and Scope

The purposes of water-quality studies in the Redwood Creek and Mill Creek basins are (1) to describe existing conditions in the main stem and tributaries and (2) to ascertain if differences exist, in the quality of water draining from various watersheds, that may be ascribed to differences in land use or the composition of the regolith (the surface mantle of unconsolidated material produced by weathering and erosion).

This report includes the interpretation of chemical-quality data collected in the Redwood Creek and Mill Creek drainage basins from September 1973 through September 1975.

The report is lengthy and detailed. Findings are summarized at the end.

Acknowledgments

This report was prepared by the U.S. Geological Survey in cooperation with the National Park Service. Arcata Redwood Co., Louisiana-Pacific Corp., Miller-Rellim Redwood Co., and Simpson Timber Co., allowed field teams general access to study stations on company properties. Lari Lopp and J. M. Burchard assisted in analyzing data and preparing and checking tables and illustrations.

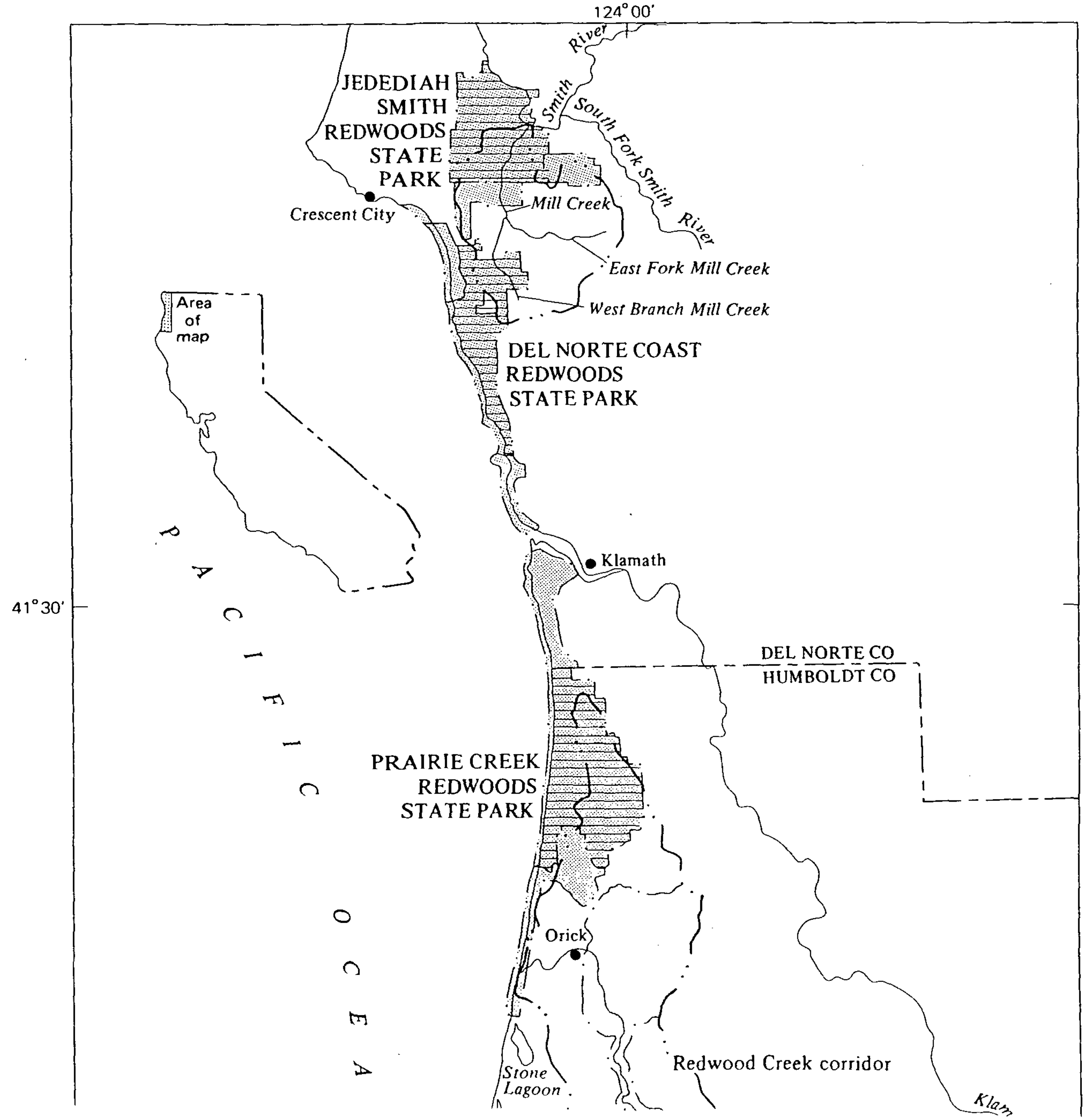
Background

The Redwood Creek and Mill Creek drainage basins (fig. 1) are along the northern California coast where the moist, mild climate and seasonally heavy rainfall are suitable for growth of the coast redwood (*Sequoia sempervire*n) and associated vegetation. Prime examples of old-growth redwood forests are found here, particularly in Redwood National Park and neighboring state parks

The forests of these basins are of major economic importance as sources of timber and wood fiber. Together with associated streams and wildlife, the forests are important recreational resources. Redwood National Park was established by the U.S. Congress on October 2, 1968. The park includes downstream areas of the Redwood Creek and Mill Creek basins.

No direct Federal control is exercised over logging operations upstream or upslope from the park boundaries. Evidence (primarily from Janda and others, 1975a) suggests that logging upstream and upslope from the park is causing numerous detrimental effects on the recreational resources of the park itself. Aggradation of stream channels by sediment, streambank erosion, and accumulation of course-grained sediments at the base of some trees, which eventually affects the root systems, has been observed. The most severe threat to old-growth redwood stands is in the 11-km-long, 0.8-km-wide corridor forming the southernmost part of the park where the effects of upstream and upslope logging are manifested (Iwatsubo and others, 1975, p. 2).

The National Park Service recognized the potential dangers to park resources from upstream logging and, soon after the creation of the park, began studies to assist in managing the park resources. R. C. Curry (U.S. Dept. of Interior, Assistant Secretary for Fish, Wildlife, and Parks, written commun., 1973) identified several potential hazards from increased erosion and recommended mitigating measures. He further recommended that the U.S. Geological Survey begin "...studies to provide the data needed in formulating management activities that would assure...the preservation of park resources" (Janda and others, 1975a, p. 5). On August 16, 1973, the National Park Service authorized a 3-year program of studies, and the Geological Survey began collecting data in September of that year.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Mill Creek
East Fork Mill Creek
West Branch Mill Creek
DEL NORTE COAST REDWOODS STATE PARK
Area of map
PACIFIC OCEA
Klamath
DEL NORTE CO
HUMBOLDT CO
PRAIRIE CREEK REDWOODS STATE PARK
Orick
Stone Lagoon
Redwood Creek corridor
Klam

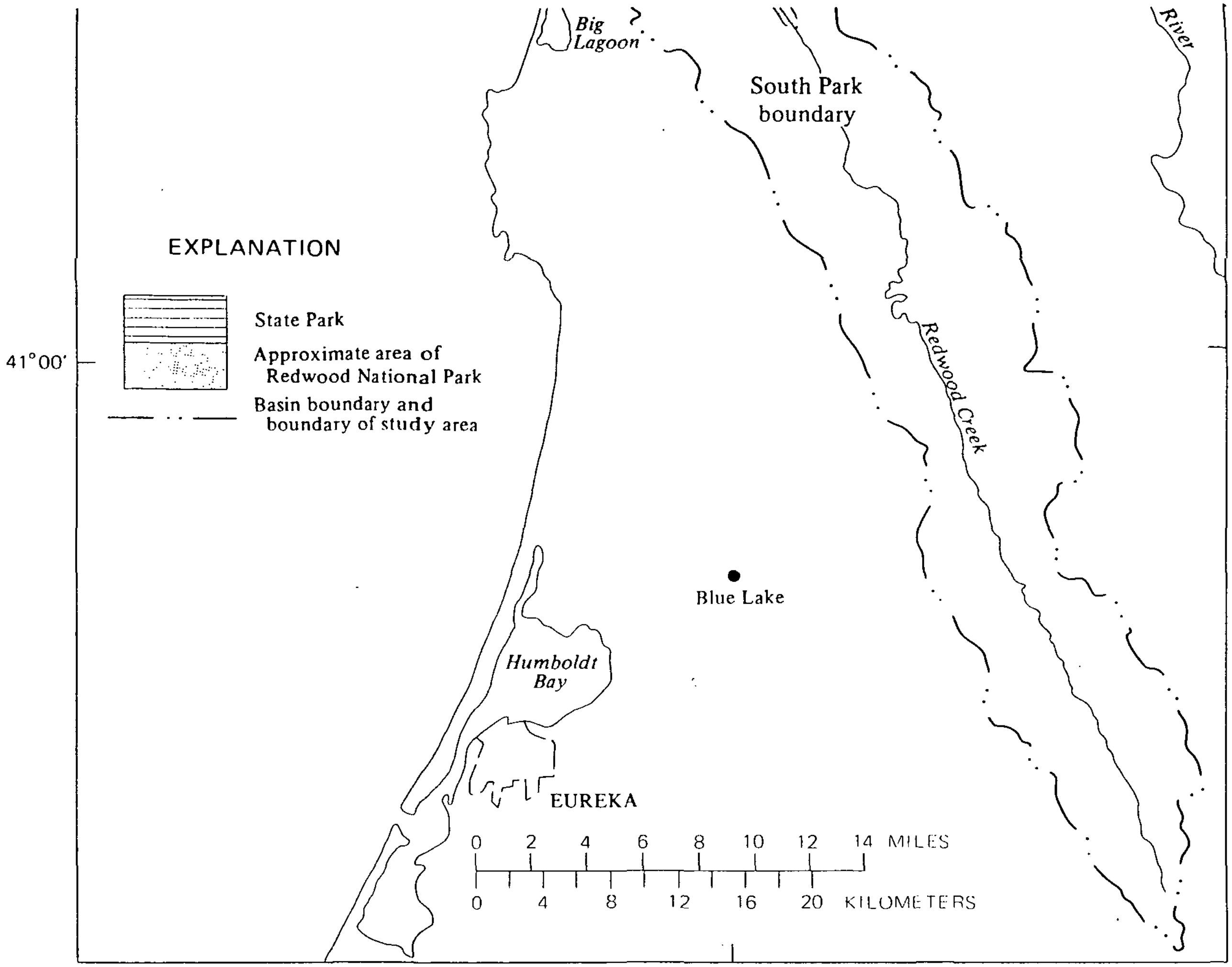


FIGURE 1.--Redwood National Park, showing location of the Redwood Creek and Mill Creek drainage basins.

Data and results of the ongoing studies have been presented in several reports. Janda and others (1975a) presented a comprehensive report on environmental conditions in the Redwood Creek drainage basin. Iwatsubo and others (1975, 1976) presented the water quality, sediment discharge, and biological data collected during the first 2 years of study. Janda, Nolan, and Harden (1975b), Lee, Kapple, and Dawdy (1975), and Averett and Iwatsubo (1975) have published interpretive reports of water and sediment discharge, rainfall-runoff relationships, and aquatic biology. Additional reports discussing sediment, water discharge, and aquatic biology are being prepared concurrently with this report.

The effects of upstream and upslope logging that are most apparent and of primary concern to the National Park Service are increased erosion and sedimentation. Effects on water quality, if there are any, are less obvious and were initially of less concern. Nevertheless, studies in the Hubbard Brook Experimental Watershed in New Hampshire (Likens and others, 1967; 1970), in the Oregon Cascades and Coast Ranges (Brown and others, 1973; Fredriksen, 1971; Fredriksen and others, 1973), in the Rocky Mountains of Montana and Idaho (Snyder and others, 1975; DeByle and Packer, 1972), and in the Washington Coast Range (Grier and Cole, 1971; McColl and Cole, 1968) all showed that common logging practices--clearcutting, road building, and slash-burning--caused changes in the quality of water draining from the affected watersheds. Thus, the observable effects of logging on water quality in the Redwood National Park could not be discounted without further study.

Description of Study Area

The Redwood Creek and Mill Creek drainage basins have been described in detail by Janda and others (1975a). The brief descriptions that follow focus on features thought to affect water quality.

Physical Features

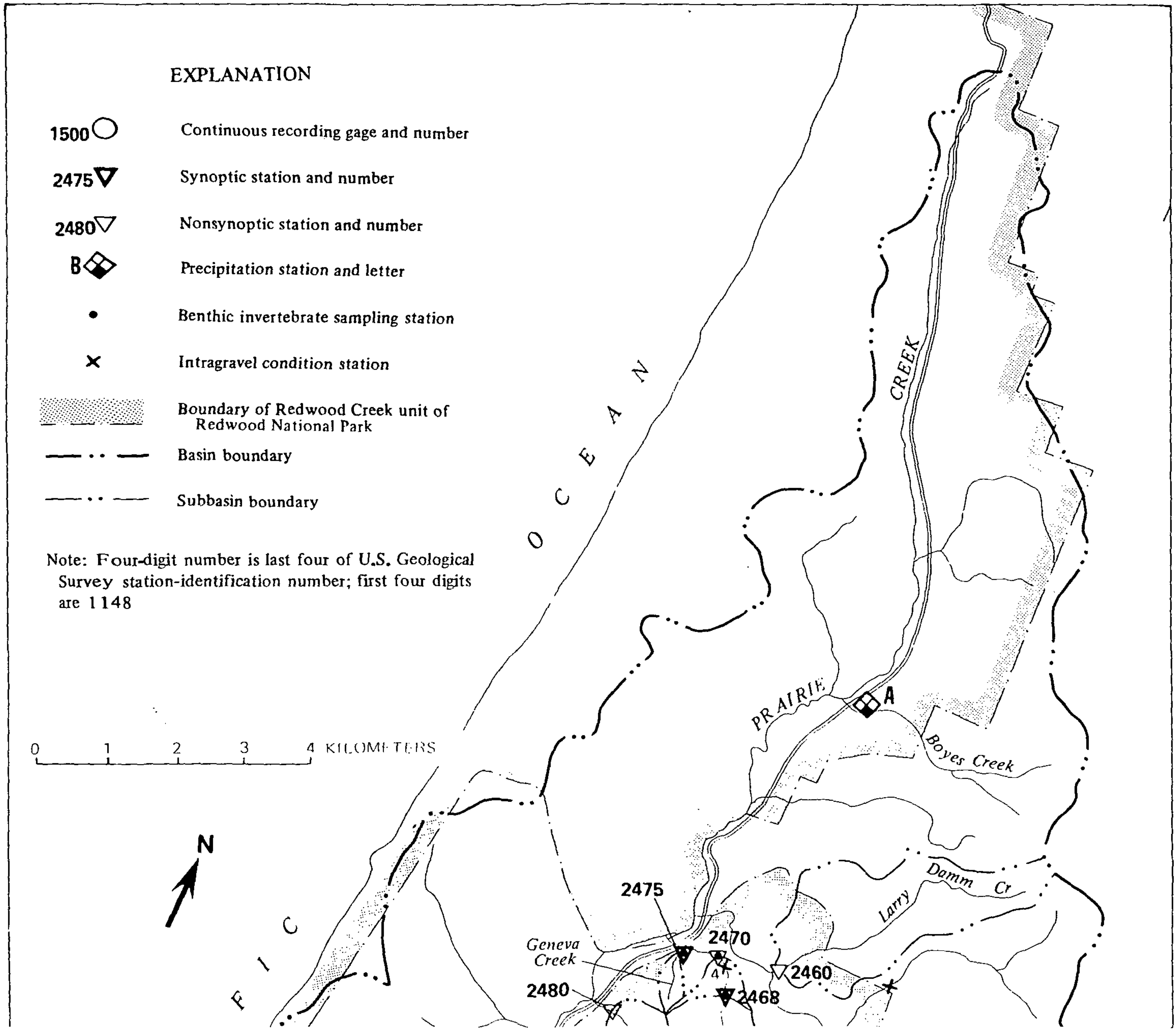
The Redwood Creek drainage basin (fig. 2) consists of 730 km^2 of generally high-relief, geologically unstable terrain in California's northern Coast Ranges. Basin elevation ranges from sea level at the northern end near Orick to 1,600 m in the southern end. The relief, in cross sections normal to the basin axis, ranges from 600 m in the northern end of the basin to 900 m in the southern end. Hill-slope gradients range from an average of 31 percent in the northern quarter to 34 percent in the southern quarter of the drainage basin. Slope gradients steepen from the drainage-basin boundary to the stream channels and in several places are nearly vertical adjacent to the streams. Flood plains along Redwood Creek are discontinuous, and most are less than 60 m wide.

The Mill Creek drainage basin (fig. 3) consists of 96 km^2 of high-relief, geologically unstable terrain. The slopes of this basin are, however, more stable than those in the Redwood Creek basin. Elevations in the basin range from 21 m, at the confluence of Mill Creek and the Smith River, to 710 m. Cross-sectional relief increases downstream from 575 m in the West Branch to 671 m near the mouth. Average hill-slope gradients range from 34 to 37 percent. The terrain at the drainage basin boundary is broad and gently sloping but steepens downslope and becomes quite steep adjacent to the stream channels.

Redwood Creek and Mill Creek are fed by numerous tributaries with steep channel gradients. Gradients in the main channel tend to be steep upstream, becoming gentle downstream. Because of the extremely steep slopes of the basins, one would expect streams to rise rapidly in response to rainfall, and the potential for erosion to be high. The steepness of channel gradients in the tributaries and main channels suggests that flowing water will be turbulent and thus generally saturated with dissolved gases--oxygen, nitrogen, and carbon dioxide. At low flow, however, photosynthesis and respiration in pools could cause alternating supersaturation and depression of dissolved-oxygen concentrations.

Climate and Rainfall

The climate in the northern part of the Redwood Creek drainage basin and in the entire Mill Creek drainage basin is influenced by the ocean. The climate is described as coastal Mediterranean, characterized by high winter precipitation (1,780 to 2,290 mm per year), mild temperatures, and short, dry summers with frequent fog. The inland southern part of the Redwood Creek drainage basin has an interior Mediterranean climate with high winter precipitation (2,030 to 2,540 mm per year), mild winter temperatures, and hot, dry summers with infrequent fog. Precipitation varies widely from year to year and is greatest at highest elevations. Most precipitation occurs as rain from large storm systems generated in the Pacific Ocean. Occasionally, snow falls at higher elevations; however, accumulations usually do not exceed 0.6 m. Near the coast, some precipitation also occurs as fog drip (Janda and others, 1975a, p. 89).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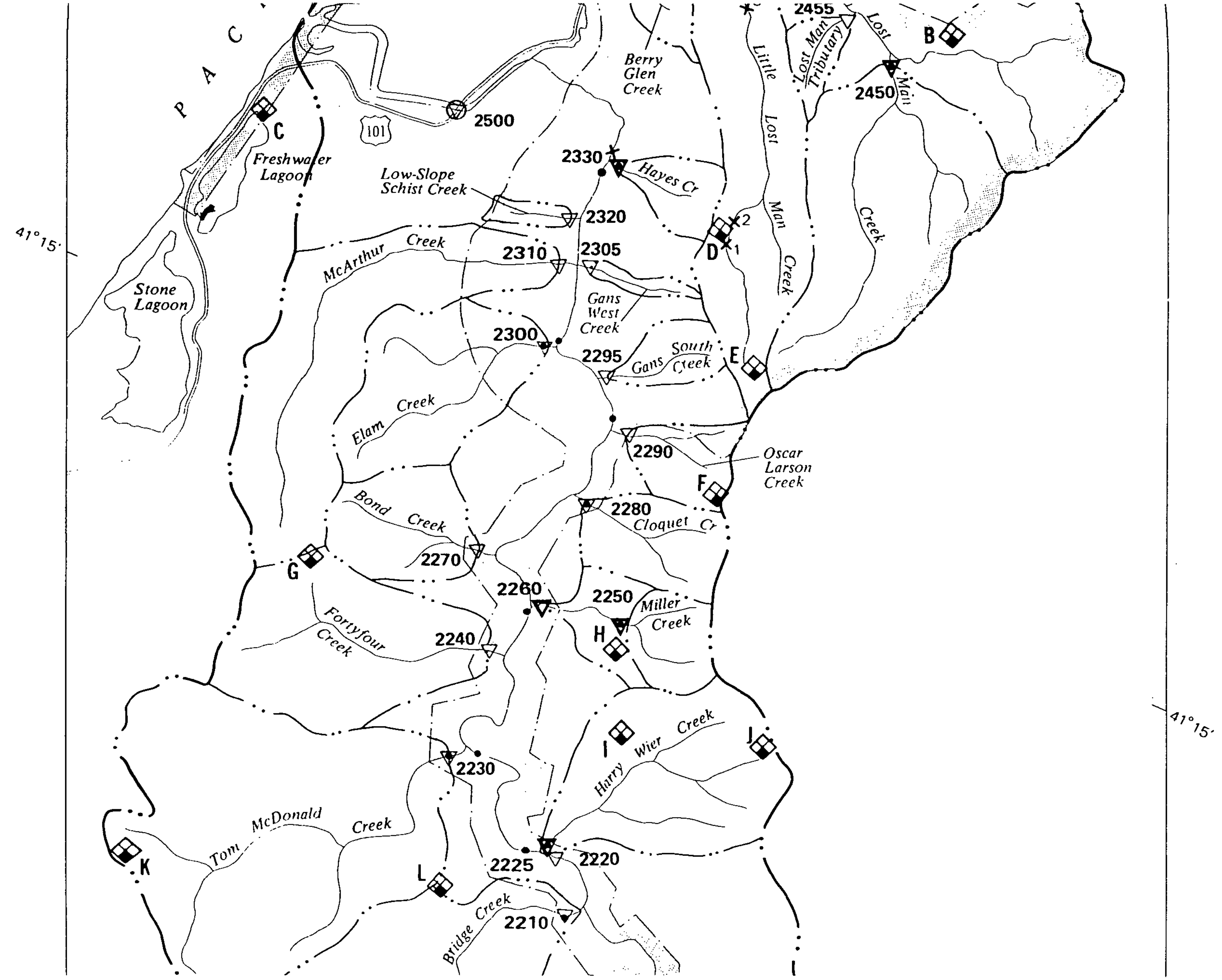
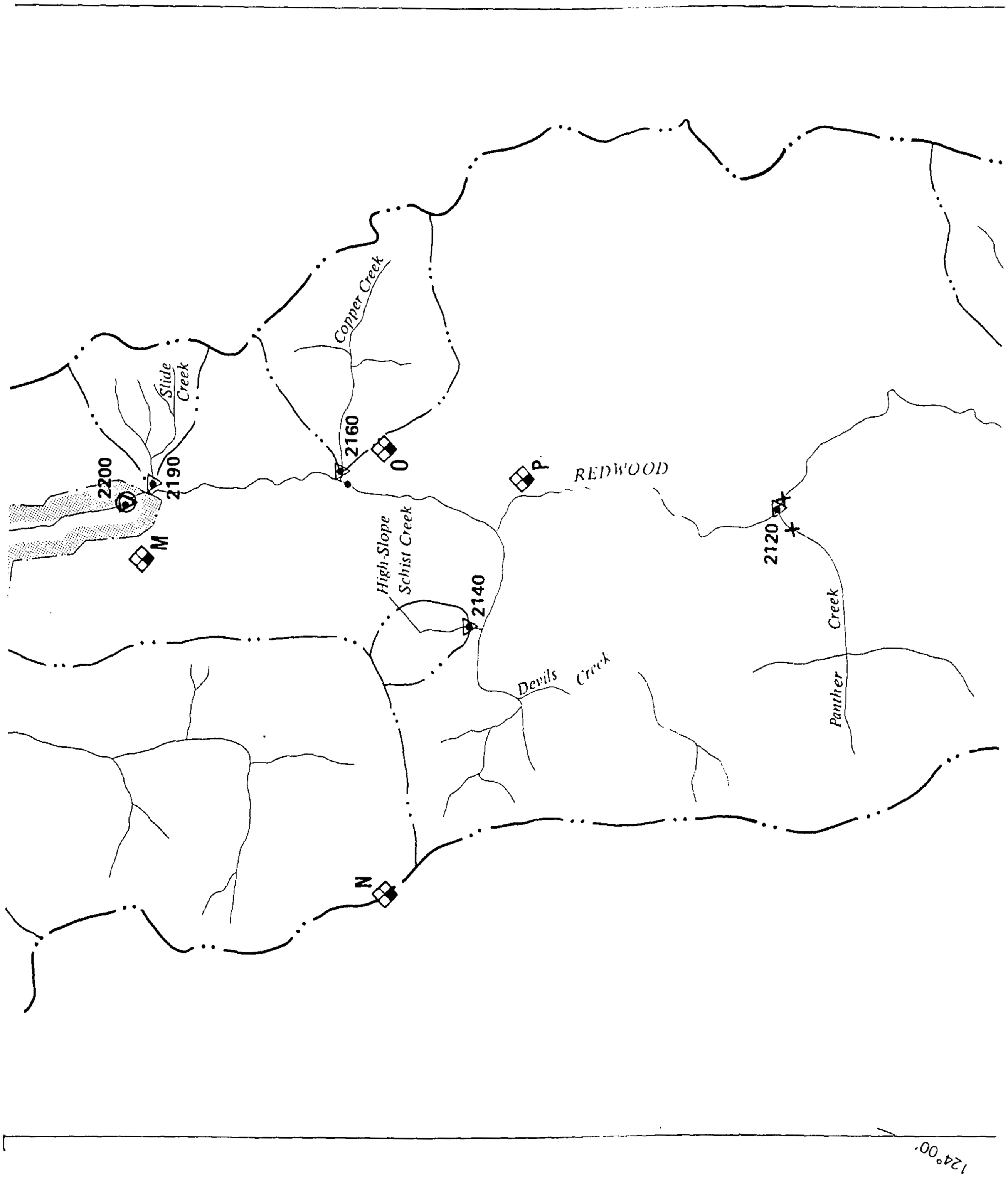


FIGURE 2.--Sampling stations in Redwood Creek area. (continued on following pages)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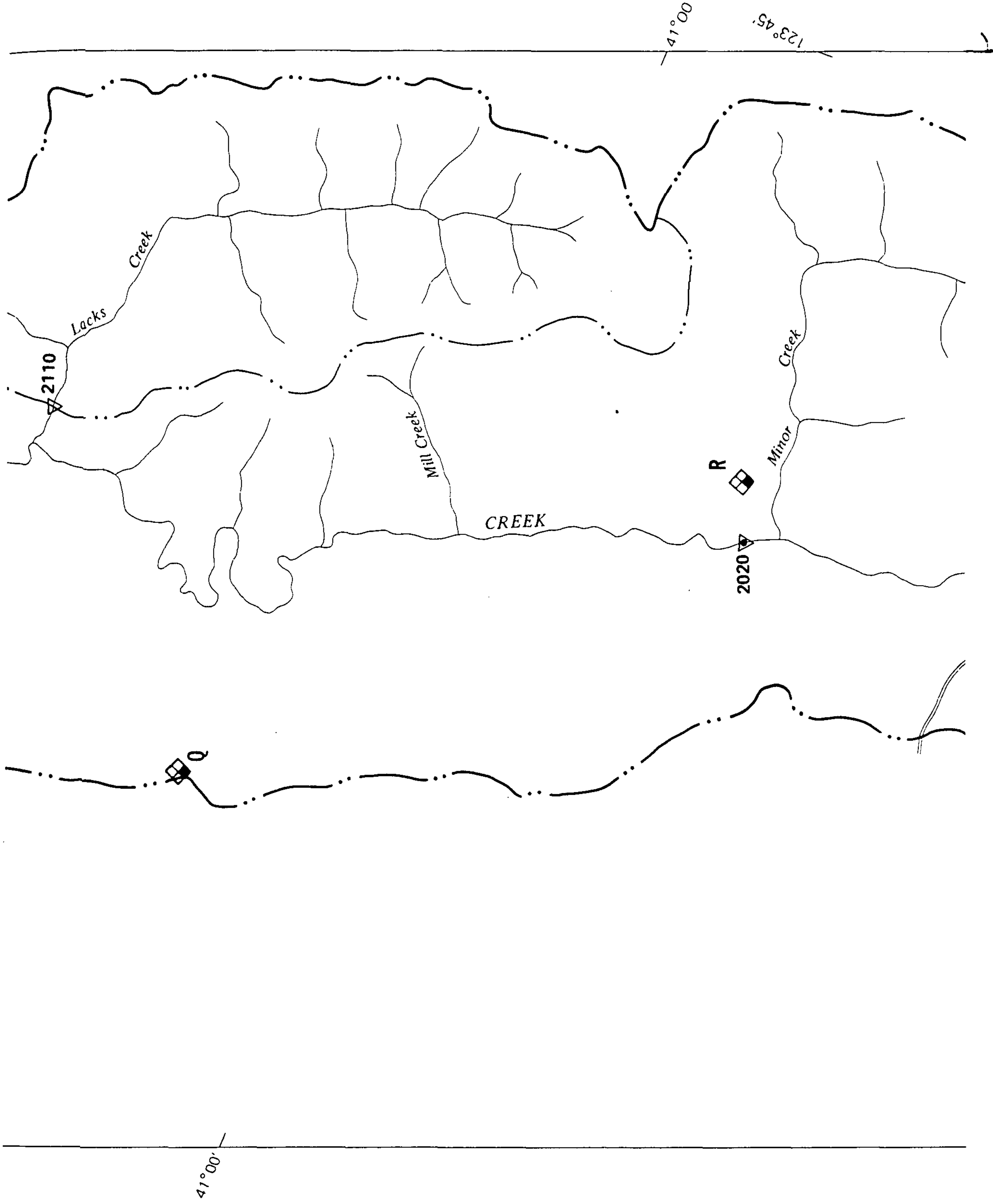
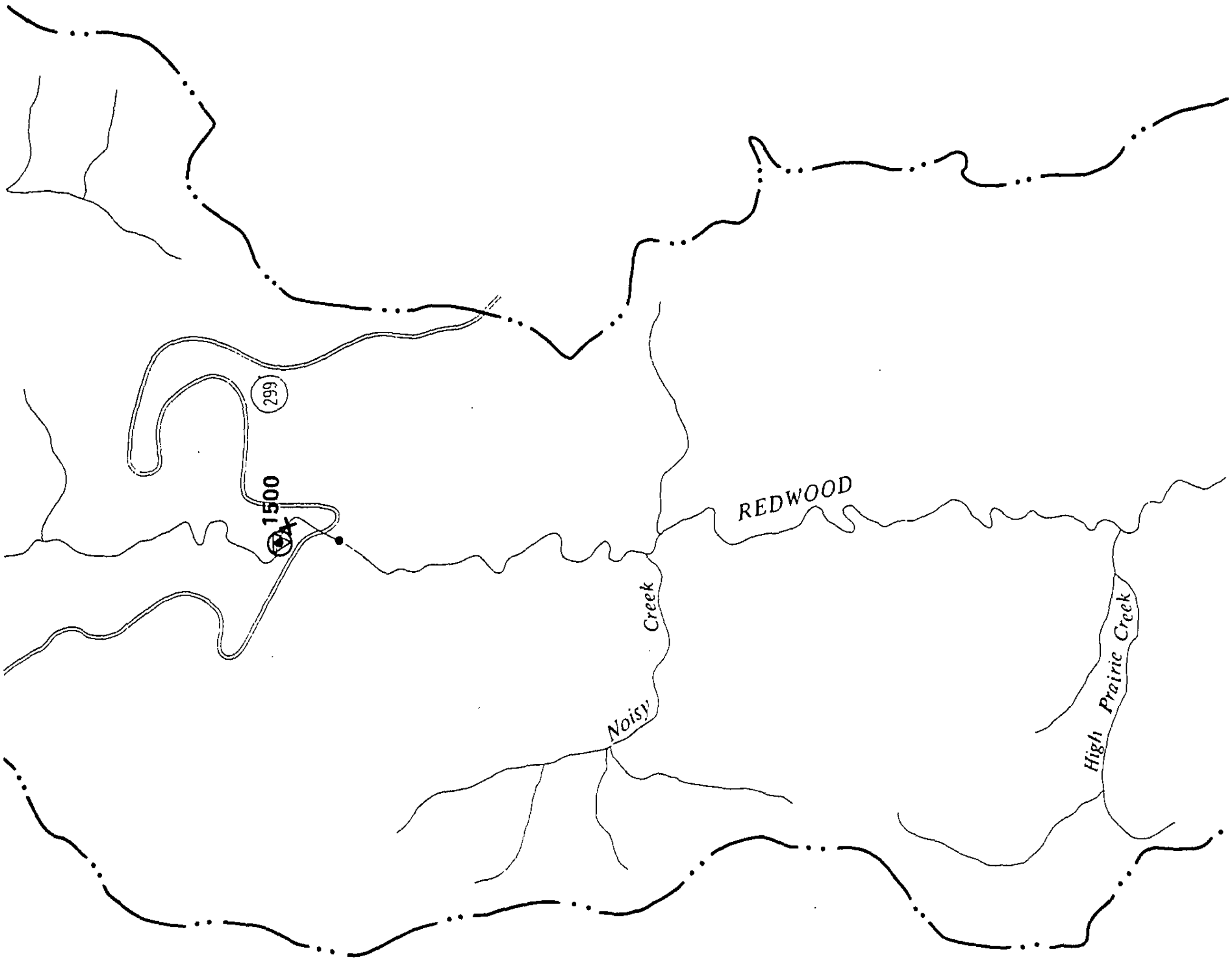


FIGURE 2.--Sampling stations in Redwood Creek area--Continued.
(continued on following pages)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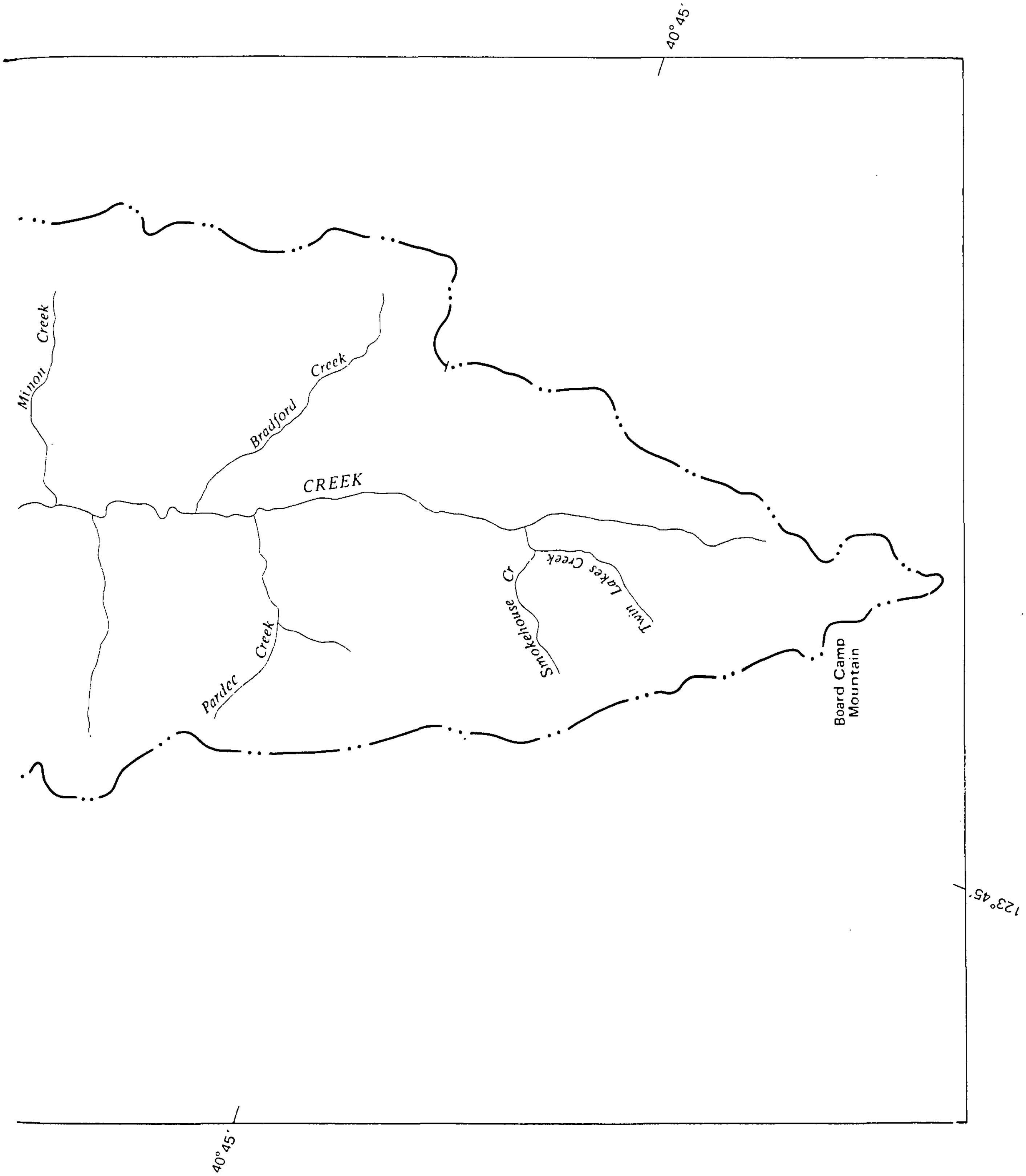
High Prairie Creek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Pardee Creek
Smokehouse Cr
Twin Lakes Creek
Board Camp Mountain
123°45'
40°45'

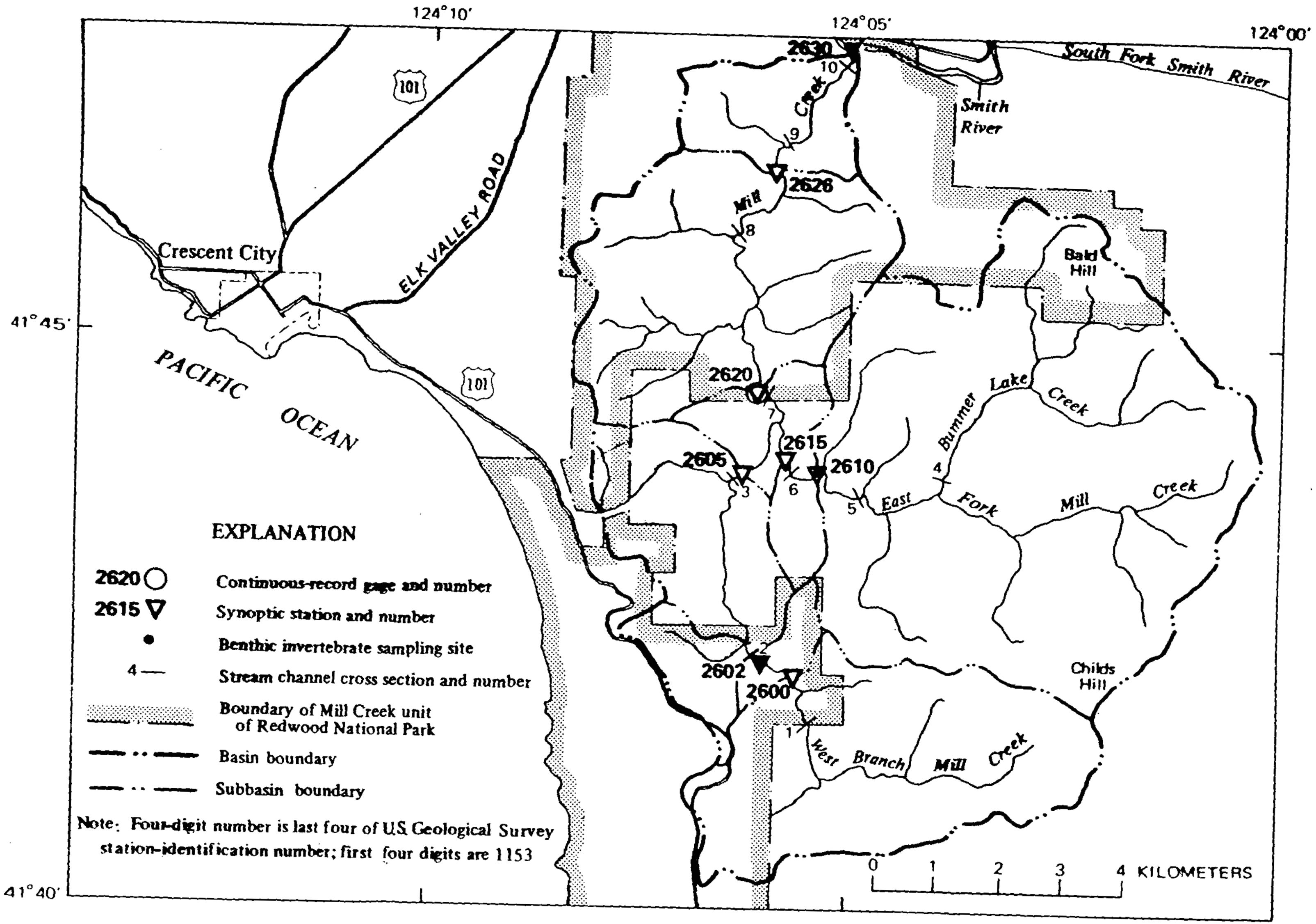

FIGURE 3.--Sampling stations in Mill Creek area.

Through much previous work and numerous data on California coastal streams, it is known that the seasonal pattern of streamflow follows the seasonal pattern of precipitation in a well-established sequence. As the dry season gets underway, usually in April or May, water stored in ponded areas and channels drains off. As the dry season progresses, streams are fed at a low and gradually decreasing rate by base flow made up of ground water with a long residence time in the soil and underlying materials. Soil moisture is depleted, and water levels in the ground-water reservoir decline.

When the rainy season returns, usually in October or November, precipitation first replenishes the soil moisture and there is little runoff. At times precipitation may be intense enough to exceed the infiltration rate and cause some runoff as overland flow, which makes little contact with the soil, or quick-return flow (Jamieson and Amerman, 1969), which has short-term intimate contact with the soil (several minutes). As the rainy season progresses soil-moisture needs are met; infiltration gradually replenishes the ground-water reservoir, causing an increase in base flow; and, the soil becomes more saturated, causing overland flow to appear more quickly in response to precipitation than earlier in the season. Also, streamflow between storms increases, owing to delayed-return flow (Kennedy and Malcolm, 1978). Delayed-return flow is water that makes contact with the soil for several hours and reemerges as surface flow (Jamieson and Amerman, 1969).

Because of differences in the sources of water feeding streams in the dry season and wet season, noticeable differences in water quality are expected. Kennedy and Malcolm (1978) observed in the Mattole River, another coastal stream, that as the wet season progressed the dissolved-solids concentration in both stormflow and base flow gradually decreased, and as the dry season progressed the dissolved-solids concentration in the base flow gradually increased. Changes in the relative concentrations of the major ions were also observed.

Stream water may also vary in chemical composition owing to proximity to the coast. Salt spray and fog containing sea salts would be expected to envelop watersheds closer to the coast more often than those farther inland, and streams may differ in chemical composition because of it.

Little is known about the chemical composition of precipitation in the study area. Data for rainwater samples collected by Iwatsubo and others (1975; 1976) are summarized in table 1. Generally, these rainwater samples showed extremely low concentrations of all constituents except phosphorus and nitrogen, which were unexpectedly high. This suggests that rainfall may be an important contributor to the nutrient budgets of the Redwood and Mill Creek basins. Likens and others (1970) also found high nitrate concentrations in bulk precipitation (dry fallout, rain, snow, and hail) in the Hubbard Brook, N.H., experimental watershed and thought this to be a major nutrient source.

TABLE 1.--*Summary of data on rainfall composition*

[Samples collected within park boundaries; maximum elevation 120 feet. Constituent values in milligrams per liter except aluminum and iron (micrograms per liter) and specific conductance (micromhos per centimeter at 25°C). Data from Iwatsubo and others, 1975 and 1976]

Constituent	Median[1]	Range	Number of samples
Silica	0.2	0.0-1.2	5
Aluminum	0	.0-30	3
Iron	20	10-40	5
Calcium	.9	0.1-1.2	5
Magnesium	.1	0.0-0.7	5
Sodium	1.2	0.3-1.8	5
Potassium	.1	0.1-0.5	5
Bicarbonate	3.5	0-7	4
Carbonate	0	0	4
Alkalinity, as $CaCO_3$	2.5	0-6	4
Sulfate	.7	0.5-2.0	5
Chloride	1.1	0.4-2.0	5
Fluoride	.0	0.0-0.1	5
Total nitrite plus nitrate, as N	.045	0.02-0.06	8
Dissolved nitrite plus nitrate, as N	.030	0.02-1.3	5
Dissolved Kjeldahl nitrogen	.095	0.02-0.53	4
Dissolved total phosphorus	.05	0.01-0.08	8
Dissolved orthophosphorus	.02	0.0-0.02	4
Dissolved solids, sum of determined constituents	8	4-12	4
Hardness, as $CaCO_3$	3.0	2-3	5
Specific conductance	30	26-35	4

[1] The median of an even-numbered set of *n* observations is the value midway between the *n*/2 and *n*/2+1 observations, ranked in value from smallest to largest.

Vegetation

Vegetation in the Redwood Creek basin varies with slope, elevation, microclimate, and several other factors. In the lower flood plain near Orick, the vegetation is a mixture of shrubs, grasses, pasture, and trees--predominantly Sitka spruce and shore pine. Redwood and Douglas-fir dominate the upland vegetation from the shore to about 15 km inland (Janda and others, 1975, p. 102). Farther inland, redwoods grow only in the moist flood plain, terraces, and lower slopes adjacent to streams. On higher ground, Douglas-fir, tanoak, and madrone become more abundant; on high ground toward the southern end of the basin, Douglas-fir, white fir, incense cedar, and black oak predominate. In contrast, the Mill Creek basin is largely covered by a dense forest of mixed redwood and Douglas-fir. Redwood-dominated groves occupy the flood plain, low terraces, and adjacent slopes in the downstream end of the basin.

The presence or absence of forest vegetation can have a noticeable effect on streamflow, temperatures, nutrient concentrations, pH, and dissolved-oxygen concentrations in streams.

Streamside vegetation restricts incoming solar radiation and outgoing back radiation, effectively reducing the temperature range. Moring (1975) found that after clear-cut logging and removal of riparian vegetation, water temperatures increased as much as 12.7°C over prelogging averages in the Alsea experimental forest, Oregon. Restricting incoming solar radiation restricts photosynthesis by algae in the water, thus decreasing diel variations in pH and dissolved-oxygen concentration.

Heavy vegetation increases evapotranspiration, thus reducing the amount of water available for leaching the soil. Likens and others (1967) found that removing the tall trees increased the base flow in an experimental tract at Hubbard Brook, New Hampshire.

Trees also assimilate substantial amounts of nutrients from the soil, nutrients that may wash out of the watershed in the absence of the trees. Likens and others (1969) noted increased nitrate washout from the Hubbard Brook watershed after clear-cut logging and attributed this to decreased nitrate uptake from the soil.

Geology

The Redwood Creek basin upstream of Prairie Creek (fig. 2) is underlain by the indurated Franciscan assemblage that shows varying degrees of metamorphism. The eastern side of the basin consists mostly of unmetamorphosed marine sedimentary rocks, largely graywacke and sandstone with lesser amounts of mudstone and conglomerate. By contrast, rocks on the western side are finer grained and consist of small, discontinuous bodies of greenstone, bedded radiolarian chert, and thick deposits of mudstone interbedded with sandstone (Janda and others, 1975a, p. 10-11). Schists, mostly light- to medium-gray quartz-mica-feldspar and quartz-mica, crop out throughout the western half of the basin.

The regoliths overlying unmetamorphosed sedimentary rocks range in thickness from about 0.5 m at higher elevations to about 4 m on lower slopes. The overlying soils have high infiltration capacity, good subsurface drainage, and moderate to high erosion potential.

Where schist and sandstone crop out together, the regolith derived from the schist is generally thicker, finer grained, and more cohesive than that derived from sandstone. The soils overlying the schistose regolith have high infiltration capacity and good subsurface drainage but contain slightly more clay, which makes them less susceptible to erosion than soils on the unmetamorphosed, sandstone-based regolith.

The Mill Creek drainage basin is underlain by unmetamorphosed sandstone of the Franciscan assemblage and some outcrops of metamorphic rocks. In contrast to the Redwood Creek drainage basin, the rocks there are less fractured and sheared and have weathered to soil series having greater cohesion. The soils are physically more stable and have a lower erosion potential than those in the Redwood Creek drainage basin. Origins of the regoliths in tributaries in this drainage basin are similar to one another.

Logging History

Logging in the late 19th and early 20th centuries was limited largely to clearing flood plains and terraces in gentle terrain to provide pasture. By 1947 less than 5 percent of the Redwood Creek basin had been logged (Janda and others, 1975a, p. 114-122). The rugged topography upslope prevented large-scale timber harvesting until the early 1950's.

Intensive logging occurred in the upper part of the Redwood Creek basin in the early 1950's and in the lower part in the late 1950's. By 1973, only about 20 percent of the basin retained old-growth redwood forest. During the 1940's, the most common logging method was selective cutting of small timber plots, but in the 1950's the clearcutting of larger blocks and yarding (gathering for loading on trucks) the logs downhill by tractor became popular. Soil disruption resulting from extensive logging probably increased erosion (Janda and others, 1975a, p. 164) and altered the hydrology of the basin (Lee, Kapple, and Dawdy, 1975).

Logging in the Mill Creek drainage basin is less well documented than that in the Redwood Creek drainage basin, but presumably it followed a similar course. By 1973, 49 percent of the basin retained old-growth redwood forest. Much of the logging was in the watershed of East Fork Mill Creek. West Branch Mill Creek has been less extensively logged, but certain sections have been clearcut.

STUDY DESIGN

Throughout this report reference will be made to the Redwood Creek and Mill Creek drainage basins, which encompass several subbasins identified by the names of the creeks tributary to the main stem. To simplify terminology, the term "drainage basin" will be used to refer only to the entire Redwood Creek and Mill Creek drainage basins. The term "watershed" will be used to refer to the area drained by tributaries to Redwood Creek and Mill Creek, and the name given to the watershed will be the name of the tributary creek.

Land-Use and Regolith Classification

The logging and regrowth history of the Redwood Creek and Mill Creek drainage basins has produced a complex present-day mosaic of old growth, advanced secondary growth, and cutover forest areas. Sampling stations were selected primarily to provide a data set representative of this broad range of land uses. Watersheds in the Redwood Creek drainage basin were assigned the following land-use codes:

Code	Description
MS	Main-stem stations: Not counted as a separate land use.
RF	Regrown, forested: Watershed first logged prior to establishing park (1968) and now substantially RF-type. Not being logged during this study.
VL	Virgin timber, logged: Watershed first logged since 1968; in some cases watershed was being logged during this study.
RL	Regrown, being logged: Watersheds first logged well before 1968 and being logged of second growth during this study.
VF	Virgin timber, forested: Largely virgin timber with small and variable amounts of advanced second growth.

In the Mill Creek drainage basin, the study objectives were accomplished by describing water-quality differences between West Branch Mill Creek, which is only about 25 percent logged (above station 11532605), and East Fork Mill Creek, which is about 52 percent logged (above station 11532615) (Iwatsubo and others, 1976).

For this study, sampling stations in the Redwood Creek drainage basin were also classified according to three broad categories of regolith composition of the watershed:

Code	Description
St	Schist: Watershed underlain predominantly by schist.
Sn	Sandstone: Watershed underlain predominantly by indurated sandstone, fractured in varying degrees, and some mudstone.
Mx	Mixture: Watershed underlain by a mixture of sandstone and schist or transitional rocks.

The regolith structure and soil-profile development do not differ significantly between the two tributary watersheds studied in the Mill Creek drainage basin.

More detailed descriptions of the watersheds upstream from the sampling stations are in Iwatsubo and others (1975; 1976). Descriptions of the sampling stations in the Redwood Creek and Mill Creek drainage basins pertinent to the classification schemes described above are listed in table 2. Locations of stations listed are shown in figures 2 and 3.

Strategy of Data Collection

In order to gain a comprehensive picture of water quality in a stream, it should be observed at three different periods--during storm runoff, over diel periods at low flow, and in periods between storms. Three data collection programs were designed to observe streams in the two basins at all three periods.

TABLE 2.--*Station description and land-use and regolith classifications of watersheds*

[Soil, mixture of types shown by /; predominant type precedes hyphen -]

Station number and name	Synoptic	Diel	Average stream gradient (m/km)	History of land use (percentage of area)			Land use classification	Soil (parent material)	Regolith classification
				Logged since establishing park	Logged prior to establishing park	Virgin and advanced second growth			
				Redwood Creek drainage basin					
11481500 Redwood Creek near Blue Lake		X	31.3	<5	>55	40	MS	Schist/sandstone and shale	-
11482020 Redwood Creek at Redwood Valley Bridge, near Blue Lake		X	26.9	<5	>60	35	MS	Schist/sandstone and shale	
11482110 Lacks Creek near Orick			57.2	10	40	50	RL	Sandstone shale-sheared sediment	Sn
11482120 Redwood Creek above Panther Creek, near Orick		X	18.8	<5	>60	35	MS	Schist/sandstone and shale	-
11482140 High-Slope Schist Creek near Orick			293.9	-	-	100	VF	Schist	St
11482160 Copper Creek near Orick			180.1	20	30	45	VL	Schist/sandstone	Sn
11482190 Slide Creek near Orick			255.9	30	40	30	VL	Sandstone and shale	Sn
11482200 Redwood Creek at South Park Boundary,	X	X	18.6	<5	65	>30	MS	Schist/sandstone and shale	-

near Orick									
11482220 Redwood Creek above Harry Wier Creek, near Orick	X	X	16.1	5	60	35	MS	Schist/sandstone and shale	-
11482225 Harry Wier Creek near Orick	X	X	145.1	40	-	60	VL	Sandstone and shale	[1]Mx
11482230 Tom McDonald Creek near Orick			70.1	6	80	14	RL	Schist	St
11482240 Fortyfour Creek near Orick			104.5	20	75	5	RL	Schist	St
11482250 Miller Creek near Orick	X	X	207.0	90	-	10	VL	Sandstone and shale	Sn
11482260 Miller Creek at mouth, near Orick	X	X	200.2	77	-	23	VL	Sandstone and shale-schist	[1]Mx
11482270 Bond Creek near Orick			137.7	27	55	18	RL	Schist	St
11482280 Cloquet Creek near Orick			219.9	55	-	45	VL	Sandstone and shale-schist	Mx
11482290 Oscar Larson Creek near Orick			283.3	23	-	77	[2]VL	Sandstone and shale-schist	Mx
11482295 Gans South Creek near Orick			271.8	-	-	100	VF	Sandstone and shale/schist	Mx
11482300 Elam Creek near Orick			89.8	40	30	30	VL	Schist	St
11482305 Gans West Creek near Orick			295.7	-	-	100	VF	Schist/sandstone and shale	Mx
11482310 McArthur Creek near Orick			47.2	30	45	25	VL	Schist	St
11482320 Low-Slope Schist Creek near Orick			241.7	-	-	100	VF	Schist	St
11482330 Hayes Creek near Orick	X		236.8	-	4	96	VF	Sandstone and shale	Sn
11482450 Lost Man Creek near Orick	X	X	103.6	-	87	13	RF	Sandstone and shale	Sn

TABLE 2.--*Station description and land-use and regolith classifications of watersheds*--Continued

Station number and name	Synoptic	Diel	Average stream gradient (m/km)	History of land use (percentage of area)			Land use classification	Soil (parent material)	Regolith classification
				Logged since establishing park	Logged prior to establishing park	Virgin and advanced second growth			
Redwood Creek drainage basin--Continued									
11482455 Lost Man Creek Tributary near Orick			243.9	-	-	100	VF	Sandstone and shale/schist	Sn
11482460 Larry Damm Creek near Orick			94.3	-	70	30	[3]RF	Soft sediment-sandstone and shale	-
11482468 Little Lost Man Creek at Site No. 2, near Orick	X	X	75.4	0	6	94	VF	Sandstone and shale	Sn
11482470 Little Lost Man Creek near Orick	X	X	66.1	-	8	92	VF	Sandstone and shale	Sn
11482475 Geneva Creek near Orick	X		242.4	-	100	-	RF	Sandstone and shale	Sn
11482480 Berry Glen Creek near Orick			261.2	-	100	-	RF	Sandstone and shale/sheared sedimentary	Mx
11482500 Redwood Creek at Orick	X	X	13.4	10	50	40	MS	Schist/sandstone and shale	-

				History of land use (percentage of area)					
				Logged as of 1974	Advanced second growth	Prairie or cleared	Virgin area		
				Mill Creek drainage basin					
11532600 West Branch Mill Creek near Crescent City[4]	X								Not classified
11532602 West Branch Mill Creek below Red Alder campground, near Crescent City[5]	X	X	64.4	39	17	0	44	Sandstone and shale	
11532605 West Branch Mill Creek at Bridge, near Crescent City	X		45.5	24	47	1	28	Sandstone and shale	
11532610 East Fork Mill Creek near Crescent City[6]		X							
11532615 East Fork Mill Creek at Bridge, near Crescent City	X		44.6	48	1	4	47	Sandstone and shale	
11532620 Mill Creek near Crescent City	X	X	37.9	38	20	3	39	Sandstone and shale	
11532626 Mill Creek at Bridge, near Crescent City	X		27.5	32	18	2	48	Sandstone and shale	
11532630 Mill Creek at mouth, near Crescent City		X	24.6	30	19	2	49	Sandstone and shale	

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[1] Regolith type does not agree with percentage of predominant soil type of parent material.

[2] Does not fit any land-use category well.

[3] Watershed is overlain by a weakly consolidated layer.

[4] Principally low-flow station. During high water, observations made at 11532602.

[5] Only one sample taken during synoptic March 17-19, 1975.

[6] Principally low-flow station. During high water, observations made at 11532615.

Synoptic Studies During Storms

Major effort was devoted to obtaining a comprehensive or synoptic overview of water-quality conditions at several stations (table 2) in the basins during several storms. In most of these synoptic studies, field measurements were made, and one to three samples were taken for laboratory analysis. Field measurements of alkalinity, specific conductance, pH, temperature, and dissolved oxygen were made at 2- to 6-hour intervals depending on the progress of the storm. Water samples for chemical analysis and measurement of other properties (listed in table 3) were collected at various times during each storm. The intent was to take samples at the rise, peak, and recession of the hydrograph. For logistic reasons, however, at times only one sample was taken.

During two storms, November 6-8, 1974, and February 5-9, 1975, at Harry Wier Creek and Little Lost Man Creek at Site No. 2, samples for laboratory analysis were collected at 1-hour or longer intervals in an intensive study of the chemograph (water-quality variations with time during storm runoff).

TABLE 3.--*Constituents*[1] *and properties measured or calculated for water samples in the study (U.S. Geological Survey Central Laboratory, Salt Lake City, Utah)*

Alkalinity (total)
Calcium
Magnesium
Sodium
Potassium
Bicarbonate
Carbonate
Carbon dioxide[2]
Sulfate
Chloride
Fluoride
Hardness, as calcium carbonate[2]
Silica

Ammonia nitrogen
Nitrate, as nitrogen[2]
Nitrite, as nitrogen
Nitrite plus nitrate, as nitrogen
Kjeldahl nitrogen
Dissolved total phosphorus (as P)
Dissolved ortho-phosphorus (as P)
Dissolved organic carbon
Suspended organic carbon

Aluminum
Cadmium
Copper
Iron
Lead
Zinc

Specific conductance
pH
Dissolved solids, sum of constituents[2]
Percent sodium[2]
Sodium adsorption ratio[2]

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[1] Unless otherwise noted, constituents are determined on a sample filtered through a 0.45-µm filter and are thus termed "dissolved."

[2] Constituent obtained by calculations from other measurements.

Diel Studies

Studies of water quality were made over diel periods (24-hours) at stations in the Redwood Creek drainage basin (table 2) July 18-19 and September 10-11, 1974, and July 30-31, 1975. Diel studies at stations in the Mill Creek drainage basin (table 2) were made July 31-August 1, 1974. Field measurements were made at 1- to 2-hour intervals.

Studies of Seasonal Variations

To determine the seasonal variations water-quality measurements and samples were taken at all stations at scheduled intervals. The resulting data is termed "regular" since it resulted from a normal program of site visits. In the Redwood Creek drainage basin, numbers of regular field measurements and laboratory analyses were about equally distributed between land-use types. More data were collected during the rainy season than the dry season, however. In the Mill Creek drainage basin, numbers were about equal between East Fork and West Branch watersheds, and between dry and rainy seasons.

METHODS

Water-Quality Measurements

The field measurements for alkalinity, specific conductance, pH, and dissolved oxygen were made by methods described by Brown and others (1970) and the American Public Health Association and others (1971). Total alkalinity was determined onsite or in a field laboratory by titrating with standard sulfuric acid to a pH of 4.5 as indicated by a pH meter. Specific conductance was measured either onsite or in a nearby field laboratory. The pH was measured onsite with meters and electrodes calibrated using two or more buffers. Dissolved-oxygen concentrations were determined by the Alsterberg azide modification of the Winkler method (Brown and others, 1970, p. 126).

The estimated precision of the field measurements are as follows: alkalinity recorded to the nearest unit (±0.5 mg/L); specific conductance, ±3 units at values less than 80 and ±5 percent above 80 μmho/cm at 25°C; pH, ±0.1 unit; temperature, recorded to the nearest 0.5°C (±0.2°C); dissolved oxygen, ±5 percent saturation.

Water samples for the laboratory analyses and measurements listed in table 3 were collected at approximately the middle centroid of flow of the stream (Guy and Norman, 1970) and were pretreated (as prescribed by Brown and others, 1970) before shipment to the Geological Survey's Central Laboratory in Salt Lake City, Utah (now known as the National Water Quality Laboratory located in Arvada, Colo.). The samples for major constituent determinations (except carbonate and bicarbonate) and trace-element determinations were filtered through a 0.45-µm pore-size membrane filter and acidified to pH<2 with nitric acid. A separate sample for carbonate and bicarbonate analysis was unfiltered and unacidified. The samples for dissolved-nutrient and Kjeldahl nitrogen analysis were filtered through the same filter into polyethylene bottles and packed, without preservative, in ice for shipment. The sample for chemical oxygen demand (COD) determination was acidified to pH<2 with sulfuric acid and packed in ice for shipment. Samples for dissolved and suspended organic carbon analysis were filtered through silver filters of 0.45 µm pore size, and both filter and filtrate were packed in ice for shipment. Methods for organic carbon analysis are described by Goerlitz and Brown (1972, p. 4).

Analysis of Water-Quality Data

Several methods were used in analyzing the water quality data. The basic statistics such as the mean, standard deviation, and skewness (defined in Snedecor and Cochran, 1967), were calculated by hand for selected sets of data or, for larger sets, by using the A140 computer program of Steele and Moody (1972). Analysis of variance as discussed by Riggs (1968, p. 31) and Snedecor and Cochran (1967, p. 258) and the Student t-test (Snedecor and Cochran, 1967, p. 59) were used to compare and contrast sets of data. The significance of differences between some sets of data was determined using the sign test described by Mendenhall (1971, p. 369) and Conover (1971, p. 121).

Regression analysis as discussed by Riggs (1968, p. 9-15) was used to determine relationships between specific conductance and dissolved-solids concentrations. Regressions for log of discharge versus log of specific conductance were also calculated using the A137 program of Steele (1973).

Trilinear diagrams (Piper, 1944, Hem, 1970, p. 268) were used to show the relative composition of the major anions and cations in water samples.

Throughout this report the arithmetic mean of a set of pH data has been employed to represent the central tendency of the set. The reader should be aware that the pH is the negative logarithm of the hydrogen ion activity, and as a consequence, the mean pH is the negative logarithm of the geometric mean of a set of hydrogen ion activities. The mean pH is not the average hydrogen ion activity, nor the hydrogen ion activity one would obtain by mixing equal volumes of the waters measured.

RESULTS

Redwood Creek Drainage Basin

Summary Statistics

A statistical summary of selected water-quality measurements obtained in this study in the Redwood Creek drainage basin is given in table 4.

The water of this basin is of excellent quality for drinking and fisheries with low dissolved-solids concentrations and low hardness. In major-ion composition it tends to be a calcium-sodium bicarbonate type, with some magnesium, potassium, chloride, and sulfate. The coefficients of variation[1] for calcium, magnesium, bicarbonate, and sulfate are larger than those for the other major ions, suggesting more variable rates of supply for those ions than for sodium, potassium, and chloride.

The set of silica (SiO_2) concentrations has a narrow range and small coefficient of variation. The sets of aluminum and iron concentrations have wide ranges and large coefficients of variation. Because these three constituents are derived from the weathering of alumino-silicate minerals, it might be expected that the coefficients of variation would be alike. Differences suggest that secondary processes such as adsorption or precipitation within the soil profile act on the three compounds differently and influence concentrations in the streams.

Dissolved ortho and total phosphorus concentrations, on the average, are high enough to support algal growth, but average nitrite plus nitrate concentrations are probably low enough, relative to phosphorus, to be the nutrient limiting growth of algal populations (Sawyer, 1947). The distributions of phosphorus and various forms of nitrogen are highly skewed positively, suggesting occasional extremely high concentrations.

The mean concentrations of four trace metals--cadmium, copper, lead, and zinc--were very near or below the detection limits of the analytical methods used. Hence, there is some question whether the values should be used in discussing the geochemical properties of those metals.[2] The data nevertheless suggest that the concentrations of these metals are very low, typical of clean streams.

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[1] The coefficient of variation is the standard deviation divided by the mean.

[2] In independent analyses made on the nearby Mattole River, Vance Kennedy (U.S. Geological Survey, oral commun., 1976), using more sensitive methods than those employed here, found concentrations which were lower by a factor of 2 for zinc, 5 for lead, and 10 for cadmium.

TABLE 4.--*Statistical summary of selected water-quality measurements, Redwood Creek drainage basin*

[Data from Iwatsubo and others, 1975 and 1976]

Constituent	Units	Mean[1]	Standard deviation	Number of samples	Maximum observed	Minimum observed	Skewness
Silica	mg/L	6.44	1.07	182	14.0	4.0	2.06
Aluminum	µg/L	36	42	161	280	0	3.3
Iron	µg/L	72	97	168	670	10	3.6
Calcium	mg/L	7.87	6.81	182	40.0	1.9	2.18
Magnesium	mg/L	1.55	.77	182	4.3	.3	.97
Sodium	mg/L	4.47	1.15	186	7.2	1.9	.05
Potassium	mg/L	.70	.25	182	2.0	.3	1.56
Bicarbonate	mg/L	30.5	19.2	177	104	8	1.55
Carbonate	mg/L	.009	.092	118	1	0	11
Alkalinity, as $CaCO_3$	mg/L	29.9	21.0	1,187	111	3	1.2
Sulfate	mg/L	4.68	4.65	183	29	.9	2.63
Chloride	mg/L	4.82	1.53	189	11	1.6	.53
Fluoride	mg/L	.13	.21	63	1.0	.0	3.13
Nitrite plus nitrate	mg/L	.087	.214	170	2.2	.00	6.82
Ammonia nitrogen	mg/L	.018	.031	108	.26	.00	5.15
Organic nitrogen	mg/L	.291	.717	108	3.3	.00	3.71
Kjeldahl nitrogen	mg/L	.257	.567	182	3.3	.00	4.64
Dissolved total phosphorus	mg/l	.030	.081	182	1.0	.00	10.2
Dissolved ortho-phosphorus	mg/l	.014	.023	80	.17	.00	4.6
Dissolved solids	mg/L	46.1	20.9	168	139	25	1.8
Hardness, as $CaCO_3$	mg/L	27.0	20.3	188	120	8.0	1.9
Specific conductance	µmho/cm at 25°C	80.2	50.1	2,494	295	17	1.6
pH		7.19	.50	1,557	8.9	4.7	-.56
Temperature	°C	10.8	3.8	2,398	25.0	4.5	1.4
Dissolved oxygen	mg/L	10.30	1.25	1,241	13.0	5.9	-.51
Dissolved organic carbon	mg/L	3.39	2.10	148	11.0	.1	.96
Cadmium[2]	µg/L	.6	.7	158	6	0	3
Copper[2]	µg/L	2.9	3.5	158	31	0	3.9
Lead[2]	µg/L	3.7	4.3	72	29	0	3.4
Zinc[2]	µg/L	18	45	161	500	0	8.5

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[1] Means reported to one additional significant figure than can be measured to avoid rounding error in statistical tests.

[2] These data have been questioned. Analyses by Vance Kennedy (U.S. Geological Survey, oral commun., 1976) suggest these values may be high by factors of 2 to 10. See more complete explanation on p. 36.

The heavy metals, including aluminum and iron, take part in many chemical and biological reactions, many of which are poorly understood and generally unquantifiable. Hence, their concentrations in natural water may not be good indicators of perturbations imposed by man and nature, except where such disturbances are sufficient to overpower natural constraints provided by such processes as adsorption, ion exchange, and chemical precipitation (C. E. Roberson, U.S. Geological Survey, written commun., 1976).

Synoptic Studies During Stormflow

Streams were studied at synoptic stations (table 2) in the Redwood Creek drainage basin simultaneously during eight storms--November 7-9, 1973, January 11-13, February 20-22, March 1-3, November 6-8, and November 20-22, 1974, and February 5-9 and February 12-14, 1975. About 360 mm of rain was recorded from two storms prior to the first storm studied on November 7-9, 1973. No substantial storms occurred in December 1973, so no studies were made.

The first storm studied in 1974, November 6-8, was preceded by only about 80 mm of rain. The second storm studied was the next storm to arrive. December 1974 and January 1975 were relatively dry months. Rainfall in February and March 1975 was intense, but only two February storms were studied.

Chemograph synoptics

The "chemograph" is defined here as the time series of water-quality measurements during periods of storm runoff.

Detailed studies of the chemograph of several chemical constituents were made at station 11482225 Harry Wier Creek near Orick (HW) (land-use type VL, regolith type Mx) and at station 11482468 Little Lost Man Creek at Site No. 2 near Orick (LLM) (land-use type VF, regolith type Sn) (see p. 20, 21). The purpose of this study was to compare and contrast the chemical characteristics of storm-associated flow from a heavily logged (HW) watershed with that from a virgin forested (LLM) watershed.

The first such study was made during the storm of November 6-8, 1974, which was the second storm of the rainy season. The first storm of the rainy season that passed through the area October 27-29, caused 76.0 mm of rain at the Prairie Creek State Park recording gage. By November 7, discharge in the two streams had returned to levels preceding the October storm. The storm of November 6-8 caused 25 mm of rain in one day, and a hydrograph of water discharge showed an easily identifiable rise, peak, and recession in both streams.

The second storm studied was February 5-9, 1975. Since October 1974, 839 mm of rainfall had been recorded at Prairie Creek State Park. A storm on February 1-5 caused 89 mm of rain. Measurements were made beginning February 5 because weather forecasts predicted a major storm would begin sometime that day. This storm did not materialize, and daily rainfalls for February 5 through February 8 were 11 mm, 13 mm, a trace, and 8 mm. Finally, 34 mm of rain fell February 8-9. The bulk of the samples taken during the study were in the period February 8-9. Hydrographs with identifiable rises, peaks, and recessions were obtained at both stations during this period.

Water discharge and concentrations of major constituents at the two stations during the synoptic study of November 6-8, 1974, are shown in figure 4. The peak discharge per unit area in HW is higher and occurs earlier than in LLM, suggesting that a larger fraction of runoff occurs as overland flow in HW than in LLM. The difference in peak discharge per unit area, and the time of the peak, may be partly due to differences in slope and land cover. The storm covered a broad area and dropped comparable amounts of precipitation on both watersheds. Differences in peak discharge per unit area (almost 3 times larger in HW than LLM) cannot be attributed to small differences in either total rainfall or short-term intensity. Likewise, the differences in timing of the two peak discharges (nearly 6 hours later in LLM than HW) cannot be attributed to differences in the timing of precipitation (Janda and others, 1975b; K. M. Nolan, U.S. Geol. Survey, oral commun., 1978).

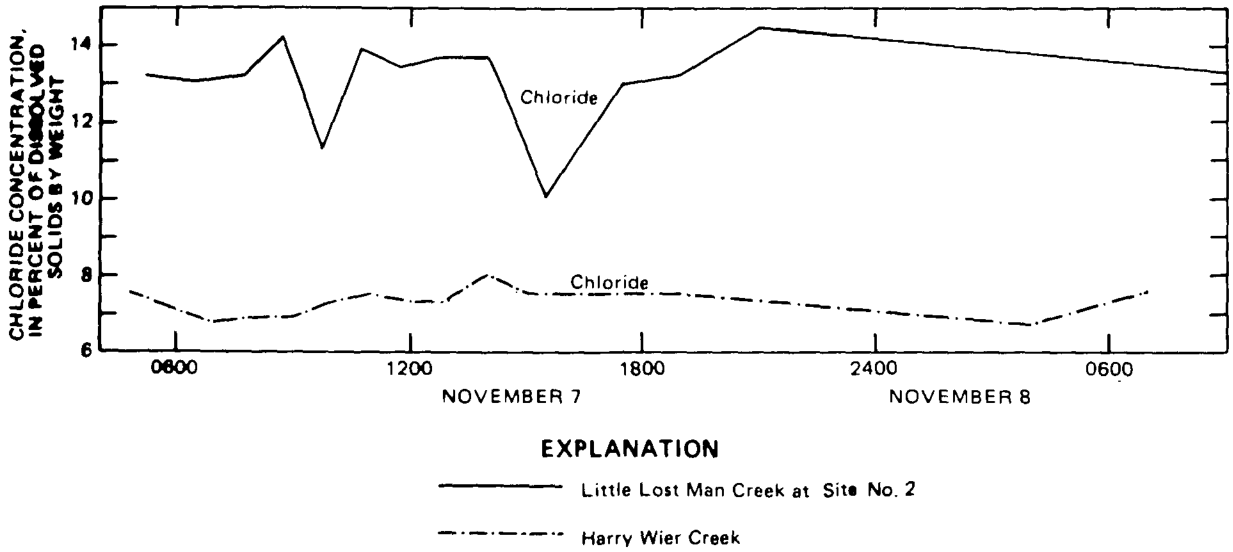


FIGURE 4.--Selected water-quality data from the synoptic study of November 6-8, 1974, Harry Wier Creek and Little Lost Man Creek at Site No. 2. No data for first day of synoptic, November 6.

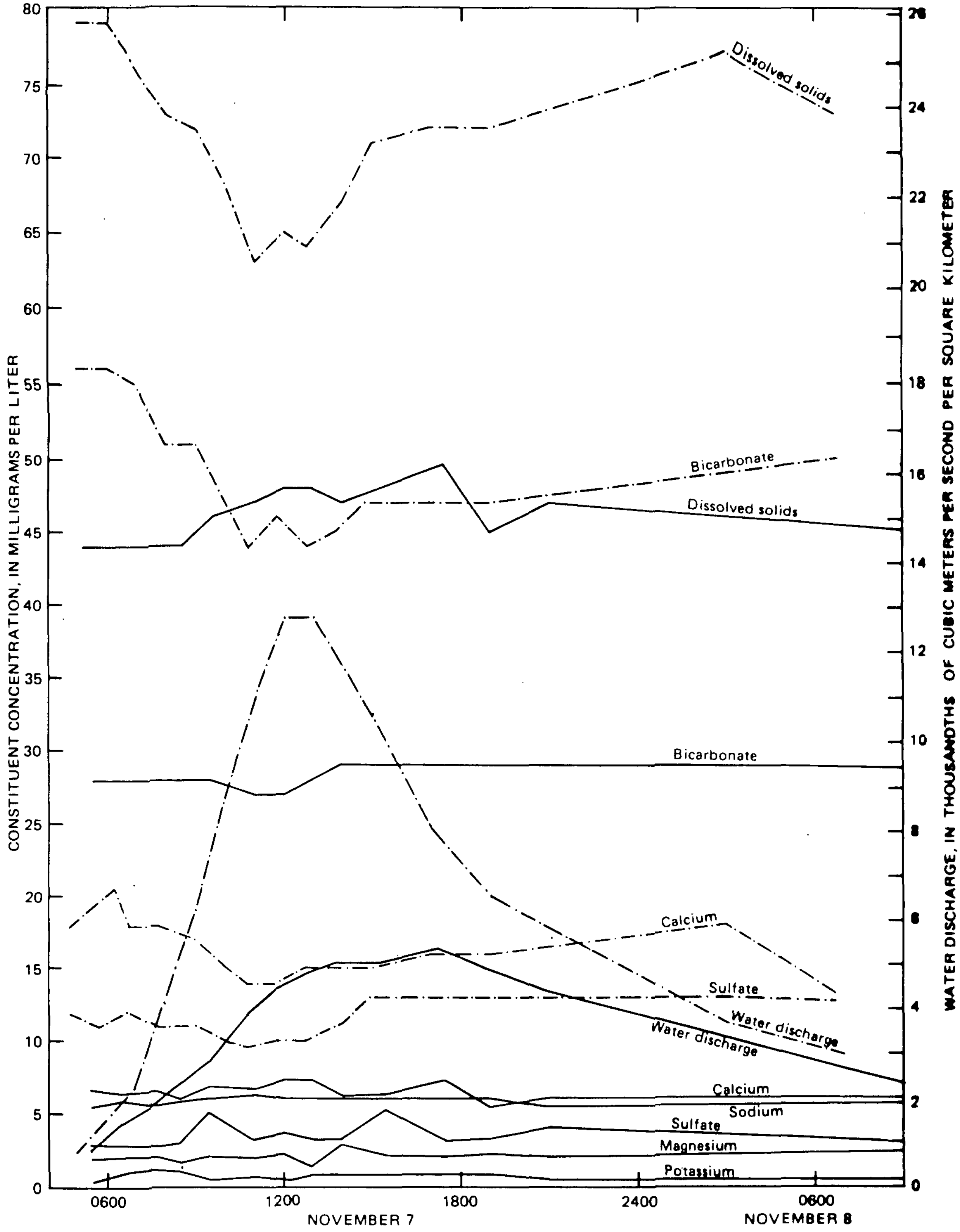


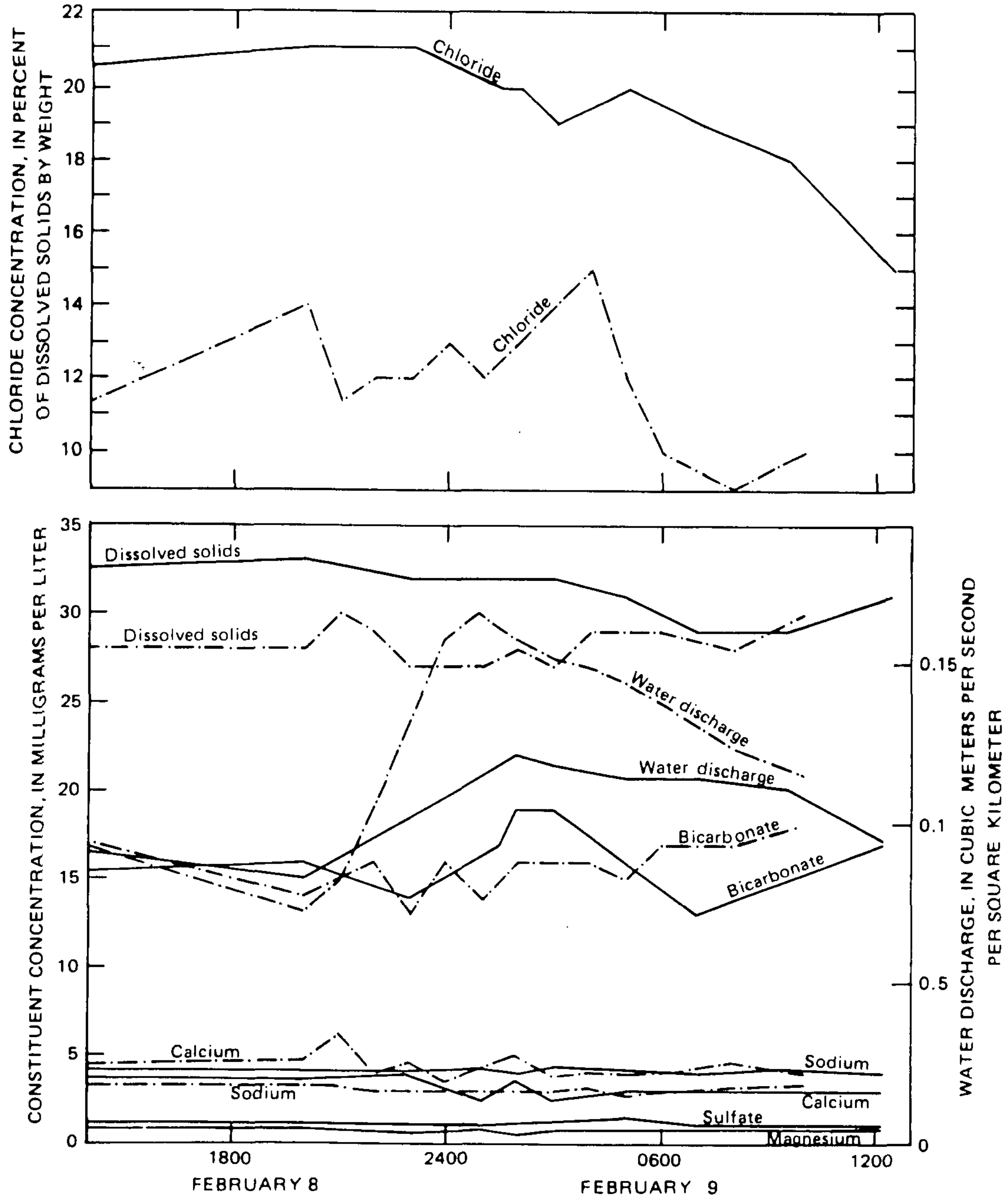
FIGURE 4.--Continued.

The concentrations of the major constituents are higher and more variable with discharge in HW than those in LLM. This suggests that the rate of rock weathering to constituents soluble in water is greater in HW. These soluble constituents were probably produced by weathering during the dry season and were easily dissolved in the early rains. The magnesium, sodium, and potassium lines are shown only for LLM. These are slight but measurable differences between the lines for LLM and HW but at the scale of the figure, the differences cannot be resolved by eye.

The concentrations of calcium, bicarbonate, and sulfate in HW all decrease steadily on the rise of the hydrograph, reach minima at or near peak discharge, and increase steadily on the recession. This suggests that as discharge increases, an increasing fraction of that discharge comes from overland flow, which has had little contact with the soil and thus contains less dissolved solids than water from other sources. By contrast, data from LLM show no discharge-related variations, suggesting that overland flow is not a major fraction of the discharge.

The concentrations of sodium and chloride are nearly equal to each other and are alike in both watersheds. Although the percentage chloride values as shown are different in the two watersheds, the chloride concentrations are approximately equal. This suggests that the source of chlorides is not rock weathering, which would have produced different concentrations in the two watersheds, as the dissolved-solids concentrations are different, but rather is sea salt either occurring as dry fallout during the summer or accompanying the rain. The latter situation probably is not the case, however. If the chloride had been supplied at a constant concentration in rainfall, the time series of percentage chloride should have been the inverse of the time series for dissolved-solids concentration. There is only slight evidence of an inverse relationship in both HW and LLM. Hence, the sodium and chloride in the runoff of the November 6-8, 1974, storm had probably accumulated in the soil through the summer from salt spray and fog drip.

The water discharge and concentrations of major constituents during the period February 8-9 of the study of February 5-9, 1975, are shown in figure 5. Potassium values are not shown because they are uniformly less than 1.0 mg/L and do not show variations at this scale. Magnesium and sulfate concentrations are shown only for LLM because the values for HW are virtually identical.



EXPLANATION

——————— Little Lost Man Creek at Site No. 2

—·—·—·— Harry Wier Creek

FIGURE 5.--Selected water-quality data from the synoptic study of February 5-9, 1975, Harry Wier Creek and Little Lost Man Creek at Site No. 2.

Streamflow prior to the February 5-9, 1975, storm was two orders-of-magnitude higher than the streamflow prior to the November storm, so that the hydrograph of the storm discharge was superimposed on a much larger base flow in February than in November. The heavy rain on February 8-9 generated hydrographs with easily discerned rise, peak, and recession portions. As in the November synoptic study, the peak streamflow per unit area was greater and occurred earlier in HW than in LLM, suggesting that a greater fraction of the runoff in HW was overland flow. Again, differences between watersheds in the peak discharge and in the time of the peak cannot be attributed to differences in total rainfall or the timing of rainfall (Janda and others, 1975b).

In the February study, the dissolved-solids concentrations in HW and LLM were nearly alike; in the November study, dissolved-solids concentration in HW was much higher than in LLM. Concentrations in both streams are substantially lower in February than in November, but more so in HW than LLM. The general decrease in dissolved solids is probably due to higher discharges; that is, more water is present in both watersheds in February to dilute the soluble material available. The differences in the magnitude of the decreases between HW and LLM suggest that in November more soluble material was available for dissolution in HW than in LLM. By the February storm, however, processes supplying soluble material were, apparently, operating alike in the two watersheds, as concentrations of individual constituents (except chloride, discussed later) are alike.

The bicarbonate and dissolved-solids concentrations in HW decreased slightly on the rise of the hydrograph, reached minima at or near the peak, and increased slightly on the recession, suggesting, as in the November storm, that overland flow was an important component of discharge. In LLM, however, the peak bicarbonate concentration coincided with peak discharge, suggesting that much of the water constituting the peak discharge is not overland flow, but is quick-return flow or water that enters the surface soil briefly and reemerges, thereby picking up more soluble salts than overland flow (Kennedy and Malcolm, 1978). This conclusion is supported by the relative shape of the two hydrographs, with LLM experiencing slower rise, lower peak, and more sustained recession than HW.

In HW, the percentage of chloride seems to rise steadily through the discharge peak, then decrease through the recession. In LLM, the percentage of chloride also decreases on the recession. In both streams, bicarbonate and dissolved-solids concentrations increase on the recession. This combination of observations suggests that, after the peak, an increasing fraction of the runoff is quick-return flow that contains higher concentrations of dissolved solids, except chloride. The chloride may be coming in primarily in rain, with little being added from the soil.

The percentage of chloride was higher in both watersheds in February than in November. In November the chloride concentrations were alike at both stations, but in February chloride was higher at LLM. It was suggested previously, that chloride salts accumulated during the summer were the dominant source of chloride in November, but rainfall was the dominant source in February. The LLM station may have had higher chloride concentrations in February because it was closer to the ocean and received more salt spray during the storm than did HW.

Changes in major-ion composition at HW and LLM between November 1974 and February 1975 are shown in figure 6. From November to February, although calcium and bicarbonate continued to be important quantitatively, there was a general shift toward a sodium chloride type water at the expense of calcium and sulfate in HW and at the expense of calcium, bicarbonate, and sulfate in LLM. LLM tended to be more of a sodium chloride type water than HW in both November and February, but probably for different reasons. In November, both watersheds probably had accumulated roughly equal amounts of chloride salts per unit area. The first runoff of the rainy season would be expected to contain nearly equal concentrations of sodium and chloride in the two watersheds (as was seen), but because of higher concentrations of other salts the water at HW was less a sodium chloride type than the water at LLM. By February, the soluble material excess in HW over that in LLM that had been seen in November was gone. The processes supplying soluble solids in both watersheds were operating about alike. But chloride in rain continued to appear in the runoff, thus causing a shift toward a sodium chloride type water. The chloride concentration in February was higher at LLM than at HW, probably because LLM is closer to the ocean. Thus, in February also, LLM water seems to have been more a sodium chloride type than HW water.

The other data collected during these chemograph studies showed very erratic behavior with time. This may be due partly to methods of treatment and analysis and partly to natural processes not yet understood. Nevertheless, treating these data by time-series offered no benefit to interpretation.

The sign test (Conover, 1971, p. 121), a nonparametric test, was used to determine whether sets of water-quality measurements made in the two streams during two separate storms had the same median values.

The data were collected at approximately the same positions on the discharge hydrographs at each station and during each storm. This collection procedure formed a natural basis for pairing the observations of each parameter between storms in the same watershed and between watersheds in the same storm.

As required in performing the test, data for each constituent collected in sequence at each station during the same storm were paired; the set having the larger median was put in the right-hand column. Ties were discarded. A plus (+) sign was assigned to each pair if the value on the right was larger and a minus (-) sign was assigned if the value on the right was smaller. The procedure was repeated for each parameter and for data collected at the same station in different storms.

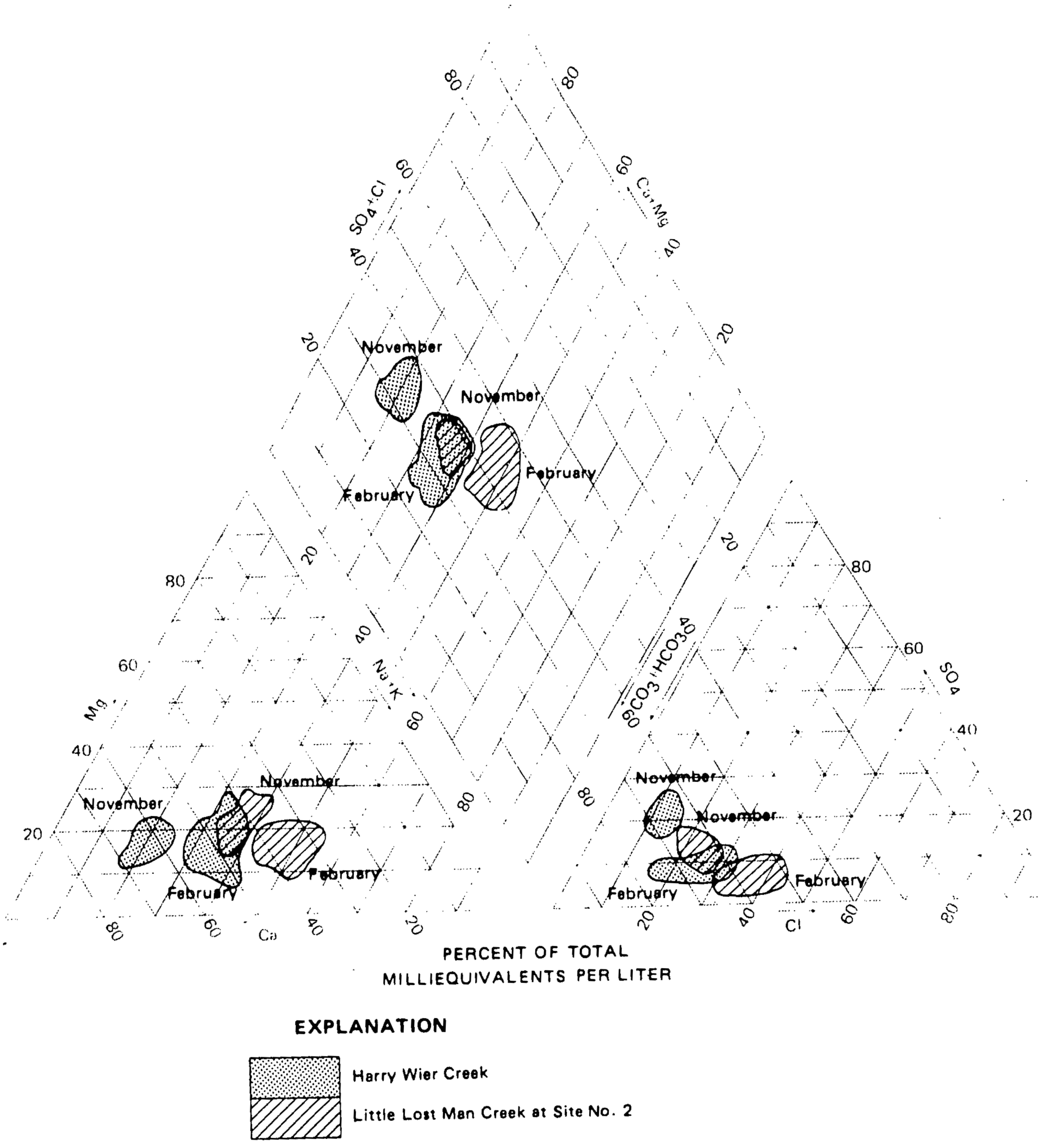


FIGURE 6.--Major-ion composition for the chemograph synoptic studies November 6-8, 1974, and February 5-9, 1975, Harry Wier Creek and Little Lost Man Creek at Site No. 2.

The test is one-tailed. The Null Hypothesis is stated: The median of the set in the left column is greater than or equal to the median of the set in the right column. The alternative hypothesis is: The median of the set in the left column is less than the median of the set in the right column. The test statistic is the number of plus (+) signs. The critical region for rejecting the Null Hypothesis at a 95-percent confidence level is given by the binomial distribution with expectation (p) 0.05, the number of observations (n) equal to the number of untied pairs, and the confidence level (α) less than or equal to 0.05.

The medians and ranges of other data collected at each station and each storm, together with the results of applying the sign test as described are shown in table 5. Medians for the two watersheds are compared at each date from left-to-right, and medians for the two dates are compared in each watershed from top-to-bottom.

The reader should note that the left and right columns of paired data used to perform the test described above do not correspond to left and right columns in table 5. An asterisk (*) in table 5 means that the hypothesis that the medians being compared are the same must be rejected at the 95-percent confidence level. A minus (-) means the hypothesis must be accepted.

Median cadmium, copper, and lead concentrations are alike in both watersheds during both storms. Median zinc concentrations were significantly lower in February than in November. In November, zinc was significantly lower in LLM than in HW. These concentrations are probably erroneously high (see footnote, table 4), and further discussion of these metals is not warranted.

Median silica concentration increased significantly between November and February in both HW and LLM. Silica concentration is significantly higher in LLM than HW. The difference may reflect the differences in fraction of the runoff that is overland rather than quick-return flow. In LLM, more of the discharge is probably quick-return flow that would be expected to contain higher silica concentrations than overland flow because of greater contact time with the soil and contact with a greater thickness of the soil column with resulting greater opportunity to entrain available silica molecules.

Median aluminum concentrations increased significantly between the November and the February synoptic study in both watersheds. This increase may be caused by increased erosion of soils and rocks resulting in increased dissolution of primary alumino silicate materials. The iron concentrations do not show the same pattern as aluminum, even though both probably come from the same sources. This suggests that secondary processes such as iron precipitation or sorption in the soil profile may influence the iron concentration.

TABLE 5.--*Medians and ranges of minor-constituent data from the chemograph synoptic studies and results of the sign test on paired data from each synoptic and station*

[Constituent value in milligrams per liter, except cadmium, copper, lead, and zinc in micrograms per liter. Asterisk (*) indicates that the sign test leads to rejection of the Null Hypothesis at a 95 percent or greater confidence level. Minus (-) means accept the Null Hypothesis]

Constituent and date of study	Harry Wier Creek (HW)		Little Lost Man Creek (LLM)		Sign test result comparing HW and LLM data sets
	Median	Range	Median	Range	
Silica					
Nov. 6-8, 1974	4.94	4.5-5.5	6.44	6.0-7.0	*
Feb. 5-9, 1975	6.08	5.5-6.5	6.77	6.0-7.5	*
Sign test[1]	*		*		
Aluminum					
Nov. 6-8, 1974	7.5	0-30	19	0-40	*
Feb. 5-9, 1975	44	30-70	39	20-80	-
Sign test[1]	*		*		
Iron					
Nov. 6-8, 1974	27	10-60	28	10-70	-
Feb. 5-9, 1975	30	10-80	28	10-80	-
Sign test[1]	-		-		
Nitrate					
Nov. 6-8, 1974	.025	0.01-0.48	.095	0.03-0.38	-
Feb. 5-9, 1975	.145	0.05-2.2	.018	0.00-0.16	*
Sign test[1]	*		*		
Ammonia nitrogen					
Nov. 6-8, 1974	.018	0.01-0.04	.019	0.01-0.04	-
Feb. 5-9, 1975	.007	0.00-0.06	.008	0.00-0.04	-
Sign test[1]	*		*		
Kjeldahl nitrogen					
Nov. 6-8, 1974	.222	0.00-0.35	.180	0.01-0.35	-
Feb. 5-9, 1975	.123	0.05-0.25	.125	0.00-1.2	-
Sign test[1]	*		-		

See footnote at end of table.

TABLE 5.--*Medians and ranges of minor-constituent data from the chemograph synoptic studies and results of the sign test on paired data from each synoptic and station*--Continued

	Harry Wier Creek (HW)		Little Lost Man Creek (LLM)		Sign test result comparing HW and LLM data sets
	Median	Range	Median	Range	
Dissolved total phosphorus					
Nov. 6-8, 1974	0.055	0.02-0.08	0.029	0.02-0.06	-
Feb. 5-9, 1975	.018	0.00-0.04	.009	0.00-0.04	-
Sign test[1]	*		*		
Chemical oxygen demand					
Nov. 6-8, 1974	11.5	4-22	7.9	0-27	-
Feb. 5-9, 1975	7.0	0-12	8.3	2-10	-
Sign test[1]	*		-		
Dissolved organic carbon					
Nov. 6-8, 1974	4.6	0-7	6.9	4-11	-
Feb. 5-9, 1975	4.6	2-7	3.6	2-9	-
Sign test[1]	-		*		
Cadmium					
Nov. 6-8, 1974	1.2	0-2	1.4	0-2	-
Feb. 5-9, 1975	1.4	0-3	1.4	0-3	-
Sign test[1]	-		-		
Copper					
Nov. 6-8, 1974	1.5	0-5	1.7	1-4	-
Feb. 5-9, 1975	1.8	1-3	1.5	0-4	-
Sign test[1]	-		-		
Lead					
Nov. 6-8, 1974	3.1	0-29	5.5	0-16	-
Feb. 5-9, 1975	1.8	0-10	2.6	0-6	-
Sign test[1]	-		-		
Zinc					
Nov. 6-8, 1974	28	10-500	13	0-260	*
Feb. 5-9, 1975	7.5	0-30	11	0-30	-
Sign test[1]	*		-		

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[1] Sign test result comparing data sets collected on November 6-8, 1974, and February 5-9, 1975.

Median ammonia, Kjeldahl nitrogen, and phosphorus concentrations generally decreased between the November and February storms, but concentrations in the two watersheds were similar in each storm. Phosphorus decreased by about a factor of 3, and ammonia nitrogen decreased by about a factor of 2. Kjeldahl nitrogen decreased by a factor of about 2 in HW and not significantly in LLM. These decreases suggest a washout and dilution as the rainy season progresses.

Median nitrate concentrations are not significantly different between HW and LLM in November, but a large significant increase in HW and a large decrease in LLM between November and February results in a large difference between the watersheds in February. This result agrees with Likens' and others' (1969) concept that large trees take up considerable amounts of nitrate. When the trees are removed, the reduction in nitrate uptake leads to a nitrate excess in the watershed, which is available to enter surface runoff and base flow.

Other synoptic studies during stormflow

As stated before, synoptic field measurements of water quality were made at one station on the main stem (11482200) and at eight stations on tributaries of Redwood Creek during eight storms (table 2). Two other main-stem stations (11482220 and 11482500) were visited only once during synoptic studies 5 through 8 (November 6-8, 1974, through February 12-14, 1975).

The time series of the synoptic field measurements proved to be of little value and are not presented here. Alkalinity and specific conductance values occurring in the rise, peak, and recession portions of the hydrographs were evaluated, however. Values for these segments are shown in table 6. The storms of February 28 to March 3, 1974, and of February 5-9, 1975, resulted in hydrographs with poorly defined rise, peak, and recession portions at all stations and are excluded from this analysis.

On the right half of table 6, symbols represent the position of each value relative to the middle value of the measurements at rise, peak, and recession. The middle is always shown with a zero. Likewise, two equal values are both represented by zeros. Alkalinity values are considered equal if they are within 1.5 units of each other, and specific conductance values are considered equal if they are within 3 units of each other. Both limits are judgments based on sensitivity of the measurements. Blanks mean no data.

Examination of the alkalinity and specific-conductance symbols (table 6) shows a preponderance of minus signs (indicating values below the median of the three measurements) at the hydrograph peaks in all the VL-type (logged) watersheds--Harry Wier Creek, Miller Creek, and Miller Creek at Mouth. Furthermore, in 18 alkalinity and in 17 specific-conductance measurements at the peak discharge in the VL-type watersheds, no plus sign occurred. The probability of various combinations of plus and minus signs occurring at the discharge peak is given by the binomial distribution for n non-zero signs. Considering alkalinity in VL-type watersheds, n = 15, all are minus signs. From a table of the binomial distribution (Conover, 1971, table 3) one can see that if plus and minus signs occurred with equal expectation (p = 0.50), in 15 trys, between 3 and 11 plus signs would occur with a 95 percent or greater confidence level. Since no plus signs occurred, it may be concluded that the expectation of plus and minus signs are not equal. Indeed, the expectation of a plus sign occurring is p = 0.20 at a 95 percent or greater confidence level. Considering specific conductance in VL-2-type watersheds, n = 14, again all are minus signs. The conclusion regarding equal expectation is the same. In this case p = 0.20 at a 95 percent or greater confidence level.

By contrast, VF- and RF-type watersheds (Hayes, Lost Man, Little Lost Man, and Geneva Creeks) show a preponderence of zero signs and small but approximately equal numbers of plus and minus signs at the peak for both alkalinity and specific conductance. This suggests that, in most cases, concentrations in VF- and RF-type watersheds at the peak discharge are not significantly or consistently diluted by overland flow.

It may be concluded that dilution at the discharge peak, due probably to overland flow, has a two to three times higher expectation in logged watersheds than in forested watersheds.

Peak discharge in virgin forested and regrown watersheds is probably dominated by quick-return flow (Kennedy and Malcolm, 1978), which could contain more dissolved solids than would overland flow; peak discharge in logged watersheds is strongly influenced by overland flow. This supposition is supported by the observation that the time of peak discharge in virgin forested (VF) or regrown (RF) watersheds lags behind that in logged watersheds by as much as several hours in November storms (Janda and others, 1975a, p. 6-20). This lag is probably due to a longer residence time of precipitation in forested watersheds than recently logged watersheds.

The difference in the lag time of peak discharge (that is, the time between precipitation and peak discharge between watershed types decreases from several hours in November to several minutes in February (Janda and others, 1975, p. 6-20). This change may occur because as the soil becomes saturated it is less able to soak up new precipitation. Thus, overland flow should predominate in peak discharge in all watershed types late in the rainy season. In table 6, plus signs at the discharge peak occur only in VF and RF watersheds and only in the two storms studied in November 1974. This suggests that quick-return flow was an important part of peak discharge only in VF- and RF-type watersheds and early in the rainy season.

TABLE 6.--*Alkalinity and specific conductance values at the beginning of the rise, at the peak, and on the recession for synoptic studies that produced hydrographs with definable features*

[Symbols used to represent the location of a value: 0, middle or equal values; +, above the middle; -, below the middle]

Station number and name	November 7-9, 1973			January 11-13, 1974			February 20-22, 1974			November 6-8, 1974			November 20-22, 1974			February 12-14, 1975		
	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession
							Alkalinity, in milligrams per liter											
11482200 Redwood Creek at South Park Boundary, near Orick	--	27	34	30	--	--	27.5	26	28	--	--	--	83	64	--	--	--	--
11482220 Redwood Creek above Harry Wier Creek, near Orick	--	--	--	--	--	--	--	--	--	94	70	82	78	83	--	--	--	--
11482225 Harry Wier Creek near Orick	15.5	11.5	11.5	18	14	15.5	17	13.5	15	47	36	40	40	31	36	--	12	16
11482250 Miller Creek near Orick	13.5	13	16	17	13	--	--	12	14	47	29	31	30	20	27	16	13	14.5
11482260 Miller Creek at mouth, near Orick	14.5	12	13.5	16	10	--	12.5	11	13	31	25	27	28	17	23	11	13.5	14
11482330 Hayes Creek near Orick	--	--	14	22	17	--	--	15	16	36	34	32	35	20	24	13	12.5	12.5
11482450 Lost Man Creek near Orick	--	11	11	14	14	--	11	11	12.5	41	35	31	31	34	24	12.5	12	11
11482470 Little Lost Man Creek near Orick, Sites No. 1 and No. 2	--	--	12	14	13	--	15	12	13	25	23	24	26	20	23	12	11	12
11482475 Geneva Creek near Orick	--	--	12	10	9	--	--	12	13	14	16	11	19	14	12	11.5	11	11

Specific conductance, in micromhos per centimeter at 25°C

11482200 Redwood Creek at South Park Boundary, near Orick	76	70	68	77	--	--	74	68	76	--	--	--	289	234	--	--	--	--
11482220 Redwood Creek above Harry Wier Creek, near Orick	--	--	--	--	--	--	--	--	--	276	242	252	250	215	--	--	--	--
11482225 Harry Wier Creek near Orick	67	36	47	62	45	60	47	40	53	137	119	137	126	104	113	51	40	46
11482250 Miller Creek near Orick	48	45	46	58	35	--	45	36	50	84	82	86	85	66	72	44	43	46
11482260 Miller Creek at mouth, near Orick	42	35	50	55	43	52	52	40	48	93	86	94	86	79	83	--	--	--
11482330 Hayes Creek near Orick	--	57	58	63	63	61	58	54	63	139	159	119	150	125	180	72	81	87
11482450 Lost Man Creek near Orick	--	37	40	42	45	--	30	33	38	100	111	98	90	145	86	37	36	35
11482470 Little Lost Man Creek near Orick, Sites No. 1 and No. 2	48	40	43	48	47	--	45	47	47	75	76	73	72	72	65	42	40	41
11482475 Geneva Creek near Orick	50	42	42	45	42	--	44	44	44	70	60	66	90	74	72	45	45	45

TABLE 6.--*Alkalinity and specific conductance values at the beginning of the rise, at the peak, and on the recession for synoptic studies that produced hydrographs with definable features*--Continued

Station number and name	November 7-9, 1973			January 11-13, 1974			February 20-22, 1974			November 6-8, 1974			November 20-22, 1974			February 12-14, 1975		
	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession	Rise	Peak	Recession
							Alkalinity, in milligrams per liter											
11482200 Redwood Creek at South Park Boundary, near Orick		-	+				0	-	0				+	-				
11482220 Redwood Creek above Harry Wier Creek, near Orick										+	-	0	-	+				
11482225 Harry Wier Creek near Orick	+	0	0	+	-	0	+	-	0	+	-	0	+	-	0		-	+
11482250 Miller Creek near Orick	0	0	+	+	-			-	+	+	-	0	+	-	0	+	-	0
11482260 Miller Creek at mouth, near Orick	0	-	0	+	-		0	-	0	+	-	0	+	-	0	-	0	0
11482330 Hayes Creek near Orick				+	-			0	0	+	0	-	+	-	0	0	0	0
11482450 Lost Man Creek near Orick		0	0	0	0		0	0	0	+	0	-	0	+	-	0	0	0
11482470 Little Lost Man Creek near Orick, Sites No. 1 and No. 2				0	0		+	0	0	0	0	0	+	-	0	0	0	0
11482475 Geneva Creek near Orick				0	0			0	0	0	+	-	+	0	-	0	0	0

Specific conductance, in micromhos per centimeter at 25°C

11482200 Redwood Creek at South Park Boundary, near Orick	+	0	0				0	–	0				+	–				
11482220 Redwood Creek above Harry Wier Creek, near Orick										+	–	0	+	–				
11482225 Harry Wier Creek near Orick	+	–	0	0	–	0	0	–	+	0	–	0	+	–	0	+	–	0
11482250 Miller Creek near Orick	0	0	0	+	–		0	–	+	0	0	0	+	–	0	0	0	0
11482260 Miller Creek at mouth, near Orick	0	–	+	0	–	0	+	–	0	0	–	0	0	–	0			
11482330 Hayes Creek near Orick		0	0	0	0	0	0	–	+	0	+	–	0	–	+	–	0	+
11482450 Lost Man Creek near Orick		0	0	0	0		0	0	+	0	+	0	0	+	–	0	0	0
11482470 Little Lost Man Creek near Orick, Sites No. 1 and No. 2	+	0	0	0	0		0	0	0	0	0	0	0	0	–	0	0	0
11482475 Geneva Creek near Orick	+	0	0	0	0		0	0	0	+	–	0	+	0	0	0	0	0

The frequency distributions and measures of distribution of the data obtained at each storm and station were also evaluated by grouping the data into classes and plotting the distributions on histograms. In the discussion that follows, the range is given from the low end of the lowest class to the high end of the highest class occupied in the grouped data, including all the data from all synoptic studies at all stations. The medians of measurements are given for each synoptic study at each station. General procedures are described in Sokal and Rohlf (1969). The sizes of class intervals are as follows: temperature, 0.5°C; dissolved oxygen saturation, 2 percent; pH, 0.2 units; alkalinity, 1 mg/L; specific conductance, 5 µmho/cm at 25°C.

Temperatures measured at all stations on all synoptic studies ranged from 5.0° to 13.5°C. Median temperatures measured during each synoptic study at each station ranged from 6.5° to 12.6°C; the highest values were in November, and the lowest were in January.

Percent saturation of dissolved oxygen measured at all stations on all synoptic studies ranged from 80 to 106. The median values of measurements made during each synoptic study at each station ranged from 85 to 103 percent, with most median values being in the range 90 to 100 percent. This high level of saturation is expected because of turbulence in the streams during high discharge.

The time series of median temperature and dissolved-oxygen concentration measured during each synoptic study at each station showed no systematic differences between watersheds. The time series of median alkalinity, specific conductance, and pH (fig. 7) showed some features of interest, however.

Alkalinity values measured at all stations on all synoptic studies ranged from 7 to 94 mg/L, and median values of measurements at each synoptic study at each station ranged from 10 to 80 mg/L, with the highest median values occurring early in the rainy season at the main-stem stations. During the 1974-75 rainy season, the range of median values decreased sharply with time. By February, median alkalinity values at the main stem and Harry Wier Creek sites decreased to less than half their November values. This pattern was not apparent in 1973-74, probably because the earliest storms in October 1973 were not studied, and the highest median values are expected in the earliest storms.

Medians of alkalinity measurements made during each synoptic study at the main-stem stations are consistently higher than the median alkalinity values in the tributaries, suggesting that the major load of alkalinity-producing dissolved solids enters the main stem upstream of the park. Geneva Creek consistently shows the lowest median alkalinity values. Median alkalinity values in Harry Wier Creek (VL-type) are nearly always higher than those of the other tributaries.

Specific conductance values measured at all stations on all synoptic studies ranged from 30 to 300 µmho. Median specific conductance values measured during each synoptic study at each station ranged from 37 to 258 µmho, with the highest values occurring early in the rainy season at main-stem stations. Through the rainy season of 1974-75, median specific-conductance values decreased sharply; the main-stem median specific-conductance values reached about one-third their November values by February. Again, this pattern is not apparent in the previous winter, probably because the earliest storms of 1973 were not studied. Median specific-conductance values in the main stem are consistently higher than in the tributaries, again suggesting that the major load of dissolved solids enters the main stem upstream from the park. Lost Man Creek has the lowest specific-conductance values except in the first two synoptic studies of the 1974-75 rainy season. The median specific-conductance values of Hayes Creek (VF-type) are consistently higher than those of the other tributaries, higher even than those of Harry Wier Creek (VL-type).

The range of pH values measured at all stations on all synoptic studies was from 5.4 to 8.6. Median pH values measured during each synoptic study at each station ranged from 6.1 to 7.9. The range in median values narrowed from November to February and March in both years, with both the initially high-pH streams decreasing and the initially low-pH streams increasing. There are almost no consistent trends maintained in these data over the entire period of synoptic studies, but Geneva Creek shows a consistent tendency to have lower median pH values than the other streams. Lost Man and Little Lost Man Creeks are also generally lower in pH than the other streams, but not consistently lower.

The significance of differences in water quality during storms between watersheds of different land use was evaluated by grouping the data from each synoptic study according to common land-use type and calendar quarter (first quarter January through March, second quarter April through June, etc.).

Differences between individual watersheds within a given land-use type and within a given quarter of the year (within-set differences) are not part of this analysis, but some differences are noteworthy based on inspection of the histograms developed from the data. The frequency distributions of specific-conductance values in Hayes and Little Lost Man Creeks (both VF-type) were different in all four quarters; the medians for Hayes Creek were always larger. Major within-set differences also occurred in the fourth quarter 1974 when the data came from the first two storms of the rainy season. This was a period of rapid change in water quality. Alkalinity values in RF- and VL-type streams varied widely. Further, the medians of the sets of specific-conductance values for Harry Wier Creek were higher than the medians for Miller Creek and Miller Creek at Mouth (VL-type watersheds).

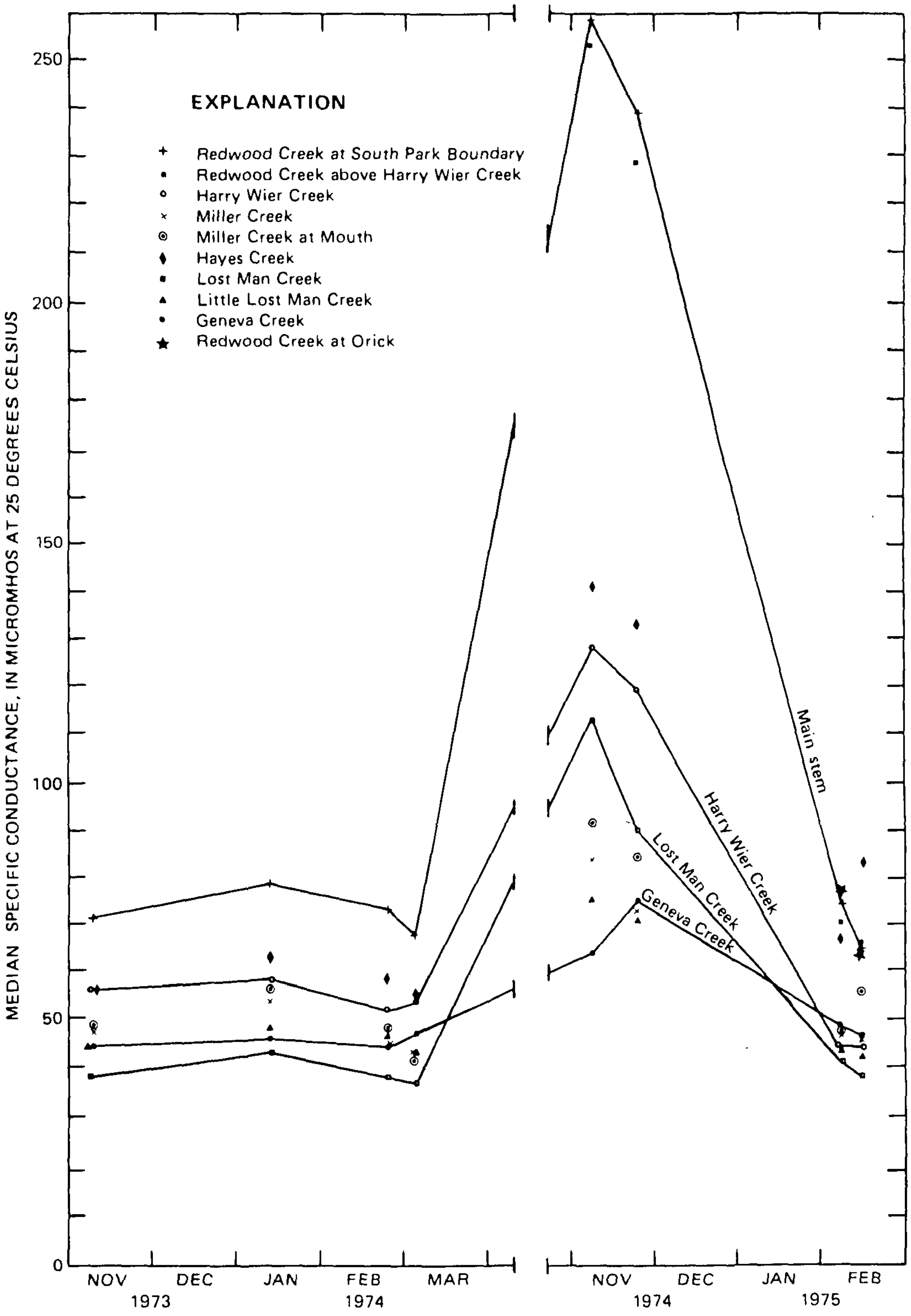


FIGURE 7.--Median values of specific conductance, pH, and alkalinity for synoptic studies during stormflow.

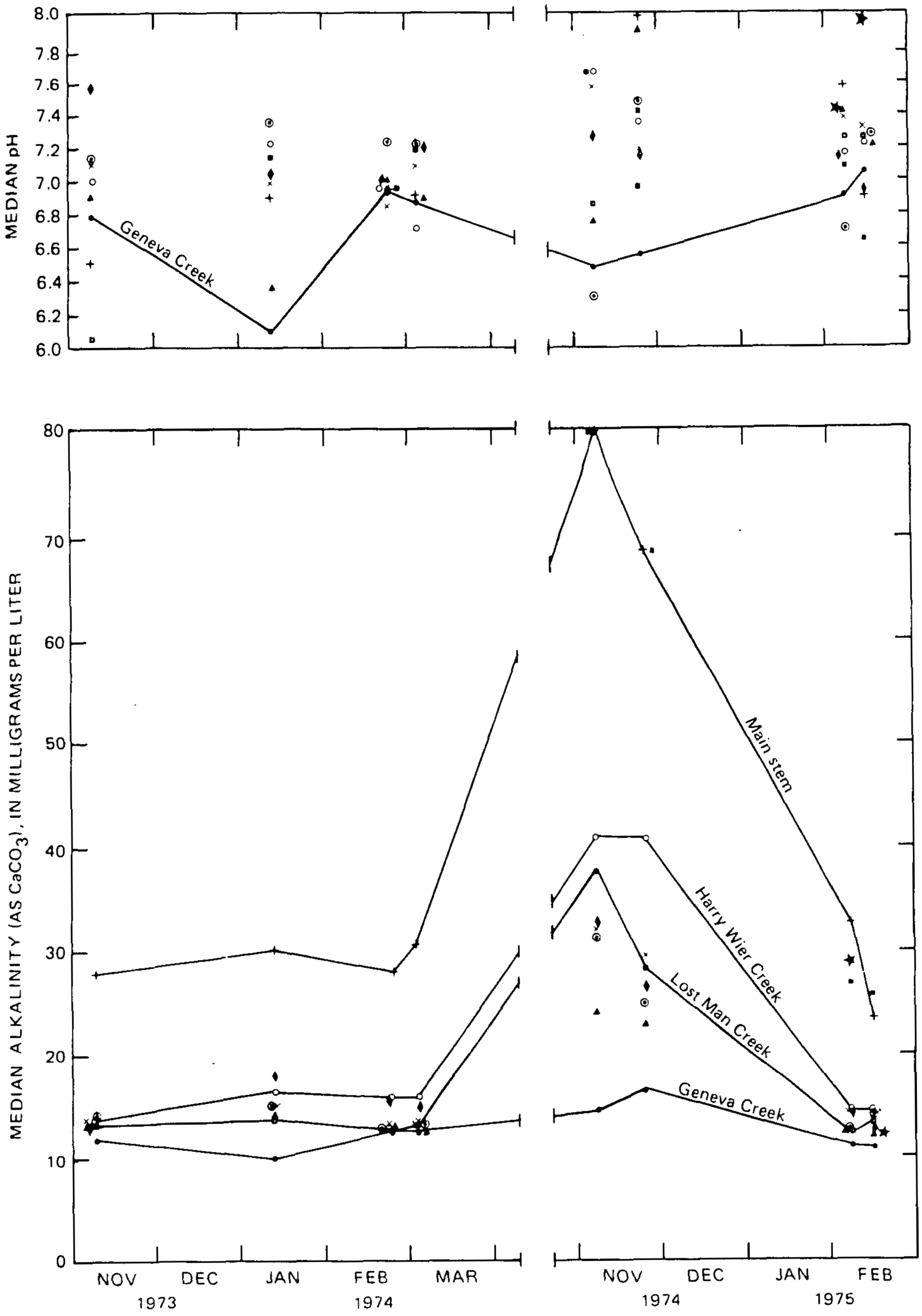


FIGURE 7.--Continued.

The common statistical measures of the combined sets of synoptic study data are listed in table 7. Calculations were made from data grouped by class interval. Calculated values are shown to one additional significant figure to avoid rounding error in subsequent statistical hypothesis testing. No mean or standard deviation is calculated for sets of less than 10 values because the sampling error of the mean and standard deviation are unduly large given only 10 values. The median and mean values are generally close to each other, indicating that most of the sets are symmetrically distributed. A Student t-test of the arithmetic means is used to test the significance of differences between sets. The standard deviations of most sets are small relative to the means, except for alkalinity and specific conductance in the fourth quarter 1974.

The mean of each data set for the RF- and VL-type watersheds and the main stem was compared to the corresponding mean for the VF-type watersheds. The differences and their significance, according to the Student t-test, are shown in table 8.

Mean alkalinity and pH vary in the same direction. Alkalinity and pH are mostly higher in VL-type watersheds than in VF-type watersheds, suggesting a faster rate of weathering of the regolith in VL-type watersheds. Alkalinity and pH tend to be lower in RF-type watersheds than in VF-type watersheds. This difference may be due to different regoliths rather than different land uses, but lack of data prevents further analysis.

Mean temperatures in RF-, VL-, and MS-type streams are significantly higher than in the VF-type streams in the fourth quarter of each year but are significantly lower in the first quarter of each year. This suggests a buffering of the VF-type streams against extremes of heat and cold. The amount of solar energy reaching the soil surface and the amount of energy radiating back to space would be expected to be greater in logged areas than in VF-type watersheds. If this is true, streams draining logged watersheds should be warmer in summer and colder in winter than streams draining VF-type watersheds. The pattern in observed temperatures is compatible with this picture.

There is clear evidence that the main stem has significantly higher alkalinity and specific-conductance values than the VF streams, suggesting that the major dissolved-solids inputs to Redwood Creek occur upstream of the park.

Mean specific-conductance values are always significantly lower in RF-type streams than in the VF streams, and are generally lower in the VL-type streams than in the VF streams. Lower mean values in VL-type streams may be due to a greater fraction of the runoff in these streams being from overland flow. Lower mean values in RF-type streams suggest a lower rate of regolith weathering than in VF streams.

Dissolved-oxygen saturation values show no particular pattern between watershed types. Dissolved oxygen is probably a function of turbulence and cascading in the stream channel. As all the streams studied are steep and rough in the main channel during high flow, this lack of a pattern is not surprising.

Diel Studies at Low Flow

Studies of the variations in alkalinity, specific conductance, pH, temperature, and dissolved oxygen over a diel period were made at several stations three times during the sampling program.

Changes in alkalinity and specific conductance can result from changes in the composition of the water due to photosynthesis and respiration. The pH and dissolved-oxygen changes parallel one another and are caused by photosynthesis in the daytime and respiration at night. Temperature changes are caused by solar heating and nighttime cooling.

The three main-stem stations studied--Redwood Creek at South Park Boundary (11482200), Redwood Creek above Harry Wier Creek (11482220), and Redwood Creek at Orick (11482500)--were fully exposed to sunlight. Little Lost Man Creek (11482470) was fully exposed, Little Lost Man Creek at Site No. 2 (11482468) was partially exposed, and Lost Man Creek (11482450) was in nearly full shade. Of the VL-type tributaries studied, Harry Wier Creek (11482225) and Miller Creek at Mouth (11482260) were also in nearly full shade. Miller Creek (11482250) was partially exposed.

TABLE 7.--*Statistical summary of field-measurement data fr*

[Means and standard deviations calculated from data grouped
conductance, 5 micromhos per centimeter at 25°C; pH, 0.2 unit

Constituent and land-use type	Fourth quarter 1973					First quarter 1974				
	Median	Range[1]	Mean	Standard deviation	Number of samples	Median	Range[1]	Mean	Standard deviation	Numbe of sampl
Alkalinity, in milligrams per liter										
Control streams	13.0	12-15	-	-	3	14.8	7-24	14.7	2.2	49
RF streams	12.8	11-14	-	-	8	13.1	9-17	12.5	1.3	60
VL streams	14.1	11-18	13.9	1.5	23	14.9	10-21	15.1	2.4	73
Main stem	28.0	27-34	-	-	3	29.5	26-32	28.9	1.6	11
Specific conductance, in micromhos at 25°C										
Control streams	48.8	40-65	50.3	7.3	16	52.9	40-90	53.4	8.6	100
RF streams	42.9	30-55	43.1	5.4	16	42.6	20-55	41.7	5.1	94
VL streams	48.6	35-85	52.2	11.2	58	49.2	30-75	51.9	7.8	172
Main stem	71.6	65-85	-	-	6	72.2	65-85	73.0	4.4	19
pH										
Control streams	6.95	6.8-7.6	-	-	3	7.00	5.8-7.8	6.92	.40	64
RF streams	6.16	5.6-7.0	6.17	.41	13	7.05	5.8-7.6	6.90	.36	71
VL streams	7.14	7.0-7.4	7.11	.11	40	7.07	6.2-7.6	7.04	.25	97
Main stem	6.50	6.2-8.2	-	-	3	6.90	6.8-7.0	-	-	8
Temperature, in degrees Celsius										
Control streams	11.3	11.0-12.0	11.1	.2	18	8.3	6.5-9.5	7.9	.6	103
RF streams	11.9	11.0-13.5	11.7	.4	29	7.5	5.0-10.0	7.3	1.0	98
VL streams	12.3	11.5-13.0	12.0	.2	56	8.0	6.0-9.5	7.7	.7	159
Main stem	12.6	12.0-13.0	-	-	6	7.6	6.0-8.5	7.2	.7	19
Dissolved oxygen, in percent saturation										
Control streams	96.7	88-102	95.9	3.3	16	97.0	84-104	95.8	3.9	57
RF streams	96.6	88-102	95.6	2.9	16	96.2	84-104	95.1	4.0	50
VL streams	99.8	98-102	99.4	1.2	17	98.3	92-104	97.9	2.1	73
Main stem	99.0	96-100	-	-	3	97.5	92-100	-	-	9

[1] The range is the low end of the lowest class to the high end of the highest class.

[2] Seven pH values taken November 6-8, 1974, at Miller Creek at Mouth are much lower than
included in this calculation. Instrument malfunction was suspected at Miller Creek at mouth.

noptic studies, grouped by calendar quarter and land-use type

ass as follows: alkalinity, 1 milligram per liter; specific
mperature, 0.5°C; dissolved oxygen saturation, 2 percent]

Fourth quarter 1974					First quarter 1975				
dian	Range[1]	Mean	Standard deviation	Number of samples	Median	Range[1]	Mean	Standard deviation	Number of samples
4.2	20-38	26.9	5.4	67	12.7	9-17	13.0	1.3	57
4.8	11-41	25.0	9.6	50	12.4	9-14	11.7	1.2	52
1.4	17-52	32.5	8.1	62	14.3	10-18	13.7	1.4	65
0.0	54-94	72.1	10.7	12	26.9	13-47	28.0	7.1	18
8.2	60-200	102.6	38.2	103	72.7	30-90	61.2	18.9	156
3.8	60-150	87.4	16.8	81	41.2	30-65	42.6	6.8	152
9.9	60-150	100.1	22.6	105	45.8	30-90	47.2	7.2	131
3.0	210-300	245.2	19.5	22	69.9	60-85	70.0	6.1	47
7.38	6.4-8.6	7.36	.43	74	7.01	6.4-7.6	7.05	.23	125
5.82	6.2-7.2	6.62	.20	50	7.19	6.4-7.6	7.06	.22	81
7.48	6.8-8.0	7.35	.21	[2]56	7.16	6.0-7.8	7.14	.27	84
7.70	7.0-8.4	7.56	.37	11	7.04	6.2-8.0	7.04	.37	18
.7	8.0-11.5	9.32	1.0	97	9.2	7.5-10.5	9.2	.6	154
.1	8.0-12.0	10.1	.8	77	8.6	6.5-10.1	8.7	.9	166
.8	8.0-12.5	9.6	.7	108	9.6	7.5-11.1	9.1	.8	129
.1	9.0-12.5	10.6	.9	24	8.2	6.0-10.5	7.9	.9	42
.9	84-104	93.4	3.7	31	97.5	92-102	96.5	2.4	48
.1	80-96	87.2	3.8	32	96.9	88-104	96.4	2.6	46
.2	84-100	93.5	3.3	50	97.6	84-104	96.3	3.1	48
.0	86-100	93.2	3.7	10	99.2	90-106	98.9	3.7	19

ermined simultaneously at Miller and Harry Wier Creeks and are not

TABLE 8.--*Results of comparing the means of field measurements from streams of common land-use type with means of field measurements from VF streams*

[The Student t-test is used to test a Null Hypothesis that the means being compared are equal. Rejection of the Null Hypothesis with level of confidence α in a one-tailed test implies that the difference shown (plus or minus) is significant at that confidence level. No data in the α column indicate acceptance of the Null Hypothesis. N means no test was performed due to insufficient sample size. Relation of subject mean to the mean for VF streams shown by +, greater than; -, less than; 0, no difference]

Period	Land-use type	Alkalinity (mg/L)		Specific conductance (μmho at 25°C)		pH		Temperature		Dissolved oxygen (percent saturation)	
		Mean	α	Mean	α	Mean	α	Mean	α	Mean	α
Fourth quarter, 1973	RF	0	N	-	0.99	-	N	+	0.99	-	
	VL	+	N	+		+	N	+	.99	+	0.99
	MS	+	N	+	N	-	N	+	N	+	N
First quarter, 1974	RF	-	0.99	-	.99	-		-	.99	-	
	VL	+		-		+	0.95	-	.95	+	.99
	MS	+	.99	+	.99	-	N	-	.99	0	N
Fourth quarter, 1974	RF	-		-	.99	-	.99	+	.99	-	.99
	VL	+	.99	-		0		+	.95	0	
	MS	+	.99	-	.99	+		+	.99	0	
First quarter, 1975	RF	-		-	.99	0		-	.99	0	
	VL	+	.99	-	.99	+	.95	0		-	
	MS	+	.99	+	.99	0		-	.99	+	.95

Generally, the diel studies showed that photosynthesis and respiration are strongly dependent on the degree of exposure of the water surface to sunlight. The main-stem stations and Little Lost Man Creek show wide changes in temperature, dissolved oxygen, and, to a lesser extent, pH. Maximum ranges observed in the main-stem stations were 8.0°C, 40 percent of dissolved oxygen saturation, and 0.6 pH units. The fully sheltered stations show only slight changes over a diel period. On the basis of data collected, water-quality changes over diel periods do not appear to be related to the extent of logging in the watersheds.

Results of Studies of Seasonal Variations

The regular data were studied using several methods. Measurements with a strong long-term time-dependent component were treated with time-series methods. The major-ion composition was studied using trilinear diagrams and regressions of dissolved solids against specific conductance. The minor constituents were analyzed by determining measures of the data sets.

Time-series analysis

Specific conductance, temperature, and alkalinity variations are strongly time dependent and thus are shown plotted against time of observation (figs. 8 through 11). The data sets used consist of all the regular observations and the medians at each site from each synoptic and diel study.

The time series of data from VF-, RF-, and VL-type watersheds are shown in figure 8. Envelopes for each variable overlap considerably for VF- and RF-type watersheds; the envelopes for specific conductance and alkalinity in VL-type watersheds have a greater range, and values tend to be higher during the summer dry season. This difference between VL and the other types of watersheds suggests that logging accelerates normal weathering processes or initiates new processes altogether, leading to greater ranges of observed values at low flow in cutover watersheds. But the effect is apparently not uniform among VL-type watersheds; otherwise, the lower limit of the VL-type envelope would have shifted upward as did the upper limit.

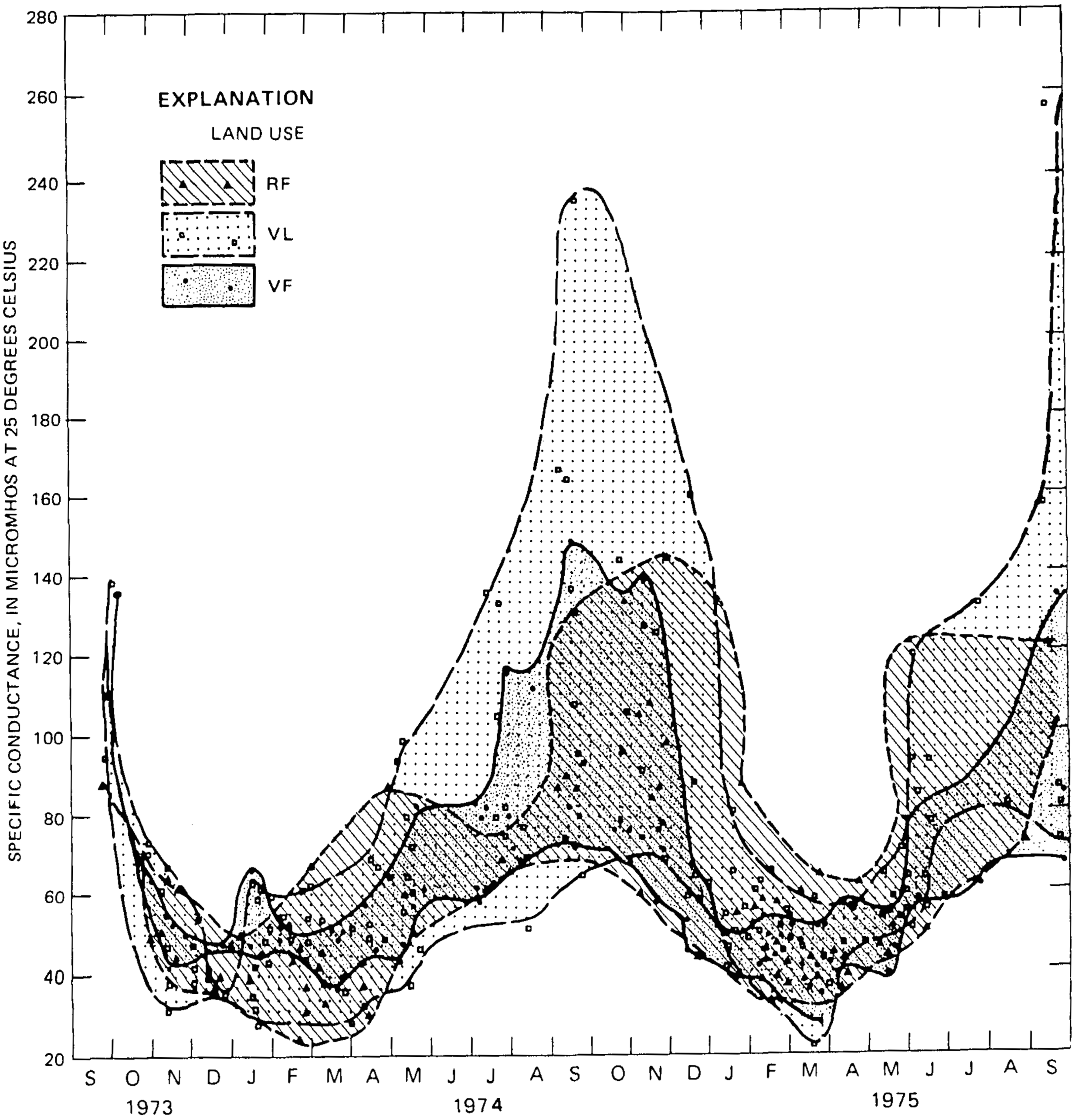


FIGURE 8.--Specific-conductance, water-temperature, and alkalinity values for VF-, RF-, and VL-type watersheds.

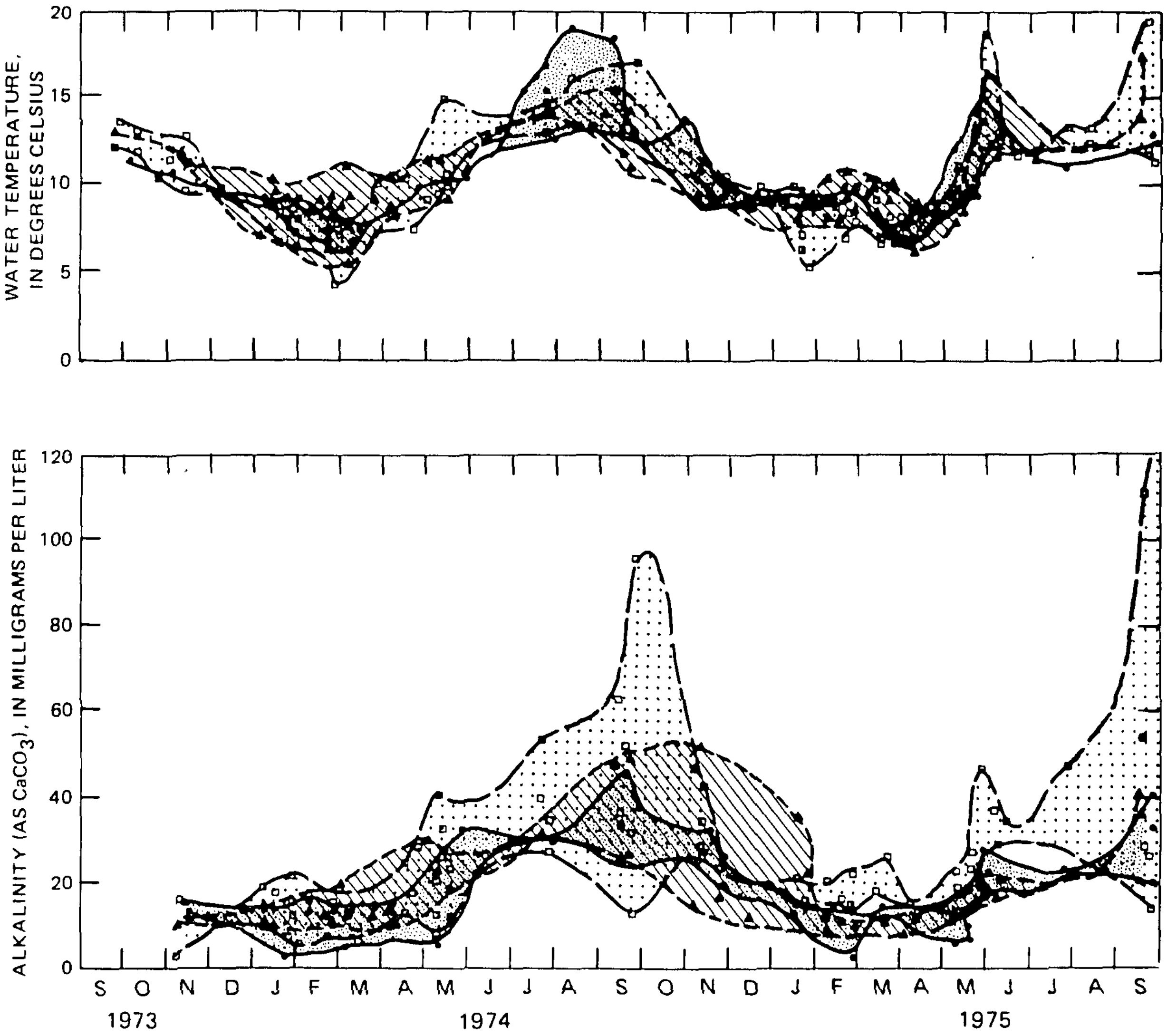


FIGURE 8.--Continued.

The time series of measurements at the main-stem stations above and below Harry Wier Creek, which approximately separates water of upstream origin from water affected by in-park tributary inflow, are shown in figure 9. Water from upstream and water within the park are alike, by this analysis, during the winter months when alkalinity, specific conductance, and temperature are all at minimum values, but water in the two areas differs considerably during the dry season. Main-stem water above the park is warmer and more alkaline and has a higher specific conductance than main-stem water within the park, indicating that the main-stem water is diluted and cooled as it passes through the park, presumably from tributary inflow, influences of the marine climate and shading.

Higher alkalinity and specific-conductance values upstream than downstream during the dry season suggest that the drainage basin upstream from the park is weathering faster than tributary watersheds within the park. Faster weathering may be partly related to slight differences in regoliths, or also to the intensity of logging activity (the drainage basin upstream of station 11482220 was 65 percent cutover as of 1973, table 2). It may also be related to exposure of the soil to the elements. According to Janda and others (1975a) vegetation in the upper basin grades upstream to prairie and sparse Douglas-fir, in contrast to the downstream part which, in its pristine state, is covered by dense stands of redwood, Douglas-fir, and heavy undergrowth.

The regular data provide an opportunity to examine the effect of differences in regolith on water quality within watersheds of common land-use type.

The time series of data from all VF-type watersheds were plotted in the same way, but no differences in values related to regolith differences were found.

Results of an analysis of data from all VL-type watersheds are shown in figure 10. During the dry season, streams with St-type regoliths seem to have the lowest alkalinity and specific-conductance values; streams with Sn-type regoliths have the highest values, and the Mx-type regoliths fall in between. This suggests that, when disturbed by logging, the sandstone-based (Sn) watersheds are more susceptible to weathering than are the schistose (St) watersheds. An examination of the data used in preparing figure 8 shows that the lower limits of alkalinity and specific conductance in VL-type watersheds during the dry season are defined by watersheds with a schistose regolith.

To examine further the characteristics of streams with schistose regoliths, all data from St-type watersheds were analyzed in a similar manner. Results are shown in figure 11. Envelopes enclosing data from VF-, VL-, and RL-type watersheds generally overlap except for Bridge Creek (RL-type), which has much higher values for alkalinity and specific conductance than all other St-type streams. The Bridge Creek watershed is one of the steepest and most susceptible to erosion and land slumping in the Redwood Creek drainage basin. Furthermore, it was logged intensively during this study. Because of the steepness of the slopes, logging caused considerably greater disruption of the surface soils there than in any other logged watershed (Deborah Harden, U.S. Geological Survey, oral commun., 1976). Perhaps intensive surface disruption has exposed deeper, less weathered soils to the elements, resulting in a greater rate of leaching of carbonate rocks.

Trilinear diagrams and regression analysis

Trilinear diagrams, which readily show the major-ion composition of a water sample, were used to examine compositional differences between land-use and regolith types. The data sets consisted of all the regular chemical analyses plus analyses of samples taken on diel and synoptic studies, excluding the chemograph data.

Preliminary evaluation indicated no differences between data sets collected in the first and fourth calendar quarters of both years. Data from these quarters were combined into one set representative of water quality during the rainy season.

No regolith-related compositional differences could be found in the rainy-season data, but land-use related differences are apparent, as indicated in figure 12.

The main-stem water is a calcium bicarbonate type; water from unlogged and RF-type areas (VF- and RF-type) is mixed sodium-calcium bicarbonate-chloride type. Water types from logged areas (VL-type) lie in between. The progression of water type from sodium chloride to calcium bicarbonate corresponds to increasing exposure of the soil to weathering, either from logging activity or natural differences in vegetation.

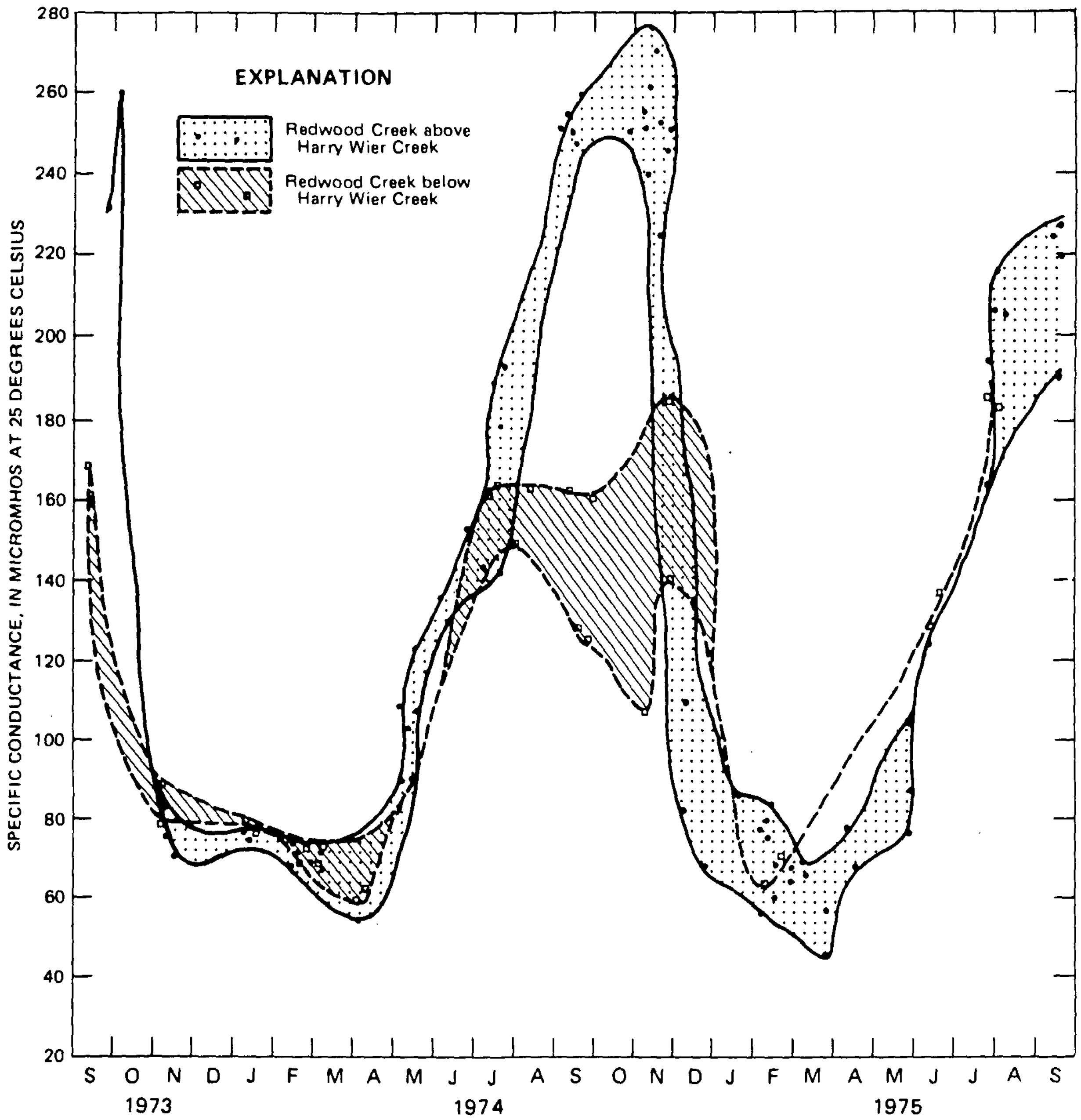


FIGURE 9.--Specific-conductance, water-temperature, and alkalinity values for main-stem stations.

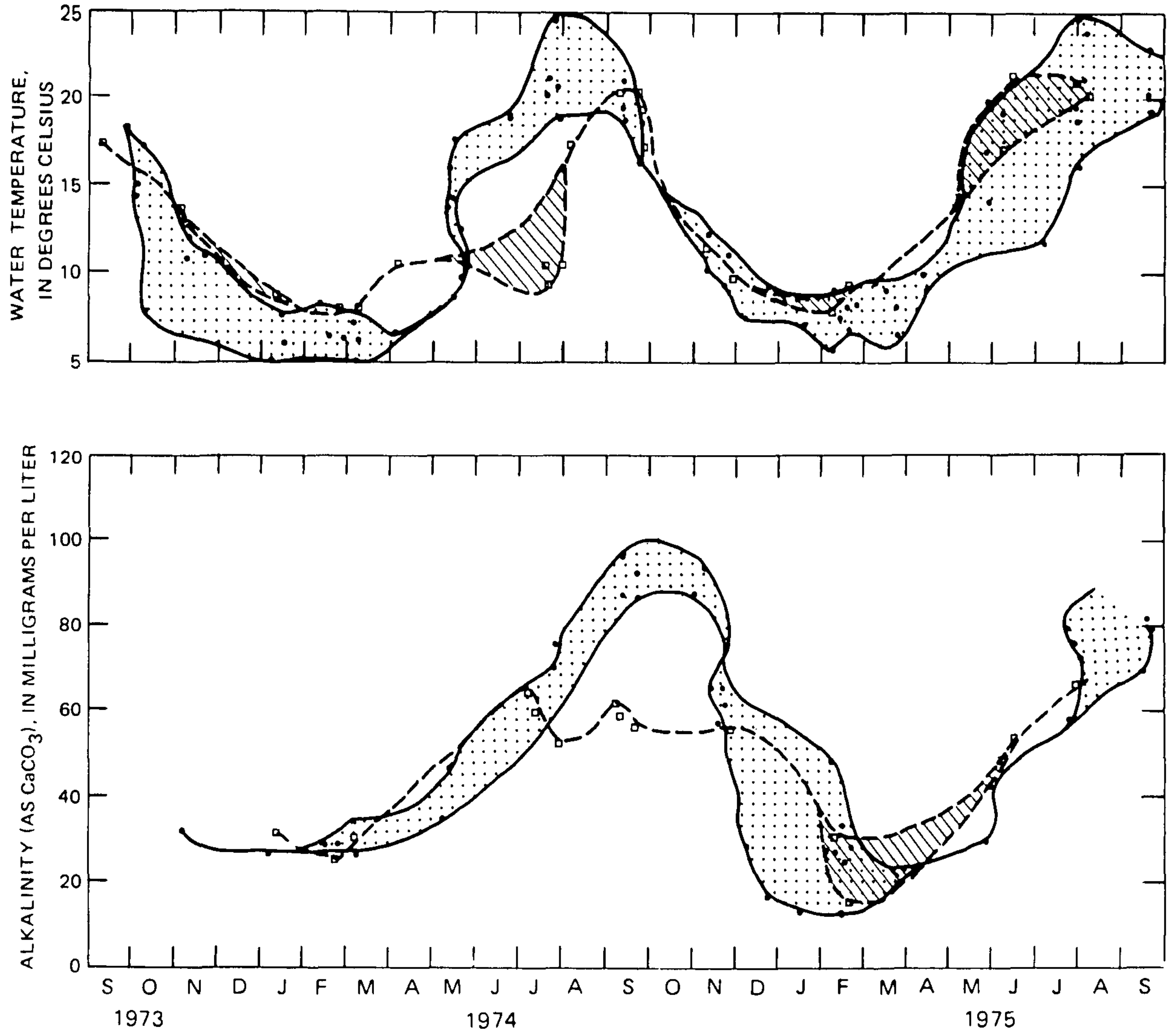


FIGURE 9.--Continued.

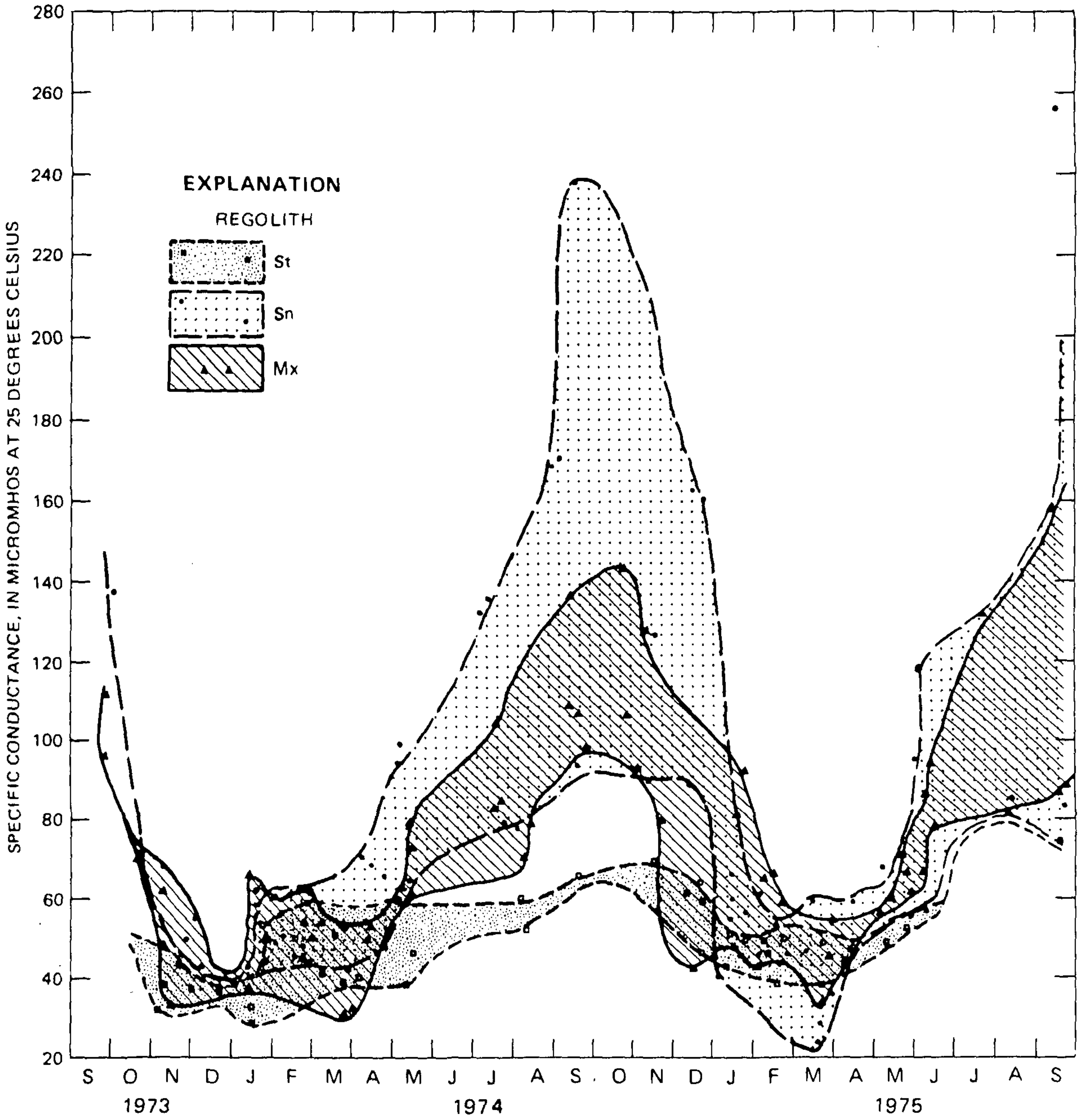


FIGURE 10.--Specific-conductance, water-temperature, and alkalinity values for VL-type watersheds underlain by St-, Sn-, and Mx-based regoliths.

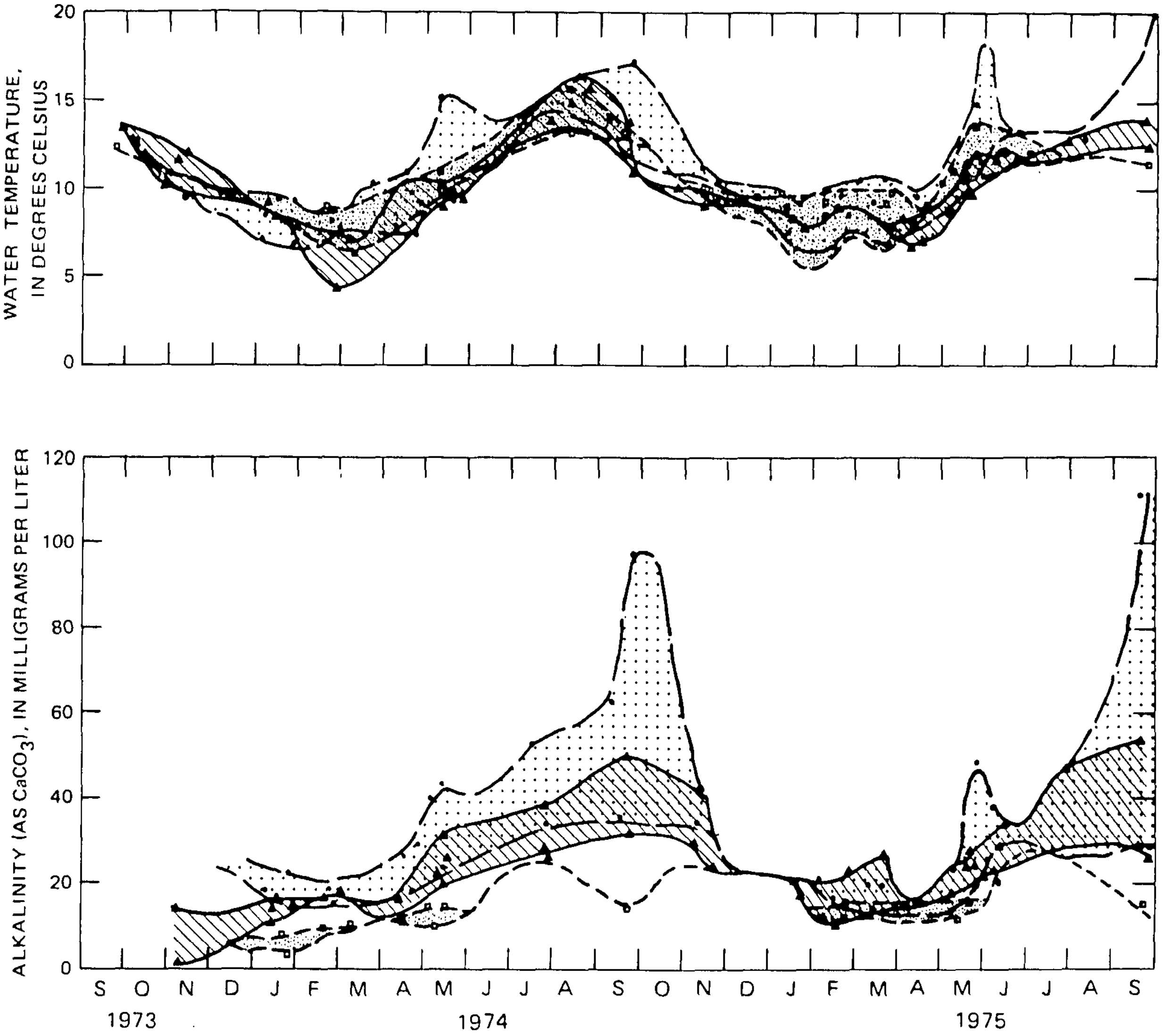


FIGURE 10.--Continued.

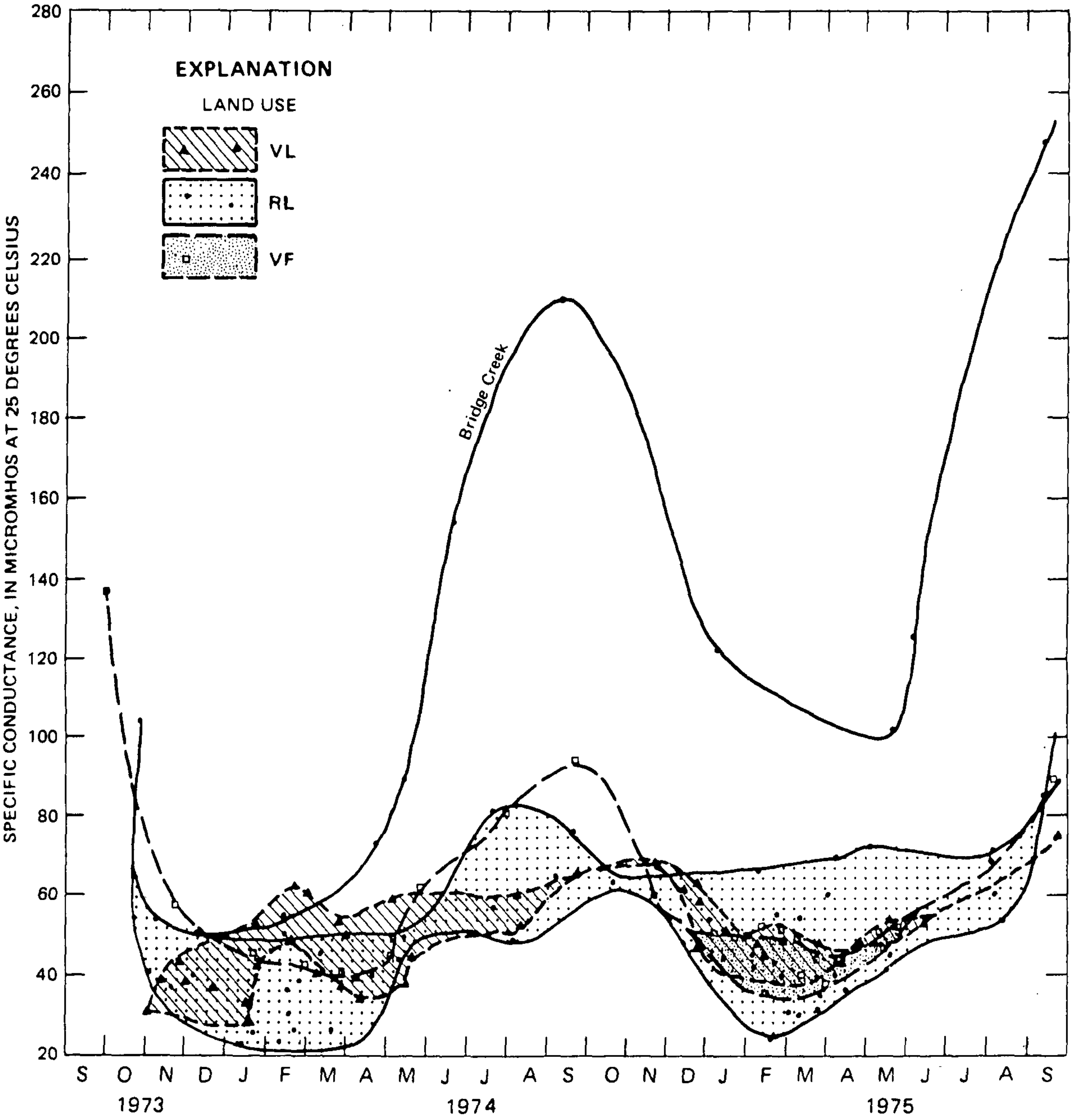


FIGURE 11.--Specific-conductance, water-temperature, and alkalinity values for St-based regoliths.

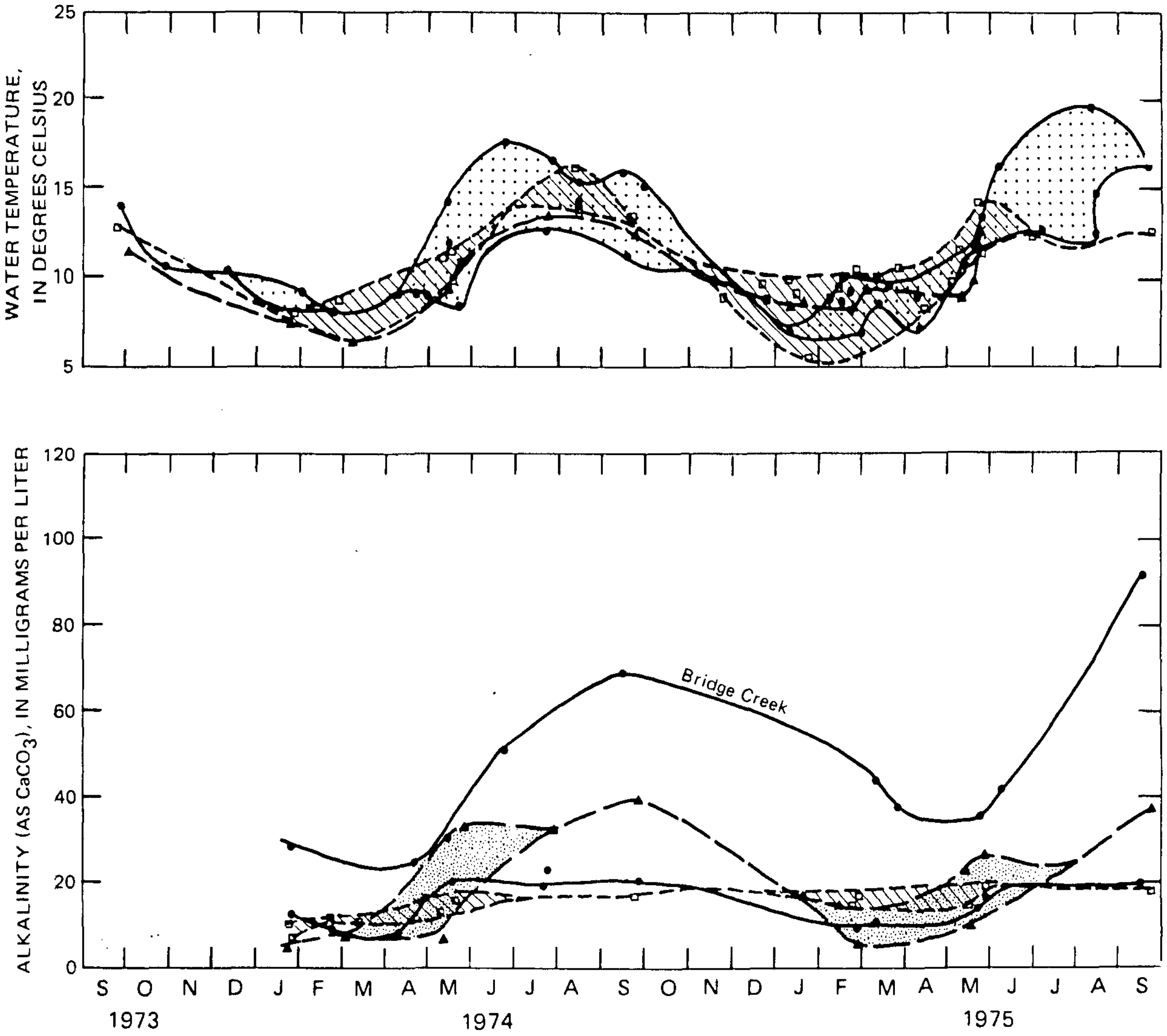


FIGURE 11.--Continued.

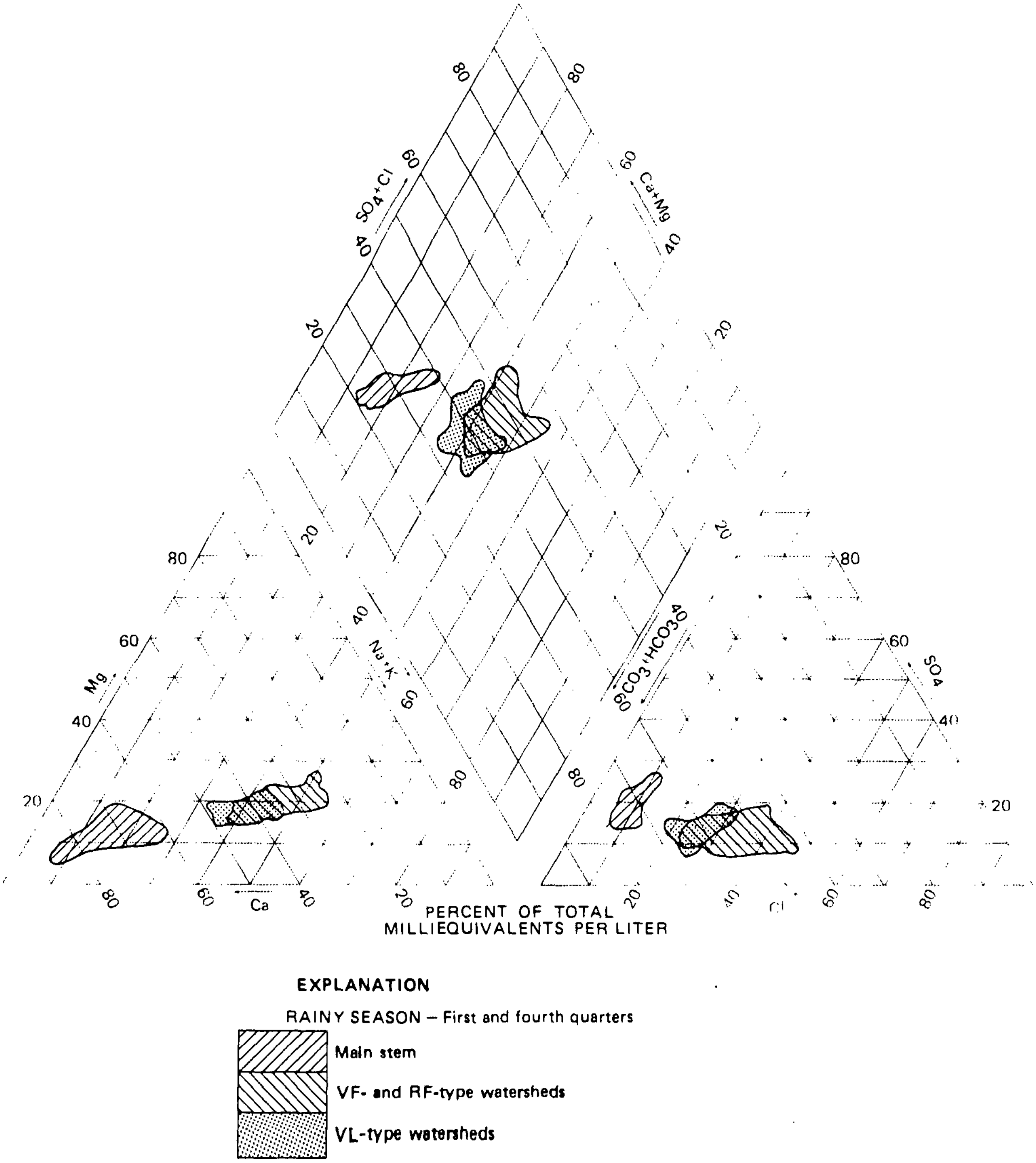


FIGURE 12.--Major-ion composition in the fourth and first quarters using the regular data, VF-, RF-, and VL-type watersheds and main stem.

Analysis of data from the second and third calendar quarters suggested there are no compositional differences between sets from VF- and RF-type watersheds and no pattern of compositional differences due to differences in regolith in the combined VF- and RF-type sets. Differences attributable to regolith were observed in VL-type watersheds only.

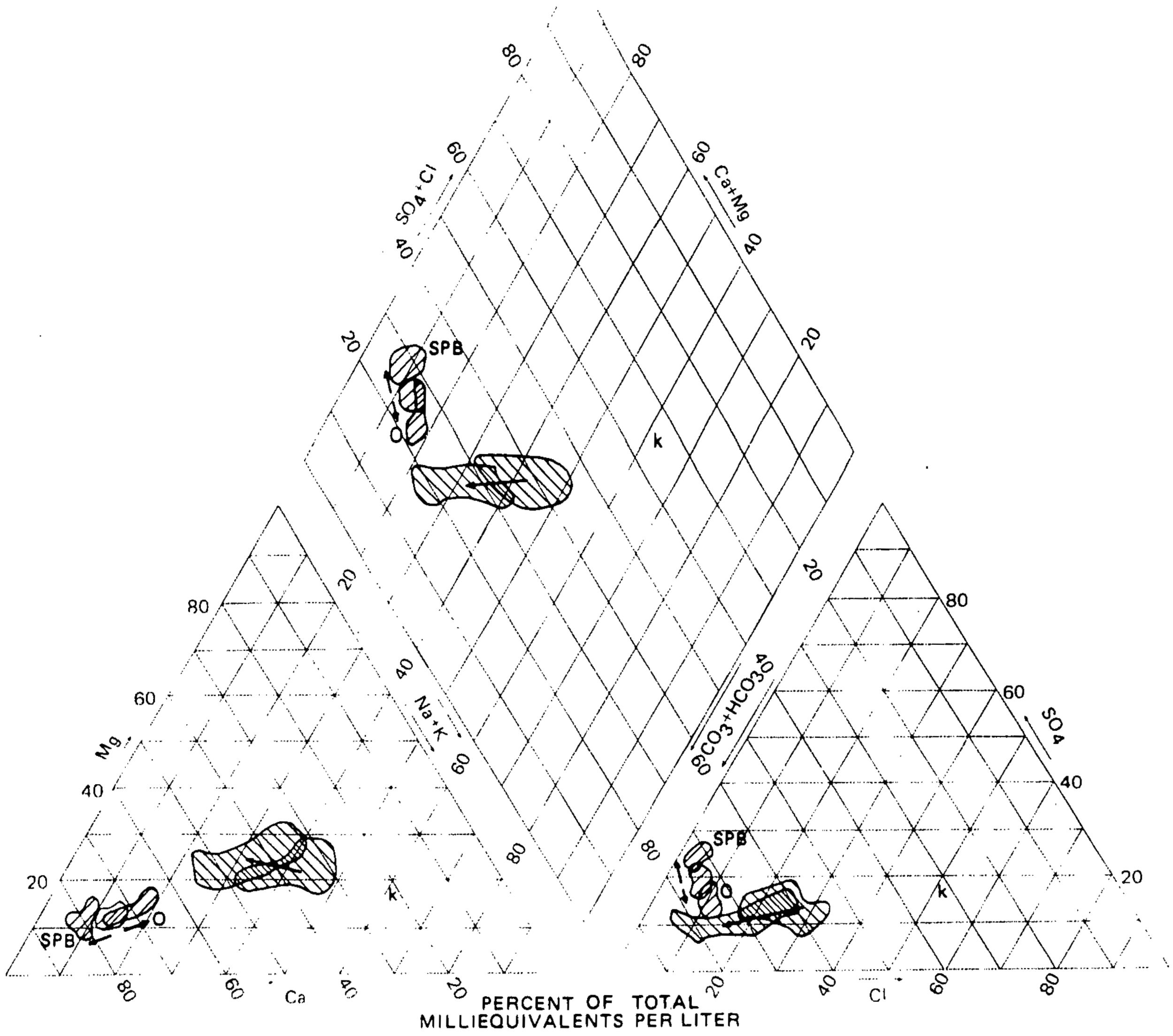
Figure 13 shows that water from VF- and RF-type watersheds shifts from the second to the third quarter toward a calcium bicarbonate type. Coincidentally, main-stem water, which is a single definable type in the second quarter, shifts to two types observable at South Park Boundary (11482200) and at Orick (11482500). The water type at Orick shifts toward that of the park tributaries, indicating the effect of tributary inflow on main-stem water quality. Low-Slope Schist Creek (VF-type land use, St-type regolith) stands out in figure 13 as a sodium chloride type water, suggesting very low weathering activity on the regolith of that watershed.

Compositional differences, apparently related to regolith differences, on logged (VL- and RL-type) watersheds can be seen in figure 14. In the second quarter, St-type watersheds have a mixed sodium chloride-bicarbonate type water; Sn-type watersheds have a calcium-sodium bicarbonate type. From the second to the third quarters the water types in both St- and Sn-type watersheds shift toward calcium bicarbonate. Again, Bridge Creek (RL-type land-use, St-type regolith) is unique among the St-type watersheds in having a calcium bicarbonate-type water.

In the second and third quarters, there is little difference in water type between the combined VF- and RF-type watersheds and the VL-type watersheds, as can be seen by comparing figure 13 with figure 14. But if the schistose (St-type) watersheds are excluded from the set of VL-type watersheds there is a tendency for the remaining VL-type watersheds to have water higher in calcium amd bicarbonate than the water of the VF- and RF-type watersheds.

The weight of evidence presented here and earlier suggests that schistose regoliths are generally more resistant to weathering than the other regolith types, which results in lower specific conductances and a more sodium-chloride type water. But, in cases of severe disruption (like Bridge Creek), the schistose watersheds can weather very rapidly which results in high specific conductances and a calcium bicarbonate-type water--the same characteristics seen in water from non-schist watersheds that have been logged.

The Mx-type regoliths do not fit clearly into the description of weathering in logged watersheds. The water type for the Mx-type regoliths should fall between that of the St- and Sn-type regoliths. The anion composition fits, but the cation composition does not (fig. 14). The lack of agreement may be due to effects that cannot be accounted for without additional data. The alkalinity and specific-conductance values during the dry season (fig. 10) in the three regolith types in logged watersheds, however, did form a regular progression from low values in St-type, through intermediate values in Mx-type, to high values in Sn-type regoliths. The lack of complete agreement between the two findings is as yet unexplained.



EXPLANATION

DRY SEASON--Second and third quarters

▨ Main stem

▨ VF- and RF-type watersheds

k Low-Slope Schist Creek

SPB Redwood Creek at South Park Boundary

O Redwood Creek at Orick

FIGURE 13.--Major-ion composition in the second and third quarters using the regular data, VF- and RF-type watersheds and main stem. Arrows indicate shifts in water types from the second to the third quarters.

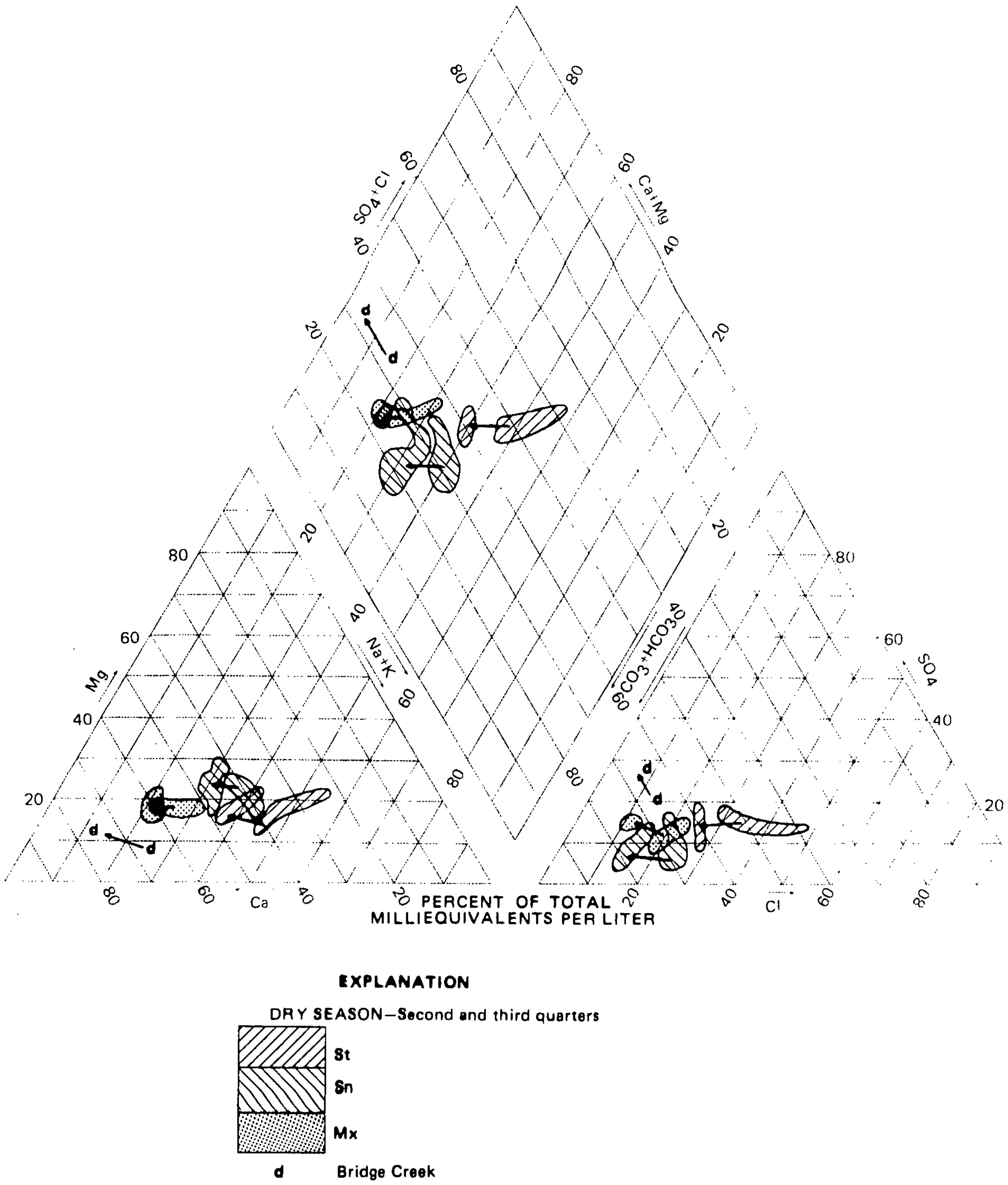


FIGURE 14.--Major-ion composition in the second and third quarters using the regular data, VL- and RL-type watersheds (St-, Sn-, and Mx-based regoliths). Arrows indicate shifts in water types from the second to the third quarters.

Figures 12, 13, and 14 show the seasonal trends in water type in the drainage basin. At the end of the rainy season, water tends to be a mixed calcium-sodium bicarbonate-chloride type. From the beginning of the dry season until the first rains in autumn there is a steady shift toward a calcium bicarbonate type. From the first rains until the end of the rainy season there is a shift back to the mixed type. For example, the water type in combined VF- and RF-type watersheds shifts from 50-55 percent calcium and bicarbonate in the first and fourth quarters to 60-63 percent calcium and bicarbonate in the second quarter to 68-72 percent calcium and bicarbonate in the third quarter.

The shift in water type with time is also reflected in the slope of the linear regression of specific conductance against the sum of dissolved solids (table 9). The slope of the regression line decreases from 1.90 in the rainy season to 1.66 in the dry season, indicating a shift in composition from more to less electrically mobile ions. Previous discussion notes the shift from sodium chloride toward calcium bicarbonate type water. The mass conductivity of sodium chloride (as NaCl) is about 2.2 millimhos per centimeter per gram and of calcium bicarbonate [as $Ca(HCO_3)_2$] about 1.3 millimhos per centimeter per gram. The shift in slope would be expected from the shift in water type (Robinson and Stokes, 1959, p. 465, and Harned and Owen, 1958, p. 697).

Analysis of distributional statistics

Data on pH, dissolved oxygen, and minor constituents (aluminum, silica, nitrite plus nitrate, ammonia, Kjeldahl nitrogen, iron, dissolved phosphorus, dissolved organic carbon, and chemical oxygen demand) had no regular predictable dependence on time, so that handling the data by time series methods yielded little information. Changes with season and differences attributable to land use or regolith type were determined by statistical analysis of the grouped data. The trace metals--cadmium, copper, lead, and zinc--are not discussed because the magnitudes of the values have been questioned (see explanation on p. 29).

In the analysis of minor constituents, the data set used included laboratory analyses of all regular samples and samples collected on diel and synoptic studies, except for the chemograph studies.

Preliminary evaluation of available data showed that the concentrations of all constituents except aluminum, iron, and Kjeldahl nitrogen were similar in the first and fourth, and in the second and third calendar quarters. Statistical measures of these combined sets are shown in table 10. The ranges of observed values in most cases cover one or two orders of magnitude, and most of the distributions are best described as exponential. Where the geometric mean (rather than the arithmetic mean) is closer to the median, the geometric mean is a better measure of central tendency in the data.

TABLE 9.--*Regression coefficients of specific conductance versus dissolved solids*

[Includes regular data and samples collected on synoptic and diel studies, except chemograph synoptic studies. Regression equation $Y = aX + b$ where Y is the specific conductance (in micromhos per centimeter at 25°C) and X is the dissolved solids (as sum of constituents in milligrams per liter). $Se(Y)$ is the standard error of the estimate of Y from X; r is the correlation coefficient]

Data set grouped by calendar quarter[1]	a	b	r	$Se(y)$	Ranges	
					Y	X
First and fourth quarter data	1.90	-14.8	0.96	3.64	36-79	25-48
Second quarter data	1.86	-10.8	.99	3.22	38-137	26-80
Third quarter data	1.66	1.2	.97	10.1	54-250	32-138

[1] Data sets were grouped by calendar quarters: first, January-March; second, April-June; third, July-September; fourth, October-December. See also tables 10, 11, 12, 13, 17, 19.

TABLE 10.--*Statistical summary of minor-constituents data from the regular samples and diel and synoptic studies, excluding chemograph synoptic studies, grouped by calendar quarter (data discussed on p. 76)*

[Constituent values in milligrams per liter except aluminum and iron in micrograms per liter]

Data set grouped by calendar quarter	Constituent	Median	Range	Mean	Standard deviation	Number of samples	Geometric mean	Range of 95-percent confidence interval about geometric mean	Standard deviation of the logarithm transformed data
A (First and fourth quarters, combined)	Silica	6.32	5.0-9.0	6.36	0.71	46	--	-	--
	Aluminum	44	10-290	66	63	44	51	1.5-1720	0.78
	Iron	64	10-680	110	112	45	66	1.4-3200	.86
	Nitrite plus nitrate	.039	0.00-1.01	.108	.203	45	.070	0.00-26	1.31
	Kjeldahl nitrogen	.166	0.00-1.55	.226	.246	46	.149	0.00-7.6	.872
	Dissolved total phosphorus	.022	0.00-0.20	.024	.031	46	--	-	--
	Dissolved organic carbon	2.50	0.0-8.0	3.00	1.78	32	2.56	0.2-35	.58
B (Second and third quarters, combined)	Silica	6.53	4.0-14.5	6.70	1.38	69	--	-	--
	Nitrite plus nitrate	.015	0.00-0.48	.033	.072	68	.015	0.00-2.7	1.15
	Ammonia nitrogen	.019	0.00-0.27	.029	.044	46	.016	0.00-2.0	1.07
	Dissolved total phosphorus	.020	0.00-1.01	.038	.127	70	.017	0.00-1.1	.914
	Chemical oxygen demand[1]	4.8	0-53	6.3	8.7	36	4.1	0-330	.97
	Dissolved organic carbon	1.82	0.0-8.0	2.22	1.48	59	1.81	0.1-40	.684

C (Second quarter)	Aluminum	37	10-150	37	25	24	--	-	--
	Iron	77	10.370	113	116	31	75	1-4770	.92
	Kjeldahl nitrogen	.100	0.00-3.35	.57	1.12	32	.150	0.00-230	1.63
D (Third quarter)	Aluminum	17	0-60	15	14	34	--	-	--
	Iron	47	10-600	88	12	34	46	1-270	.91
	Kjeldahl nitrogen	.093	0.00-0.35	.088	.075	35	.058	0.00-17	1.26

Calculation using data sets shown		Results of applying Student t-test[2]						
		Silica	Aluminum	Iron[3]	Nitrite plus nitrate[3]	Kjeldahl nitrogen[3]	Dissolved total phosphorus	Dissolved organic carbon[3]
B or C minus A	Difference in means	+0.34	-29	+9	-0.055	+0.001	+0.014	-0.75
	α	<0.90	0.95	<0.90	0.99	<0.90	<0.90	0.99
D minus C	Difference in means		-24	-29		-0.092		
	α		0.99	0.95		0.99		
D minus A	Difference in means		-51	-20		-0.091		
	α		0.99	0.95		0.99		

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[1] Calculated from data grouped into class intervals of 2 milligrams per liter width.

[2] α is the confidence level of rejecting the Null Hypothesis stated: The subject means are equal to each other. The test is one-tailed. No value for α indicates no test was performed. Values of α <0.90 should be considered not significant.

[3] The difference in means is the difference between geometric means. The test of the Null Hypothesis is performed using the mean and standard deviation of log-transformed data.

The significance of differences between sets shown was tested using the Student t-test. Results are shown at the bottom of table 10. From the rainy season (first and fourth calendar quarters) to the dry season (second and third quarters), the following significant changes occurred. Aluminum decreased significantly through the third quarter; iron did not change between the rainy season and the second quarter but decreased from the second to the third quarter; nitrite plus nitrate decreased significantly; Kjeldahl nitrogen did not change from the rainy season to the second quarter but decreased significantly between the second and third quarters; dissolved organic carbon decreased.

The regular pH and dissolved-oxygen data were grouped by calendar quarter to evaluate time trends. Results are shown in table 11. The pH means increase from the first through the third quarter and decrease into the fourth quarter. The apparent cyclic pattern of changes in pH--moving lower through the rainy season and moving higher through the dry season--may be caused by the washout and dilution of bicarbonates during the rainy season, followed by a buildup in both the soil and water during the dry season.

The decrease in iron from the rainy season to the dry season (table 10) may be caused partly by the coincident increase in pH. Increases in pH should decrease the leaching rate of iron from the soil. The decreases in iron may also be related to the corresponding decrease in dissolved organic carbon. Organic matter forms soluble complexes, especially with iron, and may affect the solubility and leaching rate of the metals (Jenne, 1968, p. 340).

Dissolved-oxygen concentrations show no pattern with time, suggesting that physical turbulence in the streams is sufficient to keep dissolved oxygen near saturation throughout the year.

Decreases in nitrite plus nitrate, Kjeldahl nitrogen, and dissolved organic carbon from the rainy season to the second and third quarters may be explained as follows. Rain washes these constituents out during the rainy season. In the dry season, these constituents build up again in the surface soils, but no rain is present to wash them downward or off the soil.

Dissolved phosphorus did not decrease from the rainy season to the dry season, contrary to what would be expected from the chemograph data. The lack of agreement between the regular data and the chemograph data cannot be explained. Alterations of the samples while enroute to the Central Laboratory for analysis may have obliterated differences. Alterations are known to have occurred in a set of samples from the Mill Creek area (see p. 89).

TABLE 11.--*Statistical summary of pH and dissolved-oxygen data from the regular measurements grouped by calendar quarter, and results of comparing the means using the Student t-test*

[Numbers in rectangle are confidence levels of rejecting the Null Hypothesis--the subject means are equal--where quarterly means of pH and dissolved oxygen data are compared. Values of 0.90 or less are considered not significant. The test is one-tailed]

Data set grouped by calendar quarter	Median	Mean	Standard deviation	Number of samples
pH				
First quarter	6.80	6.79	0.55	82
Second quarter	7.21	7.13	.49	97
Third quarter	7.37	7.36	.53	61
Fourth quarter	7.19	7.13	.56	31
Dissolved oxygen, in percent saturation				
First quarter	97.4	96.3	3.3	75
Second quarter	97.1	96.9	4.2	98
Third quarter	95.9	95.3	6.0	61
Fourth quarter	95.7	95.2	6.2	31

Quarter

pH Quarter	1	2	3	4	Dissolved oxygen
1		<0.90	<0.90	<0.90	1
2	0.99		0.90	<0.90	2
3	0.99	0.99		<0.90	3
4	0.99	<0.90	0.90		4
	1	2	3	4	

The regular data for minor constituents were grouped into subsets of common land-use and regolith types to examine how the medians of each subset varied from the median of the combined set. Medians of subsets grouped by common land-use type are shown in table 12. The same information for data grouped by common regolith type is given in table 13. The data from main-stem stations are included in the combined sets, but the properties of the MS-type subset are shown only in table 13.

Silica.--Median silica concentrations are higher in watersheds with Sn-type regoliths than in watersheds with St- and Mx-type regoliths. Median silica concentrations are also higher than the set median in VF-type watersheds, probably because VF-type watersheds have predominantly Sn-type regoliths. Higher concentrations in Sn-regolith watersheds are probably associated with generally more rapid weathering of the sandstone-based (Sn-type) than of the schistose (St-type) or mixed (Mx-type) regoliths.

Iron.--In the land-use grouping, the median iron concentration in water from the RF-type watersheds is higher than the set median during the rainy season and is lower than the set median in the VF-type watersheds during the third quarter. The RL-type watersheds as a group are also high in iron.

In the grouping by regolith, there is no pattern during the rainy season. In the second quarter, the median iron concentration in the St-type regolith is significantly higher than the set median. In the third quarter, the median of the Sn-type regolith is significantly below the set median.

The patterns of fluctuations in iron concentrations cannot be explained without further research.

Dissolved oxygen.--Further evaluation of the dissolved-oxygen data beyond that given in table 11 showed no differences attributable to either land use or regolith. As expected, because of physical turbulence in the stream, dissolved-oxygen concentrations are near saturation.

Nitrite plus nitrate.--The set median in the dry season is lower than the set median in the rainy season, and the seasonal differences are most apparent in the VF- and VL-type watersheds. The median concentration in VF-type watersheds is below the set median in both the rainy and dry seasons, but the median concentration in the VL-type watersheds is above the set median in both seasons. This pattern of changes with time and difference between watershed types is consistent with the model discussed in the section on chemograph synoptic studies. Nitrate is fixed to a greater extent in VL-type than in VF-type watersheds; this may be related to the larger amounts of mature vegetation in the VF-type watersheds. Fixed nitrate in excess of that assimilated by other plants would be expected to be washed downward during the rainy season and appear in the baseflow during the dry season. As more excess nitrate is available in the VL-type watersheds than in other watersheds, more would be found in the baseflow from VL-type than VF-type watersheds.

No pattern is seen in the data grouped by regolith type (table 13).

TABLE 12.--*Statistical summary of minor-constituents data from the regular samples, grouped by calendar quarter and land-use type (data discussed on page 78)*

[Range is from the low end of the lowest class occupied to the high end of the highest class occupied]

Data set grouped by calendar quarter	Constituent	Set median	Subset VF		Subset RF		Subset VL		Subset RL	
			Median	Range	Median	Range	Median	Range	Median	Range
First and fourth quarters, combined (rainy season)	Silica	6.32	7.13	6.5-9.0	6.38	5.5-8.0	6.19	5.0-7.5	No RL streams sampled these quarters	
	Aluminum	44	40	20-290	105	20-160	44	10-240		
	Iron	64	50	20-260	110	30-190	83	10-680		
	Nitrite plus nitrate	.039	.028	0.00-0.08	.020	0.00-36	.093	0.03-0.94		
	Kjeldahl nitrogen	.166	.117	0.05-0.35	.100	0.05-0.60	.175	0.00-1.5		
	Dissolved total phosphorus	.022	.024	0.01-0.05	.022	0.01-0.03	.023	0.00-0.12		
	Dissolved organic carbon	2.50	2.25	1.0-4.0	4.00	1.0-6.0	2.75	1.0-7.0		
Second and third quarters, combined (dry season)	Silica	6.53	7.60	6.5-8.0	7.63	6.0-14.5	6.21	5.5-8.0	5.88	5.0-6.5
	Nitrite plus nitrate	.015	.012	0.00-0.06	.025	0.00-0.48	.020	0.00-0.14	.009	0.00-0.02
	Ammonia	.019	.020	0.00-0.05	.015	0.00-0.09	.018	0.00-0.27	.053	0.03-0.06
	Dissolved total phosphorus	.020	.020	0.00-0.05	.015	0.00-0.04	.025	0.00-0.41	.017	0.01-0.04
	Dissolved organic carbon	1.82	2.00	1.8-8.0	2.83	1.0-5.0	1.94	0.0-8.0	1.83	0.0-5.0
Second quarter	Aluminum	37	35	10-50	55	20-150	34	20-50		No data
	Iron	77	35	10-180	95	30-320	80	30-370	120	70-230
	Kjeldahl nitrogen	.100	.133	0.05-3.05	.225	0.00-3.3	.094	0.00-3.3	.067	0.00-0.10
Third quarter	Aluminum	17	20	0-50	8	0-30	18	0-40	45	0-60
	Iron	47	40	10-60	28	20-600	38	20-90	160	40-310
	Kjeldahl nitrogen	.093	.100	0.00-0.35	.125	0.00-0.20	.113	0.00-0.25	.075	0.00-0.15

TABLE 13.--*Statistical summary of minor-constituents data from the regular samples, grouped by calendar quarter and regolith (data discussed on page 78)*

[Range is from the low end of the lowest class occupied to the high end of the highest class occupied]

Data set grouped by calendar quarter	Constituent	Set median	Subset St		Subset Sn		Subset Mx		Subset MS	
			Median	Range	Median	Range	Median	Range	Median	Range
First and fourth quarters, combined (rainy season)	Silica	6.32			6.80	5.5-9.0	6.18	5.0-7.0	6.05	5.0-7.0
	Aluminum	44			50	10-290	44	30-240	38	10-100
	Iron	64			60	10-260	88	10-680	60	30-150
	Nitrite plus nitrate	.039	No St streams sampled these quarters		.030	0.00-0.94	.091	0.03-0.39	.040	0.02-1.01
	Kjeldahl Nitrogen	.166			.121	0.05-0.60	.163	0.00-1.55	.225	0.10-0.50
	Dissolved total phosphorus	.022			.023	0.01-0.08	.213	0.00-0.12	.019	0.01-0.20
	Dissolved organic carbon	2.50			2.75	1.0-6.0	2.83	1.0-7.0	1.63	0.0-8.0
Second and third quarters, combined (dry season)	Silica	6.53	6.06	5.0-7.5	7.18	6.0-8.0	5.94	5.5-8.0	5.75	4.0-9.0
	Nitrite plus nitrate	.015	.011	0.00-0.02	.018	0.00-0.34	.019	0.00-0.14	.010	0.00-0.10
	Ammonia	.019	.050	0.03-0.06	.015	0.00-0.09	.040	0.00-0.27	.013	0.00-0.05
	Dissolved total phosphorus	.020	.019	0.01-0.04	.022	0.00-0.06	.019	0.00-0.42	.018	0.00-1.01
	Dissolved organic carbon	1.82	2.50	0.0-5.0	2.10	0.0-8.0	1.67	0.8-8.0	1.44	0.0-3.0
Second quarter	Aluminum	37	40	40	37	10-150	28	20-50	40	30-80
	Iron	77	175	70-370	50	10-240	40	30-140	70	30-90
	Kjeldahl nitrogen	.100	.081	0.00-0.15	.131	0.00-3.35	.075	0.00-3.35	.050	0.00-3.30
Third quarter	Aluminum	17	10	0-50	18	0-50	17	0-40	17	0-60
	Iron	47	105	30-310	32	10-60	37	20-90	60	20-380
	Kjeldahl nitrogen	.093	.100	0.00-0.15	.094	0.00-0.35	.117	0.00-0.25	.050	0.00-0.25

Ammonia.--The lack of patterns in the data grouped either by land use or regolith suggests that during the dry season the processes creating observed ammonia concentrations are virtually the same in all watershed types. Data are available only for the combined second and third quarters, however, which severely limits discussion.

Kjeldahl nitrogen.--The set medians decrease going from the rainy season through the second and third quarters, but no pattern emerges from the groupings by land-use type as shown in table 13. The median of the combined VF- and RF-type data (not shown) during the rainy season is below the set median; whereas the median of the combined VF- and RF-type data (not shown) from the second quarter is higher than the set median. This is the reverse of the pattern of combined data shown in table 10. This result suggests that Kjeldahl-nitrogen concentrations are higher in the base flow from forested and RF-type watersheds than in the base flow from logged watersheds. More of the Kjeldahl nitrogen in the surface soil may percolate downward to the water table in forested watersheds than in logged watersheds because precipitation is retained longer in forested watersheds. Thus, in the second calendar quarter, when base flow dominates surface discharge, Kjeldahl-nitrogen concentrations would be higher in streams of forested watersheds than in streams of logged watersheds.

Because materials containing Kjeldahl nitrogen are biological in origin, no pattern in median concentrations is expected when the data are grouped by regolith type. However, during the rainy season the median concentration in water from Sn-type watersheds is below the set median. This result cannot be explained from a geochemical basis.

Dissolved phosphorus.--For watersheds grouped by land use, concentrations during the dry season tend to be below the set median in RF-type and above the median in VL-type watersheds. The difference cannot be explained at this time.

No pattern in the groupings according to regolith can be seen.

pH.--Examination of the frequency distribution histograms of pH data suggested that the third and fourth quarter data could be combined without loss of detail and without biasing conclusions on time-related variations. Thus, the third and fourth quarter data were combined (not shown); then the three sets--first, second, and third plus fourth calendar quarters of data---were studied.

The only consistent and significant differences in pH observed by this analysis were that the pH values for main-stem stations were consistently higher than those for tributary stations. No patterns of differences in pH between land-use or regolith type were seen. Neither land use nor regolith seem to affect the pH systematically in streams within the park.

Dissolved organic carbon.--In the data grouped by land-use type, the median of data from the RF-type watersheds is higher than the set median in both the rainy and dry seasons. RF-type watersheds apparently supply more dissolved organic material to water than the other types of watersheds. One might also expect VF-type watersheds to follow the same pattern, but, in this analysis, they do not. An explanation is not yet available.

Earlier (p. 52) the pH of stormflow from RF-type watersheds was noted to be lower than that from VF-type watersheds. This could be caused by higher organic content of the soils in RF-type watersheds, which would by decomposition create higher partial pressures of carbon dioxide in soil. The higher dissolved organic carbon concentrations in RF-type watersheds support this hypothesis.

No pattern in the organic carbon data grouped by regolith type can be seen. Median concentration in the main stem subset during the dry season is lower than the set median. This may be due to the influence of low organic content in water upstream from the park.

Mill Creek Drainage Basin

Summary Statistics

A statistical summary of the data on water quality collected during this study in the Mill Creek drainage basin is shown in table 14.

The quality of water in the tributaries and main stem of Mill Creek is excellent for drinking and fisheries. The dissolved-solids concentration averages 33 mg/L with a maximum of 49 mg/L; hardness averages 16 mg/L; the pH is nearly neutral; and the dissolved-oxygen concentration is close to saturation. The water tends to be a calcium-sodium bicarbonate type. Concentrations of silica, aluminum, and iron, which are derived from rock weathering, are very low. Aluminum and iron distributions are skewed strongly positive. This indicates that some concentrations of these constituents are very high and that processes other than weathering affect aluminum and iron concentrations.

TABLE 14.--*Statistical summary of selected water-quality measurements, Mill Creek drainage basin*

[Data from Iwatsubo and others, 1975 and 1976]

Constituent	Units	Mean	Standard deviation	Number of samples	Maximum observed	Minimum observed	Skewness
Silica	mg/L	7.03	1.03	46	8.9	4.9	0.00
Aluminum	μg/L	46	61	46	370	0	3.9
Iron	μg/L	54	66	45	470	10	5.9
Calcium	mg/L	4.03	1.50	46	7.7	1.7	.59
Magnesium	mg/L	1.46	.62	46	3.0	.1	.55
Sodium	mg/L	3.27	.70	46	4.7	2.0	.46
Potassium	mg/L	.60	.21	46	1.3	.3	1.69
Bicarbonate	mg/L	17.5	6.8	46	32	8	1.0
Carbonate	mg/L	.0	.0	17	.0	.0	.0
Alkalinity, as $CaCO_3$	mg/L	17.5	6.0	188	35	6	.04
Sulfate	mg/L	1.98	.84	46	5.0	.9	1.62
Chloride	mg/L	3.82	.91	43	5.7	1.8	-.37
Fluoride	mg/L	.05	.07	33	.2	.0	1.05
Nitrite plus nitrate	mg/L	.379	.680	46	3.9	.00	4.01
Ammonia nitrogen	mg/L	.017	.035	13	.13	.00	3.42
Organic nitrogen	mg/L	.739	1.09	13	2.8	.03	1.42
Kjeldahl nitrogen	mg/L	.437	.634	45	2.8	.02	2.95
Dissolved total phosphorus	mg/L	.010	.011	45	.04	.00	1.02
Dissolved ortho-phosphorus	mg/l	.014	.009	36	.04	.00	.598
Dissolved solids	mg/L	32.7	7.2	46	49	21	.6
Hardness, as $CaCO_3$	mg/L	16.1	5.1	46	28	8.0	.7
Specific conductance	μmho/cm at 25°C	50.2	13.3	296	88	26	.3
pH		6.96	.364	196	7.7	5.9	-.16
Temperature	°C	13.1	4.4	287	23.0	5.0	.6
Dissolved oxygen	mg/L	9.59	1.24	188	12.1	6.3	-.14
Dissolved organic carbon	mg/L	3.55	2.06	44	9.2	.6	.97
Cadmium[1]	μg/L	.3	.5	46	2	0	1
Copper[1]	μg/L	3.5	4.2	46	20	0	2.1
Lead[1]	μg/L	2.0	1.0	3	3	1	-
Zinc[1]	μg/L	28	43	46	240	0	3.5

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[1] These concentrations are thought to be too high by a factor of 10 for cadmium and a factor of about 5 for copper, lead, and zinc (Vance Kennedy, oral commun., 1976). See more complete explanation on page 36.

Dissolved-phosphorus concentrations are generally below 0.010 mg/L, the level suggested by Sawyer (1947) above which nuisance blooms of algae might occur. The average concentration of inorganic nitrogen (nitrite plus nitrate and ammonia) exceeds the average phosphorus concentration by a factor of about 40, suggesting that on the average, phosphorus may be the nutrient limiting algal growth. The organic-nitrogen, Kjeldahl-nitrogen and dissolved organic carbon concentrations are all typical of clean streams draining forested watersheds (Fredriksen, 1971).

Concentrations of the trace metals cadmium, copper, lead, and zinc are all low, typical of clean streams. But even these low concentrations are thought to be analytically too high by a factor of 10 for cadmium, and a factor of 5 for copper, lead, and zinc (Vance Kennedy, oral commun., 1976). Routine methods of sample collection, preservation, storage, and analysis are often inadequate to obtain a representation of the true concentrations at these low levels. These trace metals will not be discussed further, and the statistics are presented for the record only.

Synoptic Studies During Stormflow

Water-quality measurements were made at five stations (table 2) during two storm events--January 6-8 and March 17-19, 1975.

Rainfall was measured at the Geological Survey rain gage at the confluence of the West Branch and East Fork of Mill Creek. The first storm caused 84 mm of rain between 1000 hours on January 7 and 1800 hours on January 8. The second storm caused 140 mm of rain between 0200 hours on March 17 and 1500 hours on March 20 (K. M. Nolan, written commun., 1976). Discharge hydrographs for both storms had well-defined rises, peaks, and recessions, but peak discharges in the later storm were about twice as high as in the earlier storm.

Preliminary evaluation of the time series of water-quality measurements during each storm showed no systematic variations in pH, temperature, or dissolved-oxygen percent saturation. Plots of these data are not shown for that reason.

Both alkalinity and specific conductance show the effects of dilution at peak flow, however. Table 15 lists the values on the rise, at the peak, and on the recession of the hydrograph of each storm. The middle value of the three is assigned a zero (0), the largest a plus (+), and the smallest a minus (-). Alkalinity values are considered equal if they are within 1.5 units of each other, and specific-conductance values are considered equal if they are within 3 units of each other. These assignments are shown at the bottom of the table. Some dilution occurred at the discharge peak in 8 of 18 observations. In no case did an increase in concentration occur at the discharge peak. This suggests that dilution or no change occurs at peak flow with greater probability than do increases in concentration. Dilution at peak flow is probably caused by a greater fraction of the discharge at the peak coming from overland flow, which would have smaller concentrations of dissolved solids than would quick-return or delayed-return flow.

TABLE 15.--*Alkalinity and specific-conductance values at the beginning of the rise, at the peak, and on the recession of the hydrographs for synoptic studies*

[Symbols used to represent the median: 0, median or equal values; +, above the median; -, below the median]

Station number and name	January 6-8, 1975			March 17-19, 1975		
	Rise	Peak	Recession	Rise	Peak	Recession
Alkalinity, in milligrams per liter						
11532602 West Branch Mill Creek below Red Alder campground, near Crescent City	11	10	9			
11532605 West Branch Mill Creek at Bridge, near Crescent City	10	10	11	12	9	11
11532615 East Fork Mill Creek at Bridge, near Crescent City	15.5	13.5	14	15	12.5	13
11532620 Mill Creek near Crescent City	13	11	12	13	10	11
11532626 Mill Creek at Bridge, near Crescent City	12	12	12	12	8	18
Specific conductance, in micromhos per centimeter at 25°C						
11532602 West Branch Mill Creek below Red Alder campground, near Crescent City	41	38	38			
11532605 West Branch Mill Creek at Bridge, near Crescent City	42	36	39	35	31	42
11532615 East Fork Mill Creek at Bridge, near Crescent City	42	42	40	40	38	36
11532620 Mill Creek near Crescent City	41	36	41	36	31	38
11532626 Mill Creek at Bridge, near Crescent City	42	44	40	39	28	36
Alkalinity, in milligrams per liter						
11532602 West Branch Mill Creek below Red Alder campground, near Crescent City	0	0	0			
11532605 West Branch Mill Creek at Bridge, near Crescent City	0	0	0	0	-	0
11532615 East Fork Mill Creek at Bridge, near Crescent City	0	0	0	+	0	0
11532620 Mill Creek near Crescent City	0	0	0	+	0	0
11532626 Mill Creek at Bridge, near Crescent City	0	0	0	0	-	+
Specific conductance, in micromhos per centimeter at 25°C						
11532602 West Branch Mill Creek below Red Alder campground, near Crescent City	0	0	0			
11532605 West Branch Mill Creek at Bridge, near Crescent City	+	0	0	0	-	+
11532615 East Fork Mill Creek at Bridge, near Crescent City	0	0	0	0	0	0
11532620 Mill Creek near Crescent City	0	-	0	0	-	0
11532626 Mill Creek at Bridge, near Crescent City	0	0	0	0	-	0

Data from the synoptic studies were grouped by storm (not shown) to determine time-related differences in the water quality. Inspection of the statistical properties of the grouped data indicated no differences between storms in alkalinity, pH, temperature, and dissolved-oxygen concentration. The mean specific conductance was significantly lower in the March storm (0.99 confidence level), probably because this storm had the heavier rainfall, and much of the soluble material available earlier in the season had been diluted and washed out of the soils by earlier rainfall.

In order to determine systematic differences in measurements between watersheds, the data were grouped into West Branch, East Fork, and main-stem sets. A statistical summary of these sets is given in table 16. When thus grouped, the statistical properties of the sets seem nearly identical. Alkalinity, however, is significantly higher in the East Fork than in the West Branch. Rocks in the East Fork watershed may be weathering faster because logging is more intense in the East Fork than in the West Branch watersheds.

Diel Studies at Low Flow

Water-quality measurements were made hourly during the diel study from 1200 hours on July 31 to 1200 hours on August 1, 1974, at the stations Mill Creek (11532620), Mill Creek at Mouth (11532630), East Fork (11532610), and West Branch below Red Alder Campground (11532602). All four stations were located in riffle reaches with partial shade.

Alkalinity showed no systematic variations related to the diel period. The pH, however, varied systematically at all but the West Branch station. The range was greatest at the East Fork station where a maximum pH of 7.5 was measured at 1200 hours, and a minimum of 6.8 was measured at 0600 hours.

Specific conductance at all stations except the East Fork station showed no systematic variations related to the diel period. Variations in specific conductance at the East Fork station seem to be related to the diel period, with the peak values at 1800 hours and minimum values at 0500 hours. The cause of this variation is undetermined.

The temperature varied systematically with the diel period at every station; the greatest range was 23.0 to 18.2°C at the Mill Creek station (11532620). The lowest temperatures and smallest variations were measured at the West Branch station.

TABLE 16.--*Statistical summary of field-measurement data from synoptic studies, grouped by watershed*

[Means and standard deviations calculated from data grouped by class intervals as follows: alkalinity, 1 milligram per liter; specific conductance, 5 micromhos at 25°C; pH, 0.2 units; temperature, 0.5°C; dissolved oxygen (percent saturation), 2 percent]

Constituent and drainage basin	January 6-8 and March 17-19, 1975				
	Median	Range	Mean	Standard deviation	Number of samples
Alkalinity, in milligrams per liter					
Main stem	12.3	8.0-19	12.3	2.1	28
East Fork Mill Creek	14.8	12-20	15.1	1.8	15
West Branch Mill Creek	10.2	6.0-18	10.4	2.5	33
Specific conductance, in micromhos per centimeter at 25°C					
Main stem	39.3	25-55	39.4	4.8	55
East Fork Mill Creek	40.6	25-50	40.1	4.8	27
West Branch Mill Creek	37.9	25-60	39.1	6.7	55
pH					
Main stem	6.79	6.0-7.2	6.73	.23	23
East Fork Mill Creek	6.83	6.2-7.8	6.79	.35	14
West Branch Mill Creek	6.77	6.0-7.8	6.79	.40	30
Temperature, in degrees Celsius					
Main stem	9.62	8.5-10.5	9.55	.44	50
East Fork Mill Creek	9.39	8.5-10.5	9.46	.49	22
West Branch Mill Creek	9.55	9.0-10.5	9.58	.34	50
Dissolved oxygen, in percent saturation					
Main stem	95.0	88-104	95.2	3.2	24
East Fork Mill Creek	95.0	90-100	94.8	2.4	12
West Branch Mill Creek	93.2	88-98	93.1	2.8	27

	Alkalinity	Specific conductance	pH	Temper-ature	Dissolved oxygen
α[1]	0.99	<0.90	<0.90	<0.90	<0.90

[1] α is the confidence level for rejecting the Null Hypothesis that the means of data from the East Fork and West Branch of Mill Creek are equal. Values of 0.90 or less are considered not significant. The test is one-tailed.

Dissolved-oxygen concentrations showed the classical systematic variation, reaching peak values at 1400-1600 hours and minimum values at 0400-0600 hours, corresponding to times of maximum photosynthesis and maximum respiration. There were no differences in the patterns of variations among the three streams. However, the highest saturation values (107 and 102 percent) were reached at the main-stem stations and the lowest value (80 percent) was reached at the West Branch station.

Results of Regular Measurements and Analyses

Field water-quality measurements were made and water samples were collected and analyzed at regular intervals. These regular field measurements and the medians of field measurements on synoptic and diel studies were combined for further study. The regular laboratory analyses were combined with analyses of samples taken on synoptic and diel studies.

Alkalinity, specific conductance, and temperature variations were strongly time dependent. This dependence is shown in figure 15. Envelopes enclose the ranges of values observed in the two tributaries and the main stem.

Alkalinity values tend to be higher in the East Fork than in the West Branch during both the rainy and dry seasons. Higher alkalinity values in the East Fork may be caused by higher rates of rock weathering brought on by land disturbance from logging. No differences in specific conductance between the tributaries and main stem can be seen. Temperature ranges in the main stem tend to be larger than in the tributaries, perhaps because the main stem tends to be more exposed to insolation and to back radiation than the tributaries. The temperature range in the West Branch is small, perhaps because of the temperature-buffering effect of forest cover which is heavier in that watershed than in the East Fork.

Changes in the major-ion composition with time and differences between tributaries are shown in a trilinear diagram (fig. 16). All available laboratory chemical analyses were used in diagramming (a total of 42 analyses).

During the rainy season, differences between the tributaries are apparent. The main-stem water is a mixture of the two types and is enclosed within the outer envelope (fig. 16). The high bicarbonate East Fork water has about equal fractions of calcium, magnesium, and sodium. West Branch water tends to be lower in magnesium and higher in chloride. In the dry season, no difference can be seen between the tributaries and the main stem, possibly because the number of observations is small for this period.

Water shifts from a sodium chloride type in the rainy season toward a calcium bicarbonate type in the dry season. This same change in water type with season was also seen in the data from the Redwood Creek drainage basin.

The minor chemical constituents, pH, and dissolved-oxygen percent saturation did not seem to have strong time-dependent variations. Therefore, differences in these variables between the rainy and dry seasons, and between the tributaries and the main stem, were evaluated by comparing the statistical properties of grouped data. The data set for the minor chemical constituents consisted of all laboratory analyses. The data sets for pH and dissolved oxygen consisted of all the regular data plus the median value from the data collected during each synoptic and diel study. Samples collected for laboratory analysis during the March storm, it was discovered later, were improperly handled resulting in serious alterations in the nitrogen, phosphorus, and organic species concentrations. These erroneous values are not included in the analysis.

Laboratory-determined analytical data from regular samples were grouped for further analysis by calendar quarter to determine gross differences in chemical properties with time. If no differences were evident from inspection of the frequency distribution histograms and performing a Student t-test of the differences in arithmetic means, the sets were further grouped into rainy season (fourth and first calendar quarters) and dry season (second and third calendar quarters). The data sets for silica, iron, and dissolved phosphorus showed no quarterly or seasonal differences and were grouped into a single set. Other data sets were evaluated separately. Summary statistics of the grouped data are listed in table 17.

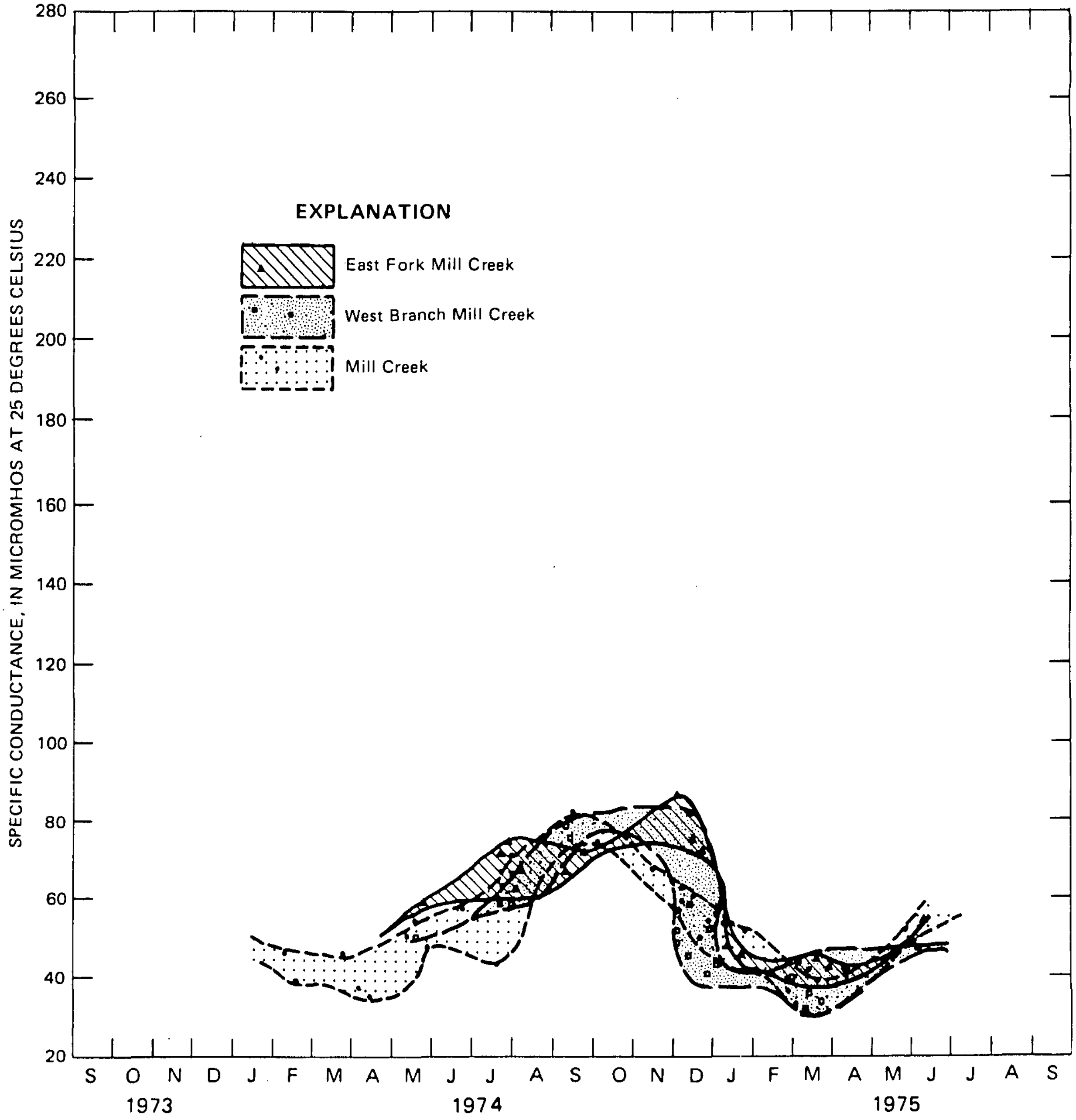

FIGURE 15.--Specific-conductance, water-temperature, and alkalinity values for main stem, East Fork, and West Branch Mill Creek.

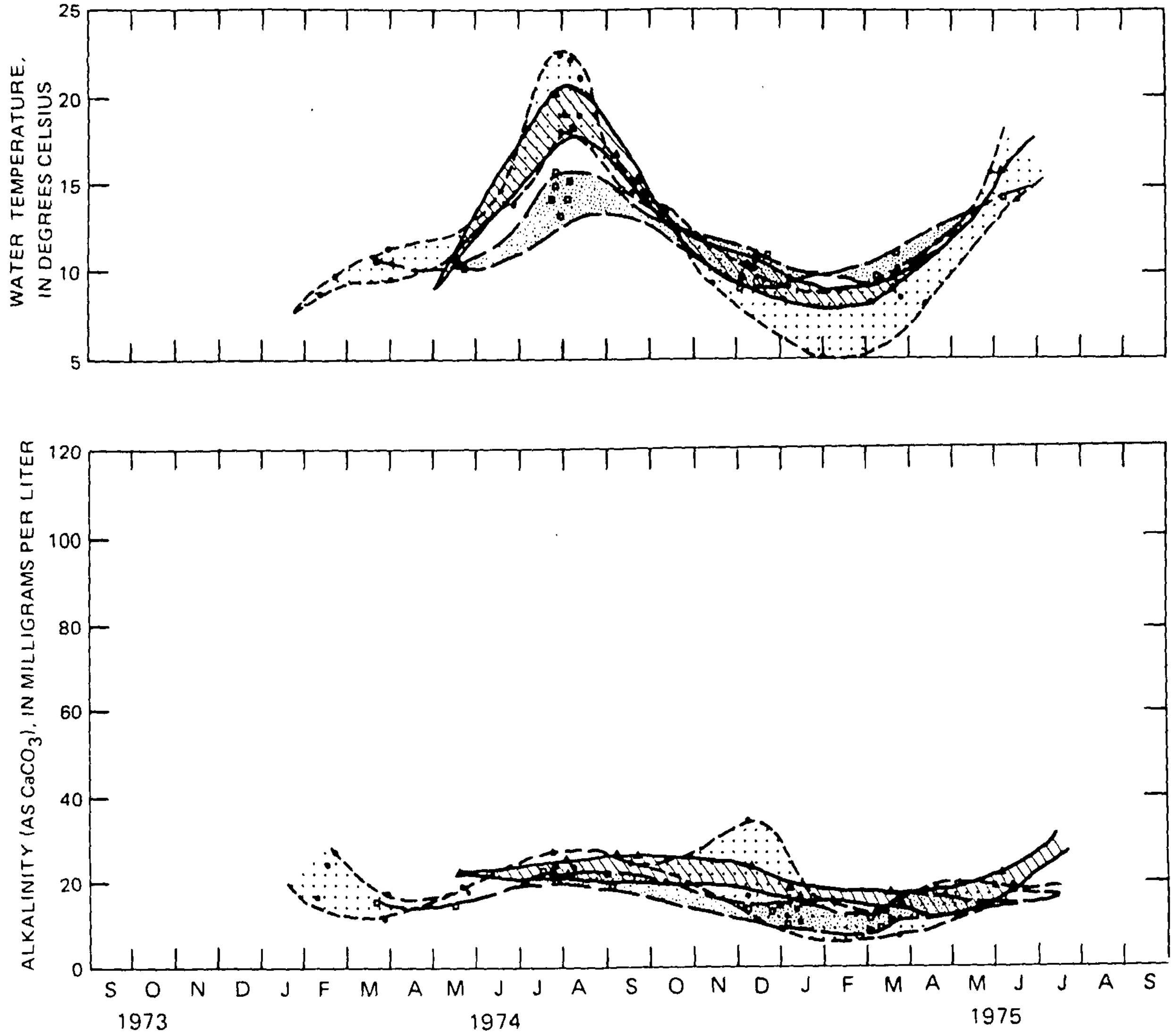

FIGURE 15.--Continued.

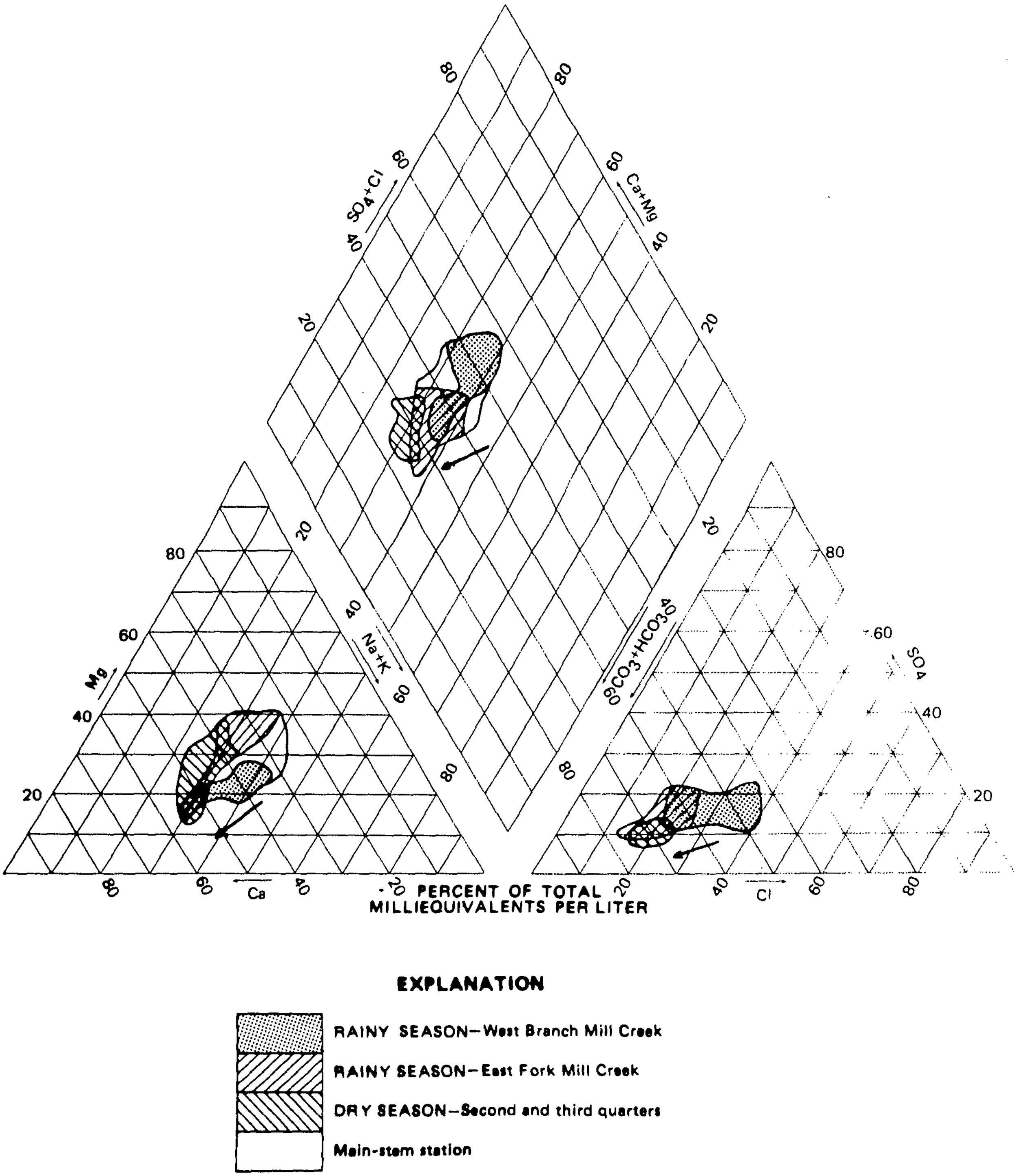

FIGURE 16.--Major-ion composition using the regular data, Mill Creek drainage basin. Arrows indicate shifts in water types from rainy season to dry season.

Aluminum, nitrite plus nitrate, chemical oxygen demand, and dissolved organic carbon all decreased significantly from the rainy season to the dry season. The decrease in aluminum, nitrite plus nitrate, and organic material may reflect the change in sources of streamflow from overland and quick-return flow during the rainy season to delayed-return flow and ground water during the dry season.

These data sets were then regrouped into East Fork, West Branch, and main-stem subsets to examine how the medians of each subset varied from the median of the combined set. Medians and ranges were shown in table 18 for each subset.

No pattern is apparent in the silica concentrations.

Iron is higher in the main stem and lower in the West Branch than the set median. The cause for these differences cannot be determined from the available data.

Dissolved phosphorus in the East Fork is higher than the set median. Both the maximum and median concentrations are both smaller in the West Branch than in the East Fork.

Concentrations of aluminum, nitrite plus nitrate, Kjeldahl nitrogen, chemical oxygen demand, and dissolved organic carbon were lower in the dry season than in the rainy season in all the streams. Among the streams, however, the only major difference is the nitrite plus nitrate concentration, which is larger in the West Branch than the set median in the rainy season. Higher nitrite plus nitrate values may be due in part to the campground located some distance upstream from the sampling station (table 2).

The first, second, and fourth calendar quarter sets of pH data were identical and were, therefore, grouped. The third quarter set was evaluated separately. This arrangement of quarterly groupings is probably needed because the second-quarter data were collected early in April, well within the rainy season. No differences in the sets of dissolved oxygen percent saturation data were found when the data were grouped by quarter or season. Therefore, the data were grouped into one set for analysis. These combined sets were then regrouped into main-stem, East Fork, and West Branch categories. A statistical summary of the grouped data is given in table 19.

TABLE 17.--*Statistical summary of minor constituents data from the regular samples*

[Constituent values in milligrams per liter except iron (micrograms per liter)]

Data set grouped by calendar quarter	Constituent	Median	Range	Mean	Standard deviation	Number of samples	Geometric mean	Range of 95-percent confidence interval about geometric mean	Standard deviation of the logarithm transformed data
All data, combined	Silica	7.00	4.5-9.0	7.03	1.03	46			
	Iron	50	10-480	54	66	45			
	Dissolved total phosphorus	.012	0.00-0.05	.008	.009	31			
Fourth and first quarters (rainy season)	Aluminum	44	10-380	60	67	33	43	1-1370	
	Nitrite plus nitrate	.330	0.00-2.64	.516	.574	19	.352	0.00-76	
	Kjeldahl nitrogen	.362	0.15-1.00	.432	.237	19	.382	.04-3.5	.49
	Chemical oxygen demand	11.9	2-16	9.4	3.7	15			
	Dissolved organic carbon	4.4	1-10	4.6	2.0	19			

Second and third quarters (dry season)	Aluminum	15	0-30	10	7	13		
	Nitrite plus nitrate	.015	0.00-0.68	.086	.184	13	.010	2.43
	Ammonia nitrogen	.014	0.00-0.14	.017	.034	13		
	Kjeldahl nitrogen	.212	0.00-2.85	.754	1.082	13	.279	1.46
	Chemical oxygen demand	3.1	0-16	3.4	3.7	13		
	Dissolved organic carbon	1.67	0.0-9.0	2.09	2.35	11		

	Aluminum	Nitrite plus nitrate[2]	Kjeldahl nitrogen[2]	Chemical oxygen demand	Dissolved organic carbon
α[1]	0.99	0.99	<0.90	0.99	0.99

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[1] α is the confidence level of rejecting the Null Hypothesis that the means of dry season and rainy season data are equal. The test is one-tailed.

[2] Determined using the mean and standard deviation of logarithm transformed data.

TABLE 18.--*Statistical summary of minor constituents data, grouped by watershed and season*

[Range is from the low end of the lowest class occupied to the high end of the highest class occupied]

Data set	Constituent	Set median	Main stem		West Branch Mill Creek		East Fork Mill Creek	
			Median	Range	Median	Range	Median	Range
Combined data	Silica	7.00	6.92	4.5-9.0	6.75	5.0-9.0	7.50	5.5-9.0
	Iron	50	56	20-480	40	10-70	50	10-90
	Dissolved total phosphorus	.012	.012	0.00-0.05	.009	0.00-0.02	.016	0.00-0.03
Rainy season data	Aluminum	44	48	20-380	45	10-130	40	10-120
	Nitrite plus nitrate	.330	.267	0.00-2.6	.490	0.28-0.92	.220	0.16-0.96
	Kjeldahl Nitrogen	.362	.334	0.15-1.0	.350	0.20-0.90	.475	0.35-0.55
	Chemical oxygen demand	11.9	12.0	4-14	11.0	2-16	9.0	6-16
	Dissolved organic carbon	4.4	3.8	1-10	5.5	2-9	4.5	4-5
Dry season data	Aluminum	15	14	0-20	15	0-30	20	0-30
	Nitrite plus nitrate	.015	.008	0.00-0.03	.140	0.03-0.68	.007	0.00-0.16
	Ammonia	.014	.013	0.00-0.03	.017	0.01-0.14	.010	0.00-0.02
	Kjeldahl nitrogen	.212	.238	0.00-2.8	.350	0.05-2.6	.175	0.05-2.55
	Chemical oxygen demand	3.1	3.5	0-6	2.7	0-4	2.5	0-16
	Dissolved organic carbon	1.7	1.3	0-3	2.0	1-3	1.7	1-9

TABLE 19.--*Statistical summary of pH and dissolved-oxygen data, grouped by watershed*

[Means and standard deviations calculated from data grouped by class intervals as follows: pH, 0.2 units; dissolved oxgyen (percent saturation, 2 percent]

Data set grouped by calendar quarter	Median	Range	Mean	Standard deviation	Number of samples
		pH			
Combined first, second, and fourth quarter	6.75	5.8-7.6	6.70	0.43	28
Main stem	6.80	6.0-7.4	6.73	.42	15
East Fork Mill Creek	6.70	6.2-7.2	-	-	5
West Branch Mill Creek	6.53	5.8-7.6	-	-	8
Third quarter	7.20	6.6-7.8	7.15	.32	16
Main stem	7.45	6.8-7.6	-	-	6
East Fork Mill Creek	7.40	7.0-7.8	-	-	4
West Branch Mill Creek	6.90	6.6-7.2	-	-	6
	Dissolved oxygen, in percent saturation				
Combined set	96.0	64-106	93.7	8.3	42
Main stem	97.0	86-106	96.0	5.6	19
East Fork Mill Creek	97.0	88-102	96.2	3.7	9
West Branch Mill Creek	92.0	64-102	88.5	11.5	14

The mean pH is significantly higher (0.99 confidence level) in the third quarter than in the combined first, second, and fourth quarters. This is probably related to the shift in water type toward a calcium bicarbonate-type water (fig. 16) and the general increase in alkalinity (fig. 15) from the rainy to the dry season.

The median pH in the West Branch is lower than at the other stations. The lower values may be related to the difference in water type--the West Branch is less of a bicarbonate water than are the East Fork or main stem (fig. 16).

Average percent-saturation values for dissolved oxygen are lower (0.95 confidence level) in the West Branch than in either the main stem or East Fork. The lower average dissolved-oxygen concentration may be caused by higher loads of allochthonous material (materials which originate outside and are brought into the waterway) from the forested watershed than from logged areas and lower exposure of the water surface to sunlight. Together, these would create a condition where respiration and decomposition rates exceed the rate of resupply of oxygen by both photosynthesis and reaeration.

SUMMARY

Hydrologic Effects of Logging

The conceptual model described by Kennedy and Malcolm (1978) that explains variations in major-ion composition with time and between watersheds for the Mattole River basin seems to apply to the Redwood Creek and Mill Creek basins. The Mattole River basin is in Humboldt County, Calif., on the north coast just south of the Redwood Creek basin.

Kennedy and Malcolm's (1978) description of the hydrology, which is based on work by Jamieson and Amerman (1969), is as follows. Stream discharge at any one time may consist of water from four different sources--base flow, delayed-return flow, quick-return flow, and overland flow. Base flow is water that percolates to depth in the soil and regolith and reemerges over a long period. Base flow dominates stream discharge during the dry season. Delayed-return flow is water that enters the soil, moves a short distance downward and laterally, and reemerges up to 24 hours later as seepage along shallow cuts in the land. Delayed-return flow dominates streamflow late in the recession part of the storm hydrograph. Quick-return flow is water that enters the soil and reemerges within one hour. Quick-return flow seems to contribute to the rise, peak, and early recession parts of the storm hydrograph and, in some cases, may dominate the rise and early recession. Overland flow is water that does not enter the soil but moves down gradient on the surface.

Kennedy and Malcolm (1978) suggest that as the rainy season progresses the soil becomes more saturated, causing overland and quick-return flows to become larger components of stormflow. Between storms, delayed-return and base flow dominate stream discharge. As the rainy season progresses, base flow becomes a larger fraction of the streamflow between storms because the ground-water reservoir is being increasingly filled.

Overland flow does not make intimate contact with the soil before entering the stream. Thus it presumably contains fewer dissolved solids than the other components of streamflow. Dissolved-solids concentration or specific conductance decreased at peak discharge a significant number of times in the VL-type watersheds but only occasionally in the VF-type watersheds. This suggests overland flow is an important part of peak discharge only in the watersheds that have been recently logged and is responsible for diluting the dissolved-solids concentrations. A statistical analysis suggests that overland flows sufficient to dilute dissolved solids concentrations at the hydrograph peak are two to three times as likely to occur in logged watersheds as in forested ones. Table 6 shows that dilution at the peak occurs both early and late in the rainy season, suggesting that overland flow is an important part of the peak discharge in VL-type watersheds throughout the rainy season.

This analysis indicates that overland flow occurs more often in a logged watershed than in a forested watershed. Intense rainfall would probably cause overland flow in a forested watershed as well, and table 6 shows that dilution at peak discharge occurred occasionally in the VF-type watersheds, but not with the regularity observed in the logged watersheds. Apparently, quick-return flow was the more important part of peak discharge in VF-type watersheds. Janda, Nolan, and Harden (1975b) found that the time of peak discharge in VF-type watersheds consistently lagged behind that in VL-type watersheds. This supports the view that quick-return flow rather than overland flow was the more important component of peak discharge in forested watersheds.

Systematic Variations in Major-Ion Composition with Time

The most important changes in chemical composition with time are a regular shift in water type from season to season and accompanying changes in the sum of dissolved solids. At the end of the dry season, streams tend to peak in specific conductance (hence, dissolved-solids concentration) (fig. 8) and to be a calcium bicarbonate type (fig. 13). As the rainy season progresses, the water type shifts steadily toward sodium chloride, and the specific conductance decreases, reaching a minimum in late March or early April. The change in water type through the rainy season is particularly evident from the chemograph data (fig. 6). Through the dry season, the water type steadily shifts back to calcium bicarbonate (fig. 13). This pattern is observed to about the same degree in all watersheds studied, although some distinction in watersheds by land use is evident. These variations are discussed later.

The probable mechanism for the changes in water type and dissolved-solids concentration is as follows. The first rains enter the soil and dissolve the soluble materials accumulated during the dry season, both products of weathering and salt spray from the ocean. A large part of this water probably percolates to the ground-water reservoir and later appears as base flow. The remainder of the water runs off, probably as quick-return and delayed-return flow. This process is repeated with each rain. As the soil becomes more saturated and the water table rises, less water percolates and more appears as overland and quick-return flows. Repeated rains also leach the soils of soluble materials. Runoff from the early rains tends, therefore, to be of the same type and dissolved-solids concentration as the base flow except where the overland flow component is large. But as the rainy season progresses, available soluble materials decrease relative to the volume of runoff. Hence, runoff from rains later in the season contains less calcium and bicarbonate derived from the weathering of the Franciscan-based soils.

At the end of the rainy season, the water stored in the soil appears as base flow. Early in the dry season, the base flow consists largely of the water from the most recent rains. As the dry season progresses, and the water table falls, an increasing fraction of the base flow consists of water percolated to the water table at various times in the rainy season just concluded.

More study is required to add detail to this simple conceptual model. In its present form the model explains the steady progression with season from high to low and back to high dissolved-solids concentration, and from calcium bicarbonate to mixed and back to calcium bicarbonate water type.

Because chloride salts are not produced in significant concentrations by the weathering of most rocks, the ocean is probably their source in runoff water. The chemograph studies suggested that chloride enters runoff water by different mechanisms early and late in the rainy season. Chloride concentrations were equal in both Harry Wier and Little Lost Man Creeks in November, and the time series of chloride concentrations were identical to the time series of other constituents. This suggests that the predominant source of chlorides was the soil before the rain. Chloride salts were probably accumulated as dry fallout during the summer.

In February, the chloride concentration was higher in Little Lost Man Creek than in Harry Wier Creek and tended to remain constant through the discharge hydrographs of both streams. This suggests that late in the rainy season the predominant source of chloride was the rain itself. The chloride concentration was higher in Little Lost Man Creek probably because that creek is closer to the ocean than Harry Wier Creek and received more sea spray in the precipitation. The water type shifts toward sodium chloride as the rainy season progresses because other salts are derived from the soil and become scarce relative to the volume of runoff whereas the chloride salts come with the rain.

The pH values also seem to vary seasonally. In the base flow and flow between storms (represented by the regular data) the median pH reaches a minimum in the first calendar quarter and a maximum in the third calendar quarter (table 11). This follows approximately, and is probably related to, the overall pattern in alkalinity--minimum in the first quarter and maximum in the third quarter (fig. 8). The seasonal patterns in pH and alkalinity are not uniform in all watersheds. Systematic differences in the patterns may be related to land use. The pH values observed during stormflow showed very weak patterns with season (fig. 7). The pH values for VL-type streams tended to be significantly higher than for the VF-type streams in the first quarter (table 8).

Variations in Physical Conditions and Major-Ion Composition between Land-Use Types and Regolith Types

Stream temperatures are more variable in watersheds with more soil surface or stream surface exposed to the open sky. Mean temperatures in RF-, VL-, and MS-type streams during stormflows are higher than in the VF-type streams in the fourth quarter and lower than in the VF-type streams in the first quarter (table 8). This pattern suggests that exposure of the soil leads to higher water temperatures in autumn and lower temperatures in winter during stormflow. This pattern is not seen in the regular data (fig. 8). Diel studies showed that exposed streams are warmed more in daytime and cooled more at night than are shaded streams.

During the summer months, the main stem is significantly warmer above Harry Wier Creek than below it. This difference may be due to the greater exposure of the main stem above Harry Wier Creek, together with the cooling effect of water entering the main stem below Harry Wier Creek from tributaries in the park.

During low flow, watersheds having more exposure to weathering (VL- and RL-type) tend to have water with higher dissolved-solid (as indicated by specific conductance) and alkalinity concentrations than the forested (VF- and RF-type) watersheds (fig. 8). Also, the main stem above Harry Wier Creek has higher dissolved-solids and alkalinity concentrations at low flow than the main stem below Harry Wier Creek (fig. 9). The drainage basin above Harry Wier Creek is highly exposed both because of heavy logging and because the natural vegetation is sparser than in the drainage basin below the creek. Within the group of logged watersheds (VL), streams from the schistose regoliths (St) have the lowest dissolved-solids and alkalinity concentrations, and streams from the sandstone-based regoliths (Sn) have the highest concentrations (fig. 10). Within the group of schistose (St) watersheds, no differences in dissolved solids or alkalinity between land-use types were discernible, except that Bridge Creek, the watershed in the study area perhaps most heavily scarred by the various activities accompanying logging, has the highest dissolved-solids and alkalinity concentrations of any stream studied (fig. 11). Other factors not investigated here may contribute to high dissolved-solids concentrations in Bridge Creek, however. Thus, a firm cause-and-effect relationship cannot be established without further study.

Differences in water types can also be seen between land-use types and regolith types. During the rainy season, water types from the forested watersheds, logged watersheds, and the main stem form a regular progression from a mixed calcium-sodium bicarbonate-chloride type to a calcium bicarbonate type (fig. 12). This progression corresponds to increasing exposure of the watershed to weathering due either to logging or to natural differences in vegetative cover. During the dry season, water from the group of VL- and RL-type watersheds (excluding the schistose watersheds) tends to be a more calcium bicarbonate type than water from the VF- and RF-type watersheds (figs. 13 and 14).

The schistose (St-type) watersheds provide less consistent results. Generally, the water in this group of streams is a mixed calcium-sodium bicarbonate-chloride type, regardless of the land-use type, but Low-Slope Schist Creek (VF-type) has a distinctive sodium chloride-bicarbonate type water. In contrast, Bridge Creek (RL-type) has a calcium bicarbonate type water (fig. 14).

The results discussed above suggest that exposure of the land surface increases the rate of weathering of the native regolith. The sandstone-based regoliths generally are most susceptible and the schistose regoliths generally least susceptible to accelerated weathering, but extensive soil disruption in the schistose watersheds, as in Bridge Creek, may overwhelm the apparent natural resistance of the schistose regolith to weathering.

Variations observed during diel studies were related to the level of exposure of the water surface locally at the study site but not to land-use or regolith differences. At sites open to the sky, considerable variation in dissolved-oxygen concentration and pH occurred. The waters are usually slightly undersaturated and seldom supersaturated with oxygen, however, suggesting that, overall, biological respiration exceeds biological productivity in these streams. It is common to find respiration exceeding production in streams from forested watersheds (Hynes, 1970).

Variations in Concentrations of Other Constituents between Land-Use Types and Regolith Types

Variations in concentrations of the plant nutrients and vegetation products--phosphorus, ammonia, Kjeldahl nitrogen, nitrite plus nitrate, and dissolved organic carbon--present a reasonably clear and consistent pattern in the chemograph studies. The pattern in the regular data is rather confusing.

In the chemograph studies, dissolved phosphorus, ammonia, Kjeldahl nitrogen, and dissolved organic carbon concentrations generally decreased, some dramatically, in both Harry Wier and Little Lost Man Creeks between November 1974 and February 1975.

In the analysis of the regular data (table 12), concentrations of nitrite plus nitrate, Kjeldahl nitrogen, dissolved phosphorus, and dissolved organic carbon decreased from the rainy season to the second or third calendar quarter. The median nitrite plus nitrate concentration is lower than the set median in VF-type watersheds and higher than the set median in VL-type watersheds. The median dissolved-organic-carbon concentration is higher than the set median in the RF-type watersheds. Dissolved phosphorus and Kjeldahl nitrogen show no pattern with land use.

The patterns observed in the chemograph studies and the regular data may be explained by the following mechanisms. Kjeldahl nitrogen, dissolved organic carbon, and dissolved phosphorus accumulate in the soil during the summer, and are subsequently diluted and washed out during the rainy season. Little of these constituents reaches the water table because of adsorption to the soil or because they are washed off of rather than down into the soil. Hence, concentrations in the base flow appearing in the second and third quarters are lower than those in the runoff during the rainy season. Higher dissolved organic carbon concentrations in the RF-type watersheds may be caused by heavy ground cover.

The occurrence of nitrite plus nitrate may follow a different mechanism from that just described. Nitrates can accumulate in soils from fixation and subsequent nitrification by leguminous weeds and shrubs. Because light penetrates to the soil more in logged than in forested watersheds, these nitrogen fixers may be more abundant in the logged watersheds. As the rainy season progresses nitrite plus nitrate accumulated by fixation and nitrification will be washed off of and leached down into the soil. In the VF-type watersheds, the nitrite plus nitrate that leaches down will be assimilated by mature trees so that little reaches the water table; hence, concentrations would be lower in the base flow from forested watersheds than logged watersheds, which is seen in the data. In VL-type watersheds, nitrite plus nitrate is not assimilated to the same extent as in VF-type watersheds. Further, as the rainy season progresses more is produced by fixation. Most of the excess thus available is carried off instead of leached down because much of the fixation occurs late in the rainy season when the soil is saturated. Hence, less appears in the base flow in the second and third quarters than appeared in the first quarter late in the rainy season. Nevertheless, more nitrite plus nitrate reaches the water table in the VL-type than in the VF-type watersheds, accounting for the higher values in the second and third quarters in streams from VL-type watersheds.

This conceptual model agrees with the finding of Likens and others (1969) that removing large trees from a watershed leads to an accumulation of nitrates which are available to wash out of the watershed.

These conceptual models of the occurrence of the plant nutrients are speculative and require a great deal more data to elaborate and verify.

Silica concentrations seem to change very little with season, according to the analysis of regular data (table 10), but a significant increase occurred between November 1974 and February 1975 in Harry Wier Creek, as observed in the chemograph studies (table 5). Median silica concentrations are higher than the set median in Sn-type watersheds and are lower than the set median in St- and Mx-type watersheds. No pattern was seen in the groupings by land use. The increase from November to February in Harry Wier Creek may have been caused by an increase in the rate of dissolution of the regolith as the soil became saturated. The higher silica concentrations in Sn-type watersheds may be related to the faster rate of weathering for the sandstone-based regoliths observed in this study, particularly in logged watersheds with Sn-type regoliths.

Aluminum concentrations increase through the rainy season (table 5) and decrease through the dry season (table 12). The pattern may be due to increased mechanical erosion of rocks and soils during the rainy season. Differences between regolith types are not observed but the median aluminum concentration in the RF-type watersheds is higher than the set median in the rainy season and lower than the set median in the dry season. This pattern is as yet unexplained.

Variations in the iron concentrations with season and between land-use and regolith types cannot be explained without further research.

Dissolved oxygen seems to be controlled by turbulence in the stream channel. No variations in the percent saturation were apparent with time or between land-use or regolith types.

The pH varied significantly with season, but no significant variations with land-use or regolith type were found. There is some indication (fig. 7) that streams in RF-type watersheds had lower pH values during the rainy season. This may be related to the higher dissolved-organic-carbon concentrations in these streams. High soil organic-carbon concentrations would be expected to cause lower soil pH which would, in turn, be observed in the streams.

The findings in the Mill Creek drainage basin can also be explained by the conceptual models speculated upon here for the Redwood Creek drainage basin.

NOTES ON THE REDWOOD CREEK ESTUARY

Downstream from Orick, Redwood Creek opens into a small, shallow estuary partly sheltered from the open ocean by a sand bar which alternately develops and recedes with changing season (fig. 17). The new channel was cut after the flood of 1964, and the remnant of the old channel carries water only at high flow. The small tributary to the north carries insignificant flow.

In the high-discharge periods of winter and spring, the sand bar is broken through at one or more points, allowing connection to the ocean. The bar rebuilds during the late spring to early autumn period and usually closes off the estuary, preventing surface discharge to the ocean.

Specific conductance was measured at several points in the estuary in May, July, and August 1974, and in May and September 1975, to determine the salinity change with depth. The sharpness of the gradient suggests the relative dominance of tidal and streamflow forces in the estuary. Although measurements were made along all three lines shown in figure 17, observations at each line are alike at each time. The findings are presented only in schematic form (fig. 18). The data from these studies are published in Iwatsubo and others (1975, 1976).

There is no evidence that saltwater enters the estuary from the ocean in May. Apparently, discharge is so high that it overwhelms the tide, preventing the saltwater wedge from entering the estuary. By July, however, flows allow creation of a sharply defined saltwater wedge which is first detected about one-half meter below the surface. At this time, fresh water is overriding the denser saltwater wedge. By August and September, tidal action is more dominant in the estuary; specific conductance values are higher both at depth and at the surface. The saltwater wedge is still well defined, however.

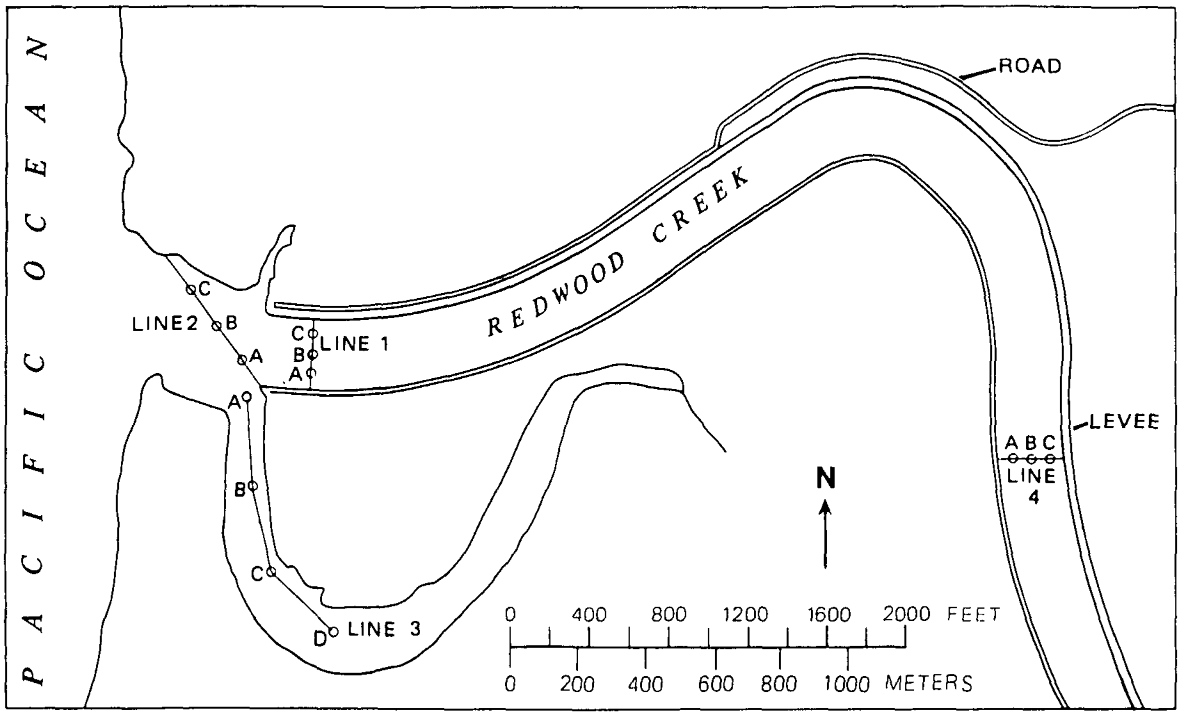

FIGURE 17.--Sampling stations in the Redwood Creek estuary area. Lines and letters show stations sampled (Iwatsubo and others, 1975, 1976). The graphs in figure 18 are based on data from these stations.

When the channel is blocked by the sand bar, a special case arises. Water may seep into or out of the lagoon through the bar, but any tidal action is strongly damped. Fresh water added to the estuary from upstream backs up into the lagoon and gradually forces the saltwater back through the sand to the ocean under a positive hydraulic gradient. Hence, the specific-conductance gradient in September (with a closed channel) shows fresh water to a depth of 0.76 m and a gentle gradient below, with a lower maximum value than in August. The Redwood Creek estuary, when an open channel, seems to be a salt-wedge estuary as described by Pritchard (1967, p. 3-6), suggesting that the ratio of tidal flow to streamflow is always less than 1.

REGRESSIONS

Regressions of specific conductance against discharge, dissolved-solids concentration against discharge, and dissolved-solids concentration against specific conductance were developed using the regression program of Steele (1973) for each of the stations in the Redwood Creek and Mill Creek drainage basins (table 20). These regressions may be used in future projects to model the concentrations of dissolved solids from the measurement of stream discharge alone.

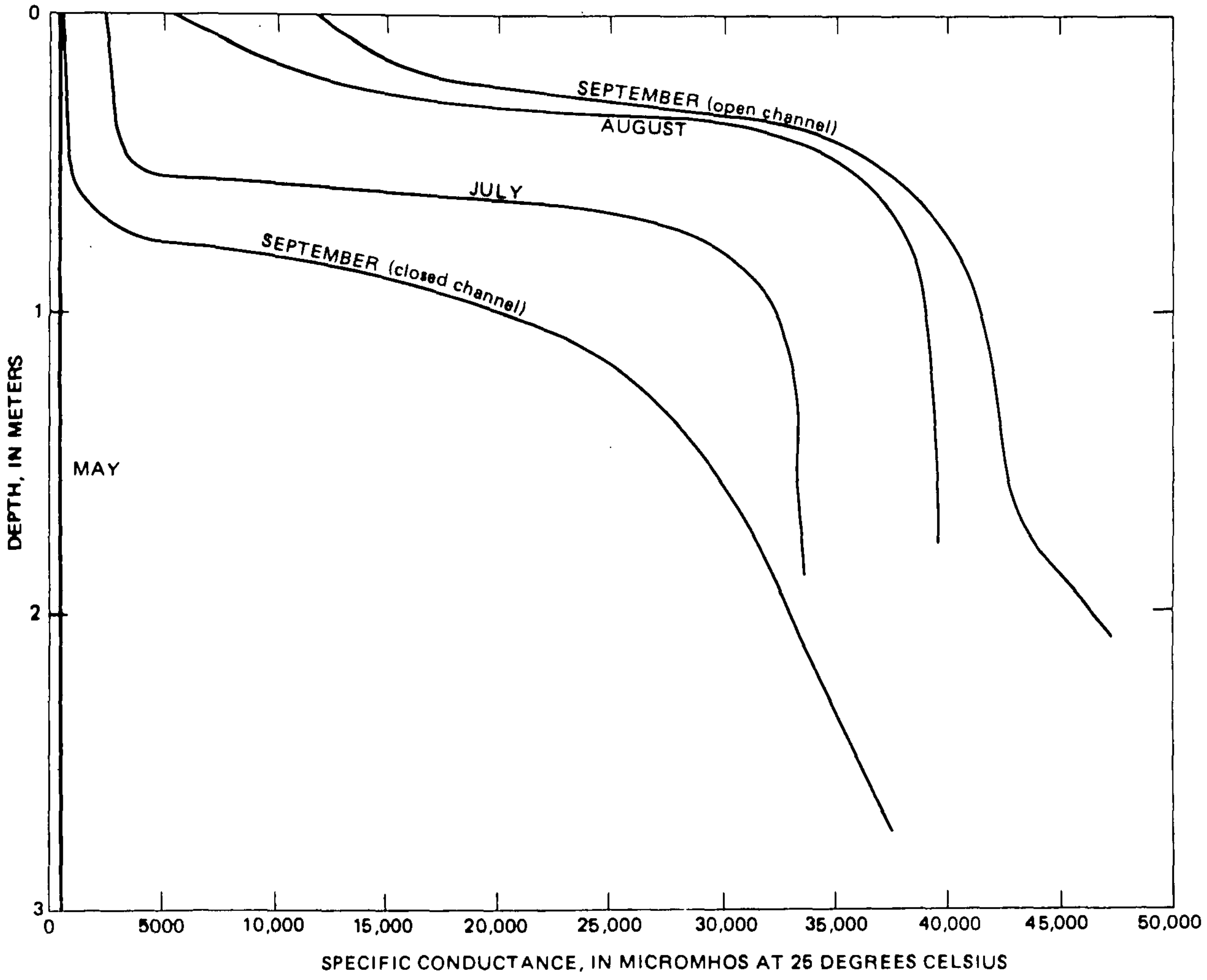

FIGURE 18.--Generalized changes in specific conductance with depth, Redwood Creek estuary.

TABLE 20.--*Regression coefficients of specific conductance against discharge, dissolved-solids concentration against discharge and dissolved-solids concentration against specific conductance for stations in the Redwood Creek and Mill Creek drainage basins*

[SC, specific conductance; DS, dissolved solids; r, correlation coefficient; SE, standard error of estimate; N, number of samples; c and k are constants; Q, water discharge]

Station number and name	$\log_{10}(SC)=\log_{10}c-k\log_{10}Q$					$\log_{10}(DS)=\log_{10}c-k\log_{10}Q$					DS=a+b(SC)				
	Log c	k	r	SE	N	Log c	k	r	SE	N	a	b	r	SE	N
11481500 Redwood Creek near Blue Lake	2.5113	0.2481	-0.97	0.0554	16										
11482020 Redwood Creek at Redwood Valley Bridge, near Orick	2.7492	.2908	-.88	.1071	15										
11482110 Lacks Creek near Orick	2.2341	.1947	-.90	.0469	25										
11482120 Redwood Creek above Panther Creek, near Orick	7.7803	.2747	-.92	.0925	14										
11482140 High-Slope Schist Creek near Orick	1.7690	.1795	-.98	.0355	10										
11482160 Copper Creek near Orick	1.9030	.1306	-.74	.0671	24										
11482190 Slide Creek near Orick	1.9653	.1613	-.63	.1360	22										
11482200 Redwood Creek at South Park Boundary, near Orick	2.6294	.2167	-.94	.0759	64	2.3399	0.1985	-0.99	0.0343	11	7.07	0.537	0.998	2.62	10
11482210 Bridge Creek near Orick	2.2155	.2021	-.69	.1431	15										
11482220 Redwood Creek above Harry Wier Creek, near Orick	2.8156	.2739	-.96	.0740	18										
11482225 Harry Wier Creek near Orick	1.9685	.1529	-.88	.0961	198	1.8066	.1955	-.91	.0793	44	8.11	.494	.994	2.32	43
11482230 Tom McDonald Creek near Orick	1.8089	.1114	-.75	.0761	28										
11482240 Fourtyfour Creek near Orick	1.7738	.1385	-.79	.0792	22										
11482250 Miller Creek near Orick	1.7796	.1118	-.85	.0706	148	1.5671	.0783	-.91	.0422	11	12.5	.424	.97	2.35	11
11482260 Miller Creek at mouth, near Orick	1.8214	.1174	-.90	.0657	171	1.5904	.0952	-.95	.0368	13	11.3	.422	.98	2.35	13
11482270 Bond Creek near Orick	1.7391	.1472	-.83	.0437	15										
11482280 Cloquet Creek near Orick	1.7846	.1050	-.95	.0375	8										

Creek near Orick															
11482295 Gans South Creek near Orick	1.7015	.0037	-.06	.0396	7										
11482300 Elam Creek near Orick	1.7584	.1056	-.91	.0371	9										
11482305 Gans West Creek near Orick	1.6978	.0766	-.79	.0328	6										
11482310 McArthur Creek near Orick	1.8682	.1282	-.70	.0605	19										
11482320 Los-Slope Schist Creek near Orick	1.6488	.0532	-.72	.0362	12										
11482330 Hayes Creek near Orick	1.8950	.1560	-.82	.0864	104	1.6511	.1015	-.90	.0528	6	8.29	.512	.992	1.76	6
11482450 Lost Man Creek near Orick	1.9171	.1825	-.84	.1043	142	1.6869	.1454	-.95	.0529	11	8.33	.519	.94	5.71	11
11482455 Lost Man Creek Tributary near Orick	1.5753	-.0846	+.59	.0262	8										
11482460 Larry Damm Creek near Orick	1.8971	.1815	-.90	.0620	21										
11482468 Little Lost Man Creek at Site No. 2, near Orick	1.8433	.1272	-.92	.0528	121	1.6370	.0917	-.91	.0349	34	14.1	.405	.98	1.67	33
1182470 Little Lost Man Creek near Orick	1.7886	.0981	-.92	.0404	65	1.5801	.0533	-.52	.0264	7	8.33	.500	.61	1.31	6
11482475 Geneva Creek near Orick	1.6627	.1138	-.74	.0539	92	1.5241	.0441	-.42	.0340	5	7.42	.575	.75	1.92	5
11482480 Berry Glen Creek near Orick															
11482500 Redwood Creek at Orick	2.4443	.1600	-.92	.0637	67	2.1540	.1304	-.90	.0594	8	6.93	.553	.95	6.89	8
11532600 West Branch Mill Creek near Crescent City															
11532602 West Branch Mill Creek below Red Alder campground, near Crescent City	1.7749	.0821	-.94	.0359	21	1.5724	.0521	-.87	.0448	7	8.23	.500	.93	2.75	8
11532605 West Branch Mill Creek at Bridge, near Crescent City	2.0146	.1590	-.91	.0292	22	1.8513	.1436	-.58	.0502	6	9.25	.477	.48	3.67	6
11532610 East Fork Mill Creek near Crescent City	1.8648	.1116	-.96	.0148	9	1.6700	.1290	-.95	.0234	4	-13.8	.880	.98	1.28	4
11532615 East Fork Mill Creek at Bridge, near Crescent City	2.1981	.2035	-.87	.0457	21	1.9583	.1630	-.66	.0484	6					
11532620 Mill Creek near Crescent City	1.9081	.1070	-.95	.0350	55	1.6676	.0621	-.80	.0519	14	18.3	.321	.80	4.03	14
11532626 Mill Creek at Bridge, near Crescent City	2.2285	.2005	-.86	.0375	12	2.4584	.2965	-.65	.1000	6	5.40	.687	.47	9.09	6
11532630 Mill Creek at mouth, near Crescent City															

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