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GEOCHEMISTRY OF THE MATTOLE RIVER OF NORTHERN CALIFORNIA

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By

Vance C. Kennedy and Ronald L. Malcolm

A study of the changes in water quality with time and stream discharge,

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ABSTRACT

There is still much to be learned about the many complex processes which, together, control the chemistry of natural streams. A detailed study of the Mattole River, which drains a 620-square kilometer area in southern Humboldt County on the northern California coast, has provided an improved understanding of the controls on major and minor dissolved constituents in a stream which is virtually unaffected by municipal pollution. The Mattole basin has relief of about 1200 meters and is underlain mainly by graywacke, sandstone, siltstone, and shale. The general northwesterly trend of the stream basin is related to the northwest strike of the folded and faulted sedimentary rocks. Ranching and logging have been the main source of income in the basin and extensive erosion has occurred, especially during the past 30 years. Vegetation is predominantly grass, second-growth timber, and shrubs. Average annual rainfall of approximately 2300 millimeters for the basin as a whole has contributed to the development of well-drained acid soils. Much of the rainfall occurs during the months of November through March and little occurs in the summer months. This results in a pronounced variation in streamflow, from about 1 m^3/s in early fall to 1000 m^3/s or more in midwinter.

Changes in water quality are closely related to the annual cycle in stream discharge. During the late spring, summer, and early fall the low rainfall permits a buildup of soluble salts at or near the land surface, both from dry fallout and from weathering reactions within the soil. When the rainy season begins there is a flushout of the Na and Cl derived principally from sea salts and of NO_3, SO_4, PO_4, and K, most of which may be released during decomposition of surficial organic matter. As the rainy season continues and soil leaching becomes more thorough, the pH of the stream decreases, the concentrations of SO_4, Na, Cl, Ca, Mg, and HCO_3 decrease, and the SiO_2 concentration increases. Although highest NO_3 values occur during storm runoff early in the rainy season, there continues to be a new pulse of NO_3 leached from the soils with each new storm throughout the rainy season. Limited data suggest that the variation in concentration of PO_4 is greatly constrained by interactions with stream sediment, although some increase in concentration apparently occurs relatively early during each individual storm-runoff period.

Trace-metal concentrations in river water appear to be controlled generally by rapid interactions with shallow soil materials and stream sediments, as modified by the degree of complexation with dissolved organics. Therefore, there is little evidence for a dilution of trace metals during storm runoff in the manner observed for Ca and Mg. In fact, Al and Fe show a distinct tendency to increase in concentration with rising stream discharge, although not to the degree that NO_3 increases.

After the rainfall decrease in late spring, the concentrations of most of the major constituents in the stream water gradually increase with falling discharge. After early August the rate of increase in dissolved electrolytes slows until the rainy season returns again. NO_3 differs from most of the other dissolved constituents by decreasing during the late spring to very low concentrations which are maintained throughout the summer. These low NO_3 levels are presumably due, at least in part, to removal by stream biota. SiO_2 concentration remains relatively high during late spring and early summer but then decreases rapidly just before the time when the dissolved electrolytes level off in concentration.

The pattern of changes in concentration outlined above for the various dissolved constituents in the Mattole River can be interpreted in terms of water sources. In late summer, before the fall rains begin, streamflow is coming primarily from ground water, which is in or near chemical equilibrium with the calcium carbonate of the bedrock. Early light rains leach soluble salts downward into the surface soils, and any runoff which occurs may be high enough in dissolved solids to cause a readily detectable change in stream water composition. With more intense rainfall, the infiltration rate of water into the surface soil in certain areas may be exceeded and some water then runs over the surface as surface runoff. However, a portion of the rain water which has entered the soil or has been in very intimate contact with the soil surface will have dissolved readily soluble salts and may contribute to storm runoff within a very short time. Such quick-return flow probably accounts for much of the increased NO_3, PO_4, SO_4, Al, and Fe observed during a stream rise. Rainfall which percolates deeper into the soil and is retained for days, weeks, or even months in the unsaturated zone above the water table before returning to the surface drainage is delayed-return flow. It provides much of the support for Mattole River discharge during between-storm periods in the rainy season and during the long slow decline in discharge in late spring and early summer. By mid-summer the delayed-return flow is depleted and most of the stream flow is probably derived from ground water.

Rainfall and dry fallout comprise the source of virtually all of the Cl carried by the river, with approximately 90 percent of the Cl being deposited during the rainy season. Inasmuch as the Cl:Na ratio in precipitation within the basin is that of sea water, the Cl serves as a convenient measure of the sea-salt input to the basin.

Rapid erosion within the river basin causes suspended-sediment concentrations to exceed 14,000 mg/L during very high stream discharge. Because the average cation-exchange capacity of the suspended sediments is approximately 18 meq/100 g, the quantity of adsorbed cations carried is significant when compared with that in solution.

In fresh-water sediments Ca is the major exchangeable cation, with lesser Mg and K and very little Na. As these sediments move into the brackish-water environment, the Ca is gradually displaced and Mg, K, and Na all increase as proportions of exchangeable cations. At a salinity of about three parts per thousand Mg achieves a maximum as a proportion of exchangeable cations, and thereafter decreases with further increases in salinity. Increased salinity causes Ca to continue decreasing while K and Na increase on the exchange sites. The net result of the change from fresh water to seawater in Mattole River sediments is to cause a pronounced decrease in exchangeable Ca, a great increase in exchangeable K and Na and relatively little net change in Mg.

The concentrations of the trace metals Cd, Cu, Pb, and Zn are all less than 1 μg/L in the Mattole because of the strong adsorption of these metals on sediments under these slightly alkaline, low salinity conditions. In the mildly acid (pH 4.5-6) soils, concentrations of these metals in interstitial water are believed to be on the order of 10 times that in the stream. This suggests a marked reduction in concentration of these trace metals as subsurface runoff moves from the soil into the stream channels. When the freshwater sediment encounters seawater a limited amount of the adsorbed trace metals are released.

INTRODUCTION

In temperate nonarid climates soils cover most of the land surface over which storm runoff travels or through which rainfall percolates on its way to the stream or the water table. It is well recognized that weathering commonly causes a vertical zonation in both the mineral and chemical composition of soils. Perhaps not so well documented is the variation in the chemistry of water contacting the various soil horizons. During heavy rainfall, when much stream flow results from water moving off the land surface, the stream chemistry should reflect the composition of rain water as modified by reactions with surface-soil materials. After rainfall ceases, water continues to drain from the soil and, with increasing time, there is an opportunity for penetration of water to greater depths in the soil before seeping out again to enter the water courses. This reasoning suggests that, for any particular stream basin, there should be consistent changes in the degree of dilution of dissolved solids and in the relative proportions of the various dissolved constituents during the stream rise and fall associated with rainfall.

As storm runoff moves through the stream channel system it carries suspended sediment which has an opportunity to react with the water to alter the content of dissolved constituents. Chemical reactions may also occur with bed sediment. The nature of these chemical reactions will be determined by the character of the sediment and the chemistry of the water. When this water-sediment mixture ultimately encounters the marine environment, a marked change in the composition of exchangeable cations will occur due to reaction with seawater. In addition to the rapid exchange reactions that occur, there are also slower reactions with sediment which can be quite significant in changing the concentration of some constituents in solution.

The interaction of rainwater first with the soil and then with the stream sediment involves complex phenomena which are not completely understood at present. As a contribution in gaining some understanding of these phenomena a detailed study was made, beginning in the fall of 1966, of the variations in solution chemistry and suspended sediment of a stream which has been relatively little affected by human activities except for logging and some ranching. The stream selected was the Mattole River, which heads in northern Mendicino County, California, and flows northwestward through an area of mature topography in southern Humboldt County before entering the ocean near Petrolia, about 50 miles south of Eureka, California (Figure 1). The purposes of the study were to determine (1) the variation of Mattole River chemistry and sediment characteristics with time and discharge, (2) the changes that occurred in the composition of exchangeable cations when the stream sediments are mixed with ocean water, and (3) possible causes for the observed changes.

Mattole Basin

The Mattole River (Figure 2) drains about 620 km^2 (240 mi^2) upstream from the sampling point. Ranching and lumbering have been the major sources of income in the area, but a little farming is done along the river. The towns generally consist of just a few buildings with other homes in the general vicinity. Population density at the time of the study was estimated as less than two persons per square kilometer.

Maximum relief is approximately 1200 meters (4,000 ft) and average relief is perhaps 460 meters (1,500 ft). Graywacke, sandstone, siltstone, shale and minor conglomerates, limestone and volcanic rocks comprise the rocks in the basin (Irwin, 1960; Nason, 1968). The general northwesterly trend of the stream basin is related to the northwest strike of the folded and faulted sedimentary rocks. The downstream half of the basin is characterized mainly by steep, grassy slopes with shrubs and second-growth trees located along some drainage lines and covering major parts of some tributary basins. The upstream half of the basin contains large areas of second-growth timber with scattered grasslands in an area of somewhat gentler topography.

Soils in the Mattole basin range from gravelly to clay loam (McLaughlin and Harradine, 1965) and have a pH generally in the range 4.5-6.0. In one 2.7 meter (9 ft) profile of upland soil sampled in this study the pH ranged from 4.8-5.2. Where relatively little recent erosion has occurred, the soil may extend to 3 meters (10 ft) or more in depth. In the last 25 years there has been extensive logging and associated road-building activity, and this has been a significant, and perhaps major, factor in the disturbance and resulting erosion of the soils. At present, erosion in the basin is rapid, and along drainage lines on some of the slopes the soil has been completely removed to bedrock. This erosion has caused aggradation of the river bed, and suspended sediment concentrations in the river may exceed 14,000 mg/L (1.4 percent by weight) during high flows.

Rainfall averages 2340 mm (92 in) per year for the basin as a whole but ranges from about 1250 to 2800 mm (1250-2800 mm) for individual points within the basin, according to Rantz and Thompson (1967). Of this, approximately 74 percent appears as runoff, based on a 33-year record. The bulk of the annual rainfall occurs in the months of November through March with intense downpours associated with some storms. Normally, little or no rain falls from late May until late October.

As a result of both the annual alternation of a period of high rainfall with a long dry summer and the geologic characteristics of the basin, the discharge range of the river is very great. In October the stream flow may be 1 m^3/s (35 cfs) or less whereas a discharge of 1,300 m^3/s (46,000 cfs) or more has been attained during periods of storm runoff only a month or two later (Jorgensen and others, 1971). Because the onset of the rainy season can be rather abrupt, the monthly average discharge commonly increases rapidly in late fall, but the gradual release of the large quantity of water held in the soils, plus the tail-off of the rainy season, combine to make the spring and summer discharge pattern a slow decrease. Because the rocks in the basin have been highly compressed during folding and faulting, porosity and permeability outside the fracture zones are rather low, so there is no large ground-water reservoir to support stream flow in late summer.

Previous Work

A large body of literature exists describing the conceptual and mathematical modeling of rainfall-runoff relationships in stream basins. Horton's (1933) view of stream discharge as being composed of just two components, overland flow and ground water, has been supplanted to a large extent by considering a stream rise to be composed of surface runoff, subsurface runoff, and ground-water contributions, or base runoff (Sugawara and Maruyama, 1956; Linsley and Franzini, 1964; Freeze, 1972).

One of the better known mathematical models describing rainfall-runoff relationships is that presented by Crawford and Linsley (1966), in which they allow for the various routes by which rainfall can enter and move through a stream basin. Rainfall is considered to either (a) move overland to rills or larger channels because it has exceeded the infiltration rate of the soil, (b) infiltrate the upper soil zone and return as shallow subsurface runoff (quick-return flow) at a lower elevation to join surface runoff, (c) infiltrate somewhat deeper soil horizons before appearing as deeper subsurface runoff (delayed-return flow) further downslope or (d) penetrate through the soil to the ground-water reservoir before ultimately returning to the surface as seepages and springs. The amount of water which enters the stream by these various routes at a particular time and location is related to the rainfall and infiltration rates. As the intensity of rainfall varies from place to place in a basin, the proportions of rainfall following the different routes to the stream also change . Thus, as the period or intensity of rainfall increases, larger and larger areas of the basin experience an excess of rainfall rate over infiltration rate and contribute storm runoff to the stream system. This reasoning has led to the variable-source-area concept in which the areas from which storm runoff is derived are believed to change with time during a storm (Hewlett, 1961; Hewlett and Hibbert, 1967; Tennessee Valley Authority, 1965; Ragan, 1968; Hewlett and Helvey, 1970). Dunne and others (1975) have summarized work on the recognition and prediction of runoff-producing zones.

The chemical implications for water quality of these ideas regarding the sources and pathways followed by water present in the stream at any particular time are evident. As might be anticipated, there has been a development in ideas regarding chemical variations in streams that parallels the ideas regarding sources of water discharge. Durum (1953) reported an essentially constant value for the product of chloride concentration and stream discharge for the Saline River in Kansas during storm runoff, but found that the relation was quite variable at both the high and low ends of the discharge range. He noted a rapid increase in concentration of dissolved constituents during initial spring runoff and attributed it to solution of materials in the channel scour and to salts deposited at low flow. Nevertheless, the relatively constant load of chloride, over a wide range of stream discharge, suggests a very high chloride concentration in base runoff compared to storm runoff. The fact that composite samples were used by Durum (1953) in the preparation of the discharge-chloride relation undoubtedly gave somewhat different results than if single samples had been used. Hendrickson and Krieger (1960) showed that, although there was a general inverse relation between concentration of dissolved solids and discharge, the relation was not a simple one. In Kentucky, the specific conductance for a particular discharge during a stream rise commonly exceeded the specific conductance for that same discharge during the recession, resulting in a cyclic curve on a plot of conductance vs discharge. The relatively slow decrease (or occasional slight initial increase) in specific conductance during

increasing discharge was attributed to the leaching of readily soluble material from the soil and stream bed as well as to shallow ground water and channel storage. On the recession, the gradual increase in specific conductance was explained as surface runoff mixed with increasing proportions of water from bank storage and high-conductivity "older" ground water. The authors noted a change in the proportion of anions in the dissolved salts on a seasonal basis and stated that the sulfate:bicarbonate ratio in the Salt River was generally higher during high flows than at low flows. The increased SO_4 was attributed to leaching of surficial salts and removal of weathering products of sulfide minerals from shales and limestones.

In a study of the Columbia River basin Gunnerson (1967) related, on a seasonal basis, the concentration of various individual dissolved constituents, as well as the total of dissolved constituents, to stream discharge and observed an elliptical "doughnut" pattern on a plot of concentration vs discharge. The pattern shape varied in different headwater streams. These patterns near the headwaters were altered by mixing with tributary waters in a downstream direction. He pointed out that seasonally rising flows flush accumulated salts from the basin and seasonally falling flows remove only newly leached salts. Edwards (1973) used weekly samples to investigate the changes in water chemistry of several rivers in Norfolk, England as related season and stream discharge. He found that NO_3 and SO_4 concentrations increased with increasing discharge and attributed this to leaching from the upper part of the soil profile. Large increases in NO_3, SO_4, K, Na, Cl and SiO_2 occurred at the beginning of the fall rainy season with accumulated weathering products being flushed from the soil. SiO_2 was relatively insensitive to discharge but during spring and summer it was depleted by diatoms.

Hart and others (1964) in an attempt to explain the variation of dissolved solids with discharge in the Russian River of northern California assumed varying contributions of surface runoff, interflow and ground water, each having a characteristic composition, and were able to obtain a good correlation between quality and quantity of river flow. La Sala (1967) estimated with some success the dissolved solids content of several streams at various levels of flow from the discharge and measured average dissolved solids content of "overland runoff" and ground water. Actually, La Sala's "overland runoff" probably represented a combination of the overland flow and the quick-return flow of Jamieson and Amerman (1969). Cleaves and others (1970) studied the chemistry of rainfall and stream flow in a small basin in the Piedmont of Maryland and found evidence for components of storm runoff to be (1) rain falling directly into the channel, (2) rain falling onto the flood plain and displacing existing soil water, (3) rain passing through soils on the hillsides and, finally, (4) water which has reached the water table and enters the streams as base flow. Kennedy (1971) was able to explain the variation of SiO_2 concentration with discharge in streams of the Mattole River basin on the basis of overland flow, subsurface flow and ground water. The subsurface flow referred to by Kennedy (1971) included both the quick-return and delayed-return flow referred to in this report (see section on rainfall-runoff terminology).

An investigation of the chemistry of stream flow from a 24-hectare forested basin in the Piedmont region of Georgia was done by Ayers (1976), who concluded that, "variations in stormwater quality are largely explainable in terms of the physical and chemical processes operating in the soils that form the source areas of subsurface stormflow. In accordance with the variable source area concept, these soils may occupy only a small and varying percentage of the watershed area, chiefly along the perennial channel and its storm period extensions."

Glover and Johnson (1974) studied the lag of the minimum in dissolved constituents behind maximum stream discharge during storms at several points along a river. They found an increasing lag with distance downstream which was attributed to the fact that the velocity of a kinematic wave is always greater than the mean water velocity, so the discharge peak tends to outrun the dissolved solids minimum. A following paper by Walling and Foster (1975) pointed out that the lag observed by Glover and Johnson (1974) was due not only to travel time effects in the stream but to other important factors. Walling and Foster (1975) found a significant inverse correlation between the lag and amount of stream rise, preceding discharge, soil moisture deficit and a seasonal index which was related to the recency of soil leaching. This explanation is similar to the one given by Hendrickson and Krieger (1960) except that Walling and Foster mentioned that additional complexities are involved as evidenced by the fact that NO_3 and K concentrations often increase during flood events. Miller and Drever (1977) also found evidence for rapid solution of K from soil materials during the study of runoff from a single storm in the mountains or northwestern Wyoming. They concluded that storm runoff could be attributed to a combination of overland flow and a subsurface flow component. Hyne (1975), in an interesting review paper, emphasized the great effect of biota and decaying organic matter on stream chemistry due to reactions in the stream and in the soils of the surrounding land area.

Recently, increasing use has been made of oxygen isotope ratios in the attempt to determine the source of storm runoff. The O^{18}/O^{16} ratio in rainfall can vary considerably from storm to storm, whereas the ratio for ground water is much more stable and can be significantly different from that of rain during any one particular storm. Thus, for storms in which the O_{18}/O_{16} ratio differs greatly between rain and soil or ground water, the proportion of rain in storm runoff may be measurable. The technique holds considerable promise. In a study of a stream basin in Ontario, Canada, Bottomley (1974) presented results indicating that about 50 percent of the stream flow during storm periods was derived from prestorm storage water on valley slopes and from a shallow ground-water zone on the valley bottom. Such a view coincides with the suggestion of Hewlett and Hibbert (1967) that displacement of prestorm soil water may contribute to storm runoff. Although the soil permeability and hydrologic conditions in the Mattole basin are greatly different from those studied by Bottomley (1974), his results certainly suggest that a significant fraction of storm runoff in the Mattole basin may be displaced soil water during the latter part of the rainy season, for then the soils should be thoroughly wetted.

After the water enters a stream channel, there is an opportunity for continuing interaction of the solutes and solids as the stream flows along. This interaction has been verified in many studies. For example, Dall'Aglio (1971) found dissolved mercury in natural waters is almost totally adsorbed by stream sediments in less than an hour, and the rate of uptake is related more to grain size and surface area than to mineral type. Gunnerson and Morris (1964) found evidence for solution of suspended sediment in the increased conductivity of sediment-bearing water in canals and aqueducts. Kunishi and others (1972) reported PO_4 decreased downstream from 200 to 15 µg/L P (613 to 46 µg/L PO_4) as a result of adsorption on stream sediment. Kennedy (1965) showed that in some streams the exchange capacity of suspended sediment in a unit volume of water can equal or even exceed the quantity of cations carried in solution during high-flow periods when suspended-sediment concentrations are at a maximum. During low-flow periods in some shallow streams the exchangeable cations in the upper few millimeters of bed sediment can equal the cations in the water above the bed, thus indicating that these sediments can exercise significant stabilizing action on the composition of dissolved cations. Malcolm and Kennedy (1970) demonstrated that the rate of cation exchange for Mattole River sediment varied greatly with particle size. Approximately 50 percent exchange occurred in the clay-size fractions in less than 2 seconds but 50 percent exchange required over 10,000 seconds for 4-9.5 mm gravel.

When a freshwater-sediment mixture constituting stream flow enters brackish and marine environments the result is a change in the proportion of different exchangeable ions on the sediment. The nature of this change has been investigated by use of both radioisotopes and ordinary chemical analyses. In the case of Columbia River sediments, Evans and Cutshall (1973) found that suspended material placed in contact with seawater released 15-45 percent of the sorbed Zn^{65} and 30-60 percent of the Mn^{54} Bed sediments lost some Mn to solution but no detectable Zn. More than 90 percent of the Cr^{51} and Sb^{124} initially added to the river water remained in solution under freshwater conditions and their concentration varied inversely with salinity on entering the ocean. Muller (1964) studied the changes in the character of the major exchangeable cations on sediments on going from freshwater to the brackish and marine environments. He found, as salinity increased, exchangeable Ca decreased steadily, Mg increased gradually to a maximum in brackish water and then decreased with further increase in salinity. Na, K, and the Na:K ratio of exchangeable cations increased with increasing salinity. Under freshwater conditions Ca, Mg, K, and Na comprised 50, 30-35, 5, and 5 percent, respectively, of the exchangeable cations; whereas under marine conditions, these elements comprised 0, 20, 20-25, and 50 percent of the exchangeable cations. This distribution of exchangeable cations conflicts with the results of Carrol and Starkey (1960) in which Mg was found to be the major absorbed cation after suspending various clay minerals in seawater for 10 days.

Recently, Sayles and Mangelsdorf (1977) reported on the exchange reactions when freshwater sediments move into the marine environment. They stated that the rinsing of the sediment samples mixed with seawater prior to desorption of cations will cause gross errors in the relative proportions of measured exchangeable cations. A comment on this problem had also been made by Kennedy (1975) in a short note. As shown by Kennedy and Brown (1965), the rate of exchange on some clays is very rapid, with 50 percent of Mg-for-Na exchange occurring in 0.1 - .3 seconds and 90 percent within 1-2 seconds. Thus, equilibration of the seawater saturated clays with dilute leaching solution would occur very rapidly. To the extent that Ca, as well as Mg, were available in the diluted seawater, they would displace Na as the solution was diluted and be determined as exchangeable Ca and Mg. Therefore, the exchangeable cations on seawater-equilibrated clays, as determined by the method of Carrol and Starkey (1960), would depend upon the specific method of washing with distilled water. Other authors (Powers, 1959; Russel, 1970; Toth and Ott, 1970; Spears, 1973) have used a similar leaching technique on saline saturated samples without noting that simple dilution of the solution in contact with an exchanger can greatly change the relative proportions of the ions adsorbed (Helffrich, 1962, p. 156-158). The commonly reported excess of Mg over Na in exchangeable cations on seawater-saturated sediments thus is greatly in error. One can use the distilled-water washing technique only on homoionic sediments when the pH is near or above neutral, for then the H^+ ion concentration should be of little consequence.

Rainfall-runoff terminology of this report

The paths that rain follows from the time it strikes the land until it arrives at the outlet of the stream basin are not well understood, and this has contributed to the confusion in terminology describing the sources of water causing stream flow. Because there is no universally accepted terminology it is necessary to define the terms used in this report. Where feasible, a reference is given for the origin of each definition. Many of the terms have implications as to source, time and chemical composition.

Runoff - That part of the precipitation that appears in surface streams. It is streamflow unaffected by diversions, storage or other works of man (Langbein and Iseri, 1960).

Surface runoff - overland flow -

That part of the runoff which travels over the soil surface to the nearest stream. It is the part of the runoff that has not passed beneath the surface since precipitation (Langbein and Iseri, 1960). This is primarily a source term, but surface runoff should normally occur during, and for only a short period after, the rainfall. Chemically, surface runoff will reflect rain composition as modified by leachates from vegetation and reactions with suspended solids.

Subsurface runoff - interflow -

Rainfall that enters the soil but returns to the surface or appears in channels at a lower level without entering the permanent water table (modified from Joint Editorial Board, 1969). A source term with little implication as to time or depth of penetration. Chemically, the term implies intimate contact with soil and (or) rock with a resultant increase in dissolved salts.

Quick-return flow - That part of subsurface runoff entering stream channels shortly (in this report, within 24 hours) after the rainfall causing the flow has occurred (modified from Jamieson and Amerman, 1969). A time term with both source and chemical implications. The brief contact period allows relatively shallow penetration of the soil or a short path length of water movement through the soil subparallel to the land slope. The chemical constituents added to solution normally are those characteristic of surface soils.

Delayed-return flow - That part of subsurface runoff which enters stream channels beginning well after (more than 24 hours in this report) the rainfall causing the flow has occurred (modified from Jamieson and Amerman, 1969). Such flow can continue for months after rainfall ceases. A time term with both source and chemical implications. The time available permits penetration to considerable depth into the soil or rocks overlying the permanent water table.

Storm runoff - The runoff entering stream channels promptly after rainfall or snowmelt (Langbein and Iseri, 1960). This is a time term with little or no implication as to source or chemistry other than that rain penetration is slight and reaction with the soil is limited.

Ground water - Subsurface water below the permanent water table (modified from Joint Editorial Board, 1969). A source term with both time and chemical implications. Normally, ground water is assumed to have percolated slowly through soils and rocks with ample time to dissolve earth materials.

Base runoff - That part of the inflow to a stream derived from the permanent saturated ground-water flow system (Langbein and Iseri, 1960). This is a source term with implications of time and chemistry. The time of contact with rocks or soils is normally relatively long, and chemical near-equilibrium with earth materials is common.

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METHODS

Stream Water and Sediment

Field analyses and sample processing were done in a field laboratory prepared for that purpose. A steel building 3.7 m by 9.1 m was constructed near the river and a house trailer was placed adjacent to the steel building to provide additional laboratory space. Commercial power normally was available for operations except during very severe storms when power failure was common.

Stream-water samples obtained in this study were collected near midstream in polyethylene bottles during 1966-68 and filtered through 0.45 µm Millipore [1] membranes (through 0.1 µm membranes after 1968) as soon as possible after collection, using compressed air (Skougstad and Scarboro, 1968). Normally, samples of 4-8 liters were passed through a 102 mm diameter filter and the first 1-1.5 liters were discarded. Except under conditions of unusually clear water, the filter was partially clogged by sediment before any filtrate was retained, so the effective pore size of the filter was probably less than 0.2 µm for most samples. When samples containing more than 5000 mg/L of suspended sediment were filtered, the time for filtration occasionally exceeded 6 hours but commonly 2-4 hours were required. After filtration, 4 mL of reagent grade concentrated HNO_3 were added to each 3.5 L (1 gallon) of filtrate in a polyethylene bottle and the sample was held thus until it was analyzed for major constituents. Atomic absorption spectrophotometry was used for the determinination of Ca, Mg, Na, K and Sr. The Thorin method (Brown and others, 1970) was used for SO_4 in stream water and for rain samples analyzed prior to 1971. Rain samples collected in 1972 were analyzed for SO_4 using Stephen's (1970) method, but the turbidity was measured in a spectrophotometer instead of nephelometrically. Thereafter, stream water was analyzed for SO_4 by autoanalyzer using a modified version of the methyl thymol blue method (Technicon, 1971). A Technicon autoanalyzer was used for the determination of NO_3 (Technicon, 1970), Cl (O'Brien, 1962), PO_4 (Bernhardt and Wilhelms, 1967), and also for SiO_2 (Mullin and Riley, 1955) in those samples collected after 1968. SiO_2 analyses made in 1967 and 1968 were done by the method of Rainwater and Thatcher (1960) in the U.S. Geological Survey Sacramento water quality laboratory. Alkalinity (Rainwater and Thacher, 1960), pH and conductivity measurements were made in the field immediately after pressure filtration.

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[1] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Freeze-drying was used as a means of concentrating the dissolved salts from aliquots of selected samples taken prior to acidification, and the resulting residue was analyzed by emission spectroscopy (Barnett and Mallory, 1971). The sensitivity of the technique is great, but even so, "less than" figures were obtained for some trace elements. Although the use of "less than" figures does not yield an actual numerical value, it does show an upper limit on concentration. Elements determined in this fashion included Ag, Ba, Be, Bi, Cr, Ga, Sr, Sn, Ti, and V.

Major cations could be determined without pre-concentration, but an extraction step was required for the trace metals during most of the work. Ag, Cd, Co, Cu, Mo, Ni, Pb, and Zn were first chelated with ammonium pyrrolidine dithiocarbomate (APDC), extracted into methyl isobutyl ketone (MIBK) at pH 3, then analyzed by atomic absorption methods. Al, Fe, and Mn were chelated with 8-quinolinol, extracted into MIBK, and analyzed as for the other metals (Kennedy and others, 1974). Beginning in 1974 many of the analyses for trace metals were done using a flameless attachment to an atomic absorption spectrophotometer and, because of the increased sensitivity of the flameless method, no extractions were required except for analyses of seawater.

Suspended-sediment samples were obtained at low flow by compositing water samples collected at three points in the stream cross section. Under higher flow conditions sampling was done at five points equally spaced in the cross section. The sampling device, a DH-59 hand sampler (Inter-Agency Committee, 1963), was passed through the water column at the same rate at each sampling point so that the water collected represented the integrated effect of stream velocity and depth. Thus, all five samples could be composited to represent the average sediment concentration in the stream as a whole. Under very high flow conditions, when water velocities near the surface approached 4.5 m/s (G. W. LaRue, Oral Commun., 1970), only samples of the upper one-half meter (1.5-2 ft) of flow could be obtained. However, the extreme turbulence under such conditions should have caused sufficient vertical mixing that the samples truly represented the average concentration of transported sediment of fine-sand size and smaller. The load of coarse sand and gravel moving near the stream bed, which must have been large during high flow, was not sampled. Suspended-sediment samples were taken within 15-20 minutes of the collection of water samples.

The use of a bronze sediment sampler equipped with a brass nozzle and rubber gasket prevented the use of composited sediment samples for determination of exchangeable trace elements because of potential contamination. However, a 9 L (2.5 gallon) sample of river water was obtained in a polyethylene bottle immediately preceding or following the collection of the suspended-sediment composite, and this large sample was filtered to obtain sediment usable in determining exchangeable cations.

Sediment samples to be used for determination of exchangeable cations were filtered and the solids freeze-dried and stored for later extraction. The exchangeable cations were displaced using 0.5 N NaCl of pH 8.0 in most instances. A 5 g portion of sediment was treated with 20 mℓ of NaCl solution five times in succession. Each time after centrifuging, the supernatant solution was removed, fresh NaCl solution added, and the suspension thoroughly mixed. The suspension was centrifuged immediately after stirring during the first three leaches and was allowed to stand for one-half hour after stirring on the last two leaches.

The Na -saturated sediment was washed first with distilled water, then with ethanol until Cl free as determined by a $AgNO_3$ test. A solution of 1 N ammonium acetate (NH_4OAc) was used to desorb the exchangeable Na from the Na-saturated sediment in the same manner the exchangeable cations were orginally displaced, and the Na was measured to determine Na-exchange capacity.

A separate aliquot of the freeze-dried stream sediment was leached with 1 N NH_4OAc to determine the original exchangeable Na on the sediment. In a few cases 1 N NH_4OAc at pH 7 was used as the desorbing solution in the same manner as for NaCl (see above) and then all major cations were measured in one solution.

Sediment samples which had been in brackish or marine water were considered to have enough interstitial water remaining after filtering to prevent determination of exchangeable cations in the regular manner. These samples were extracted successively with 1 N NH_4OAc, and the Cl concentration in the acetate leachate was determined. Analyses of Cl in the water previously contacting the sediment (assuming negligible sorbed chloride) therefore permitted a calculation of the quantity of interstitial water present before drying. Other dissolved constituents in the water contacting the sediment were also determined based upon the ratio of Cl to other ions in sea water. This calculation permitted the correction for various cations in interstitial water to be made, thus resulting in the measurement of cations held in true exchange position. As indicated earlier, washing out the interstitial solution with distilled water is not feasible because of the rapid change in proportions of adsorbed cations when this is attempted.

Some samples of stream sediment were analyzed by a six-step semi-quantitative emission spectrographic method in which concentrations are reported as (0.1, 0.15, 0.2, 0.3, 0.5, 0.7) x 10^n (Myers and others, 1961). A number of these samples were analyzed by a rapid-silicate method for major constituents (Shapiro and Brannock, 1962), for As by colorimetry (Ward and others, 1963), and for Cd, Cu, Ni, Pb, Zn, and Hg by atomic absorption (Ward and others, 1969; Vaughn and McCarthy, 1964). When separation of individual size fractions was required, this was done by sedimentation in distilled water without chemical dispersants after air-jet dispersion (Chu and Davidson, 1953).

Rain

Rain samples were collected in several ways, depending upon the type of information desired. During the rainy seasons of 1966-67 and 1968-69, an inverted 500 mL polyethylene bottle, from which the bottom had been removed, was used as a collector for most samples. The collector was mounted at the top of a wooden post 1.5-2 m above the ground. A Tygon tube attached to the base of the collector allowed rain water to flow downward into a 3.5 L polyethylene bottle for storage. The storage bottle contained 5 mL of concentrated HNO_3 which served as a preservative. This type of sampler was used for the collection of total precipitation during successive periods of a few weeks at the field laboratory near Petrolia and at Honeydew, Ettersburg and Thorn.

Because analyses of the rainfall collected in 1966-69 showed considerable variation with time and sampler location, samplers were designed for obtaining separate sequential samples for each 1.4-5.4 mm increment of rainfall. These samplers were used during a storm in January 1972 to collect rainfall at two points in the Mattole watershed as well as at Menlo Park, California.

RAINFALL

Composition

The composition of bulk precipitation (dry fallout plus rainfall) in a total of 40 samples collected at Petrolia, Honeydew, Ettersburg, and Thorn is shown in table 1A for the period January 16, 1967-June 3, 1967 and in table 1B for the period October 1, 1968 to April 24, 1969. An average composition for the total precipitation in the basin during these two time periods was obtained as follows: the analyses were weighted according to normal annual rainfall at the sampling site and also according to the amount of rain falling during the collection period of a single sample compared to that falling during the entire period of precipitation collection. The average composition of the total precipitation during these two periods and the expected composition of the rain, if it were sea water diluted to a point where Cl was 1 mg/L, are shown in table 2.

Table 1. Average composition of bulk precipitation in mg/L at various sites in the Mattole River basin.

Part A. January 16 - June 3, 1967

Constituent	Sampling Site [1]				
	Petrolia	Honeydew	Ettersburg	Thorn	Weighted [2] Average of all sites
Na	1.3	1.1	1.1	0.9	1.1
Cl	2.6	2.2	1.6	1.6	2.0
Ca	1.8	4.3	7.7	7.5	5.5
SO_4	5.5	4.7	7.7	7.1	6.2
Mg	0.3	0.4	0.5	0.4	.4
K	0.1	0.4	0.1	0.1	.2 [3]
SiO_2	0.2	0.2	<0.1	0.1	0.1 [4]

Part B. October 1, 1968 - April 24, 1969

Constituent	Sampling Site				
	Petrolia	Honeydew	Ettersburg	Thorn	Weighted [2] Average of all sites
Na	1.2	.9	.8	.8	0.9
Cl	2.3	1.7	1.6	1.6	1.8
Ca	3.6	1.5	3.3	1.0	2.3
SO_4	2.9	3.6	4.6	5.8	4.2
Mg	0.3	0.4	0.2	0.2	.3
K	0.1	0.2	0.1	0.1	0.1 [3]
SiO_2	<0.1	<0.1	<0.1	<0.1	<0.1

[1] Distance from sea (SE): Petrolia, 7 km; Honeydew, 23 km; Ettersburg, 40 km; and Thorn, 50 km. Prevailing winds are from the northwest.

[2] Weighted on the basis of the isohyetal curves shown by Rantz and Thompson, 1967.

[3] One of the individual rain samples representing the bulk precipitation for about one month exceeded the average concentration by more than a factor of 15. The value was discarded and an average value for the three other stations for that period was substituted.

[4] Concentrations for 2 of 12 samples were deleted. If these two values (1.5 and 3.9 mg/L) are included, the average weighted concentration is 0.4.

Table 2. Relative proportions of dissolved constituents in seawater [1] compared to that in precipitation in the Mattole River basin, normalized to unit Cl concentration.

Water type	Constituent						
	Na	Cl	Ca	SO_4	Mg	K	SiO_2
Seawater	0.556	1.0	0.021	0.14	0.067	0.021	<<0.01
Precipitation, January 16-June 3, 1967	.553	1.0	2.8	3.1	.20	.10	0.05
Precipitation, October 1, 1968-April 24, 1969	.514	1.0	1.3	2.4	.16	.08	<0.1

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[1] Riley and Chester, 1971.

Composite rain samples obtained at four points in the basin during early 1967 and for the entire 1968-69 rainy season showed some consistent patterns. In general, the average concentration of dissolved salts in rain during a collection period decreased with increasing rainfall, and the decrease in Ca and SO_4 concentration was much greater percentagewise than for Na and Cl. Comparison of the average composition of dissolved solids in bulk precipitation in the Mattole basin with sea water normalized to unit Cl content shows that Na is essentially unchanged, Mg and K are increased in bulk precipitation by a factor of 2-5, SO_4 is increased by a factor of 20, and Ca by a factor of 100.

Both Na and Cl concentrations tend to be highest in precipitation near Petrolia whereas Ca and SO_4 show a slight tendency to be more concentrated in precipitation at Ettersburg and Thorn. The proximity to the ocean and prevailing winds from the northwest are believed to be partly responsible for the higher Na and Cl concentrations near Petrolia. A 1000-1200 m mountain range between the sea and the middle and upper Mattole basin may also contribute to the trend in rain composition within the basin. The Ca and SO_4 are thought to be largely land-derived because of their distribution within the basin, their tendency to increase in concentration in samples collected during relatively dry periods, and because Ca:Cl and SO_4:Cl ratios far exceed those in sea salts.

Because of the wide variation found in the composition of short-period rain samples obtained in 1966 and 1967 (Na=0.1-5.8 and Cl= 0.2-9.9 mg/L), an investigation of the detailed compositional changes during a single storm was made in January 1972. A Lucite funnel approximately 0.9 m (3 ft) on a side was used to collect the rain and each successive 2.6 mm (0.1 in) of rain filled a 2 L pyrex bottle at one site near Petrolia. A 0.45 m (18 in) funnel was used with 1 L bottles at Honeydew to collect each successive 5.3 mm (0.2 in) of rain. A recording rain gage at Petrolia was used to relate composition of particular samples to specific periods of rainfall. It was not possible to do this at Honeydew, except in a general way, because of the method of recording rainfall.

A plot of Cl concentration versus time is shown in figure 3 for the rainfall collected near Petrolia. The time span in which Cl concentration is shown as constant indicates the period required to accumulate 2.6 mm of rain in a single bottle. There is a distinct tendency for the Cl concentration to vary inversely with precipitation rate (figure 3) as has been reported elsewhere (Gatz and Dingle, 1971). However, the magnitude of the variation observed during this storm was somewhat surprising, Cl ranged from less than 0.02 to 38 mg/L, a factor of more than 1900 within one general storm period. The 38-mg/L sample was collected mainly during a short hail storm, which was accompanied by high winds, at the very end of the rainy period. Although wind direction was not monitored, the proportions of the various ions in this high-chloride sample certainly suggest that sea salts were being swept in from the ocean 6 km to the west. For example, if seawater were diluted to give 38 mg/L Cl, it would contain 21 mg/L Na, 2.5 mg/L Mg, 0.8 mg/L Ca, 0.76 mg/L K and 5.3 mg/L SO_4. In fact, the hail-rain sample contained 21 mg/L Na, 2.5 mg/L Mg, 0.9 mg/L Ca, 0.7 mg/L K and 5.2 mg/L SO_4. The agreement between theoretical and measured values is within analytical precision. Similarly, the last rain sample taken near Honeydew, which included the time of the hail storm near Petrolia, contained quite high Cl (28 mg/L) and also contained major dissolved constituents in the same proportions as seawater. Because the Honeydew collection station is located 16 km southeast of Petrolia, this suggests that the high-salt rain was widespread within the Mattole basin. The average Cl content of the 183 mm of rain collected during the period January 18 to January 24, 1972 at Honeydew was 1.47 mg/L, if all the samples are considered, but only 0.80 mg/L if the last sample containing the very high Cl rain is deleted. Similarly, the average Cl in 137 mm of rain at Petrolia was 1.18 mg/L if the hail [rain] samples is included but was 0.53 mg/L with that sample excluded.

The composition of the rainfall at Petrolia and Honeydew for the storm of late January, 1972, is presented in detail in table 3. The correlation coefficient r, between Cl and Na for 26 samples containing Cl values exceeding 0.02 mg/L at the Petrolia site was 0.99996, with the slope of the regression line indicating a ratio of Na:Cl of 0.547 compared to a ratio of seawater of 0.556 (Riley and Chester, 1971). A similar calculation for 28 samples at the Honeydew site yielded an r of 0.9996 with a ratio of Na:Cl of 0.564. The data are plotted in figure 4 to show graphically the relation of the Na:Cl ratio in rain to that of seawater.

Correlation between Cl and Ca is not as good as for Cl and Na but is still highly significant. The r for 27 samples from Petrolia was 0.982 and for 28 samples at Honeydew was 0.957. The ratio of Ca to Cl for the Petrolia samples was always higher than the 0.021 value for seawater (see table 3a). At Cl concentrations below about 2 mg/L the Ca:Cl ratio is considerably greater than at higher chloride concentrations. This tendency for an increased ratio of Ca to Cl in rain with low dissolved salts is not as pronounced for Mg,

Table 3a Composition of successive increments (2.65 mm) of rainfall near Petrolia, California, January 18-24, 1972.

Sample Number	Collection period[1] Date Time	Specific Conductance umho/cm at 25°C	pH[2]	Constituents in solution (mg/l)																Cl deposition rate gm/ha/hr
				Na	Cl	Ca	SO_4	Mg	K	NO_3-N	NH_4-N	Al	Cd	Cu	Fe	Mn	Pb	Zn	Ca/Cl[3]	
M2-1	1/18/72, 1500-1900	4.5	5.35	0.08	0.12	.09	0.2	0.01	0.03	0.04	0.05	0.001	0.0002	0.001	0.002	0.002	0.004	0.004	0.74	0.8
M2-2	1/18/72, 1900-1/19/72, 0200	4.2	5.25	.14	.23	.07	.2	.02	.03	.06	.06	.002	<.0001	<.001	.001	<.001	.004	.001	.31	.9
M2-3	1/19/72, 0200-1330	4.9	5.31	.31	.53	.03	.2	.04	.02	.02	.04	.002	.0001	<.001	.001	<.001	.002	.001	.051	1.2
M2-4	1/19/72, 1330-1/20/72, 0530	12.7	5.24	1.30	2.3	.09	.6	.16	.03	.06	.07	.002	.0001	<.001	.001	<.001	.004	.001	.040	3.8
M2-5	1/20/72, 0530-0745	3.6	5.38	.19	.34	.07	< .2	.03	.02	.02	.02	.006	<.0001	<.001	.014	<.001	.001	<.001	.20	4.0
M2-6	1/20/72, 0745-1230	12.6	5.14	1.26	2.2	.10	.6	.16	.02	.05	.07	.000	<.0001	<.001	.001	<.001	.003	<.001	.046	12.2
M2-7	1/20/72, 1230-2145	15.1	5.12	1.65	2.8	.14	.6	.19	.03	.04	.03	.009	.0001	.001	.016	.001	.002	.002	.048	8.0
M2-8	1/20/72, 2145-2345	13.8	4.95	1.22	2.1	.11	.6	.15	.02	.08	.04	.000	.0001	<.001	.002	<.001	.001	.001	.052	27.6
M2-9	1/20/72, 2345-1/21/72, 0035	4.6	5.33	.19	.34	.02	< .2	.03	-	.04	.04	.002	.0003	<.001	.002	<.001	-	.001	.050	10.7
M2-10	1/21/72, 0035-0155	5.1	5.28	.17	.32	.05	< .2	.03	-	.03	.03	.014	.0003	<.001	.024	<.001	-	.001	.16	6.4
M2-11	1/21/72, 0155-0225	2.1	5.24	.15	.28	.03	< .2	.02	-	.02	.03	.002	.0002	<.001	.001	<.001	-	<.001	.11	14.7
M2-12	1/21/72, 0225-0250	2.6	5.45	.04	.08	.04	< .2	.01	-	.01	.04	.002	.0002	<.001	.001	<.001	-	.001	.48	5.0
M2-13	1/21/72, 0250-0310	2.0	5.49	.01	<.02	.04	< .2	.00	-	.04	.05	.001	.0002	<.001	.001	<.001	-	.001	>2	<1.6
M2-14	1/21/72, 0310-0330	1.6	5.47	<.01	.02	.04	< .2	.00	-	.01	.02	<.001	.0002	<.001	.002	<.001	-	<.001	>2	<1.6
M2-15	1/21/72, 0330-0350	2.2	5.47	.02	.02	.01	< .2	.00	-	.02	.03	.002	.0002	<.001	.001	<.001	-	.001	>.7	<1.6
M2-16	1/21/72, 0350-0410	2.0	5.49	<.01	.02	.03	< .2	.00	-	.02	.02	.001	.0002	<.001	.001	<.001	-	<.001	>1.3	<1.6
M2-17	1/21/72, 0410-0435	1.8	5.58	<.01	.02	.03	< .2	.00	-	.01	.02	.003	<.0001	<.001	.001	<.001	.002	<.001	>1.6	<1.3
M2-18	1/21/72, 0435-0455	2.0	5.51	<.01	.02	.05	< .2	.00	-	.02	.03	-	<.0001	<.001	.002	<.001	.004	<.001	>2.5	<1.6
M2-19	1/21/72, 0455-0515	2.0	5.51	.01	.02	.04	< .2	.00	-	.02	.03	.001	<.0001	<.001	.001	<.001	.002	.001	>2	<1.6
M2-20	1/21/72, 0515-0530	4.1	5.32	.01	.02	.02	< .2	.00	-	.01	-	.001	<.0001	<.001	.002	<.001	.004	.001	>.8	<2.1
M2-21	1/21/72, 0530-0550	1.6	5.50	.01	.02	.03	< .2	.00	-	.02	-	.009	<.0001	<.001	.001	<.001	-	<.001	>1.6	<1.6
M2-22	1/21/72, 0550-0605	1.7	5.52	<.01	.02	.04	< .2	.00	-	.01	-	.003	<.0001	<.001	.011	<.001	-	<.001	>1.9	<2.1
M2-23	1/21/72, 0605-0630	1.7	5.45	<.01	.02	.02	< .2	.00	-	.03	-	-	-						>1.1	<1.3
M2-24	1/21/72, 0630-0700	1.8	5.46	.01	.02	.02	< .2	.00	-	.07	-	-	-						>1.2	<1.0
M2-25	1/21/72, 0700-0745	1.8	5.44	.02	.02	.04	< .2	.00	-	.01	-	-	-						>1.9	<.7
M2-26	1/21/72, 0745-0830	1.8	5.53	.02	.02	.04	< .2	.00	-	.02	-	-	-						>2	<.7
M2-27	1/21/72, 0830-0915	2.0	5.49	.01	.02	.03	< .2	.00	-	.02	-	-	-						>1.4	<.7
M2-28	1/21/72, 0915-1025	2.1	5.50	<.01	.02	.02	< .2	.00	-	.05	-	-	-						>1.1	<.5
M2-29	1/21/72, 1025-1225	2.2	5.45	<.01	.02	.03	< .2	.00	-	.02	.04	-	-						>1.3	<.4
M2-30	1/21/75, 1225-1555	4.0	5.30	.11	.19	.03	< .2	.01	-	.02	.03	-	-						.17	1.5
M2-31	1/21/72, 1555-1/22/72, 0115	16.9	4.94	1.63	3.0	.16	.8	.16	.05	.07	.05	.001	.0002	.001	.002	.002	-	.01	.052	8.5
M2-32	1/22/72, 0115-0400	14.3	5.08	1.38	2.5	.11	.6	.12	.04	.05	-	.001	.0001	<.001	.001	<.001	-	.002	.043	24.3
M2-33	1/22/72, 0400-0445	5.6	5.18	0.28	0.54	.03	< .2	.03	.01	.03	-	<.001	.0002	<.001	.001	<.001	-	.001	.057	18.8
M2-34	1/22/72, 0445-0545	5.2	5.18	.18	.34	.05	< .2	.02	.00	.02	-	.002	.0002	<.001	.001	<.001	-	.002	.14	8.9
M2-35	1/22/72, 0545-0630	2.9	5.36	.06	.11	.02	< .2	.01	.03	.02	-	<.001	<.0001	<.001	<.001	<.001	-	<.001	.18	3.8
M2-36	1/22/72, 0630-0715	2.0	5.46	.01	.02	.02	< .2	.00	.00	.02	-	-	-	-	-	-	-	-	>1.1	<.7
M2-37	1/22/72, 0715-0830	2.1	5.48	<.01	.02	.00	< .2	.00	-	.02	-	<.001	<.0001	<.001	<.001	<.001	<.001	.001	-	<.7
M2-38	1/22/72, 0830-0955	2.4	5.48	<.01	.02	.00	< .2	.00	-	.01	-	<.001	<.0001	<.001	.001	<.001	<.001	<.001	-	<1.3
M2-39	1/22/72, 0855-0930	1.6	5.43	<.01	.02	.00	< .2	.00	-	.04	-	.001	<.0001	<.001	<.001	<.001	<.001	.001	-	<.9
M2-40	1/22/72, 0930-1000	1.5	5.43	<.01	.02	.03	< .2	.00	-	.01	.02	<.001	.0001	<.001	<.001	<.001	<.001	<.001	-	<1.0
M2-41	1/22/72, 1000-1040	1.6	5.47	.01	.02	.00	< .2	.00	-	.00	.02	<.001	<.0001	<.001	.001	<.001	<.001	<.001	-	<.8
M2-42	1/22/72, 1040-1145	1.7	5.47	<.01	.02	.00	< .2	.00	-	.00	.01	<.001	<.0001	<.001	.001	<.001	<.001	<.001	-	<.5
M2-43	1/22/72, 1145-1225	2.1	5.38	.01	.02	.00	< .2	.00	-	.00	-	-	-	-		-	-	-	-	<.8
M2-44	1/22/72, 1225-1315	1.9	5.44	.01	.02	.00	< .2	.00	-	.02	-	-	-	-		-	-	-	-	.6
M2-45	1/22/72, 1315-1350	2.1	5.39	.02	.03	.00	< .2	.00	-	.00	-	-	-	-		-	-	-	-	1.3
M2-46	1/22/72, 1350-1420	1.8	5.46	.00	.02	.00	< .2	.00	-	.02	.02	-	-	-		-	-	-	-	1.0
M2-47	1/22/72, 1420-1445	1.9	5.44	.02	.04	.01	< .2	.00	-	.00	-	-	-	-		-	-	-	.38	2.5
M2-48	1/22/72, 1445-1520	2.2	5.44	.03	.07	.01	< .2	.01	-	.02	-	-	-	-		-	-	-	.14	3.1
M2-49	1/22/72, 1520-1555	2.1	5.48	.04	.04	.02	< .2	.00	-	.00	-	-	-	-		-	-	-	.50	1.8
M2-50	1/22/72, 1555-1710	2.8	5.24	.03	.06	.01	< .2	.01	-	.01	-	-	-	-		-	-	-	.22	1.3
M2-51	1/22/72, 1710-1/23/72, 1145	35.8	5.02	4.47	8.3	.31	1.1	.55	.16	.02	-	-	-	-		-	-	-	.038	11.6
M2-52	1/23/72, 1145-1/24/72, 1300	146	-	20.7	37.8	.86	5.2	2.47	.72	.03	-	.003	.0002	<.001	.002	<.001	-	-	.023	39.6

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[1] Based upon information from a recording rain gage and occasional observations during the collection period.

[2] Because of the very low ionic strength, precision was only about 0.1 pH unit. Procedure for each group of samples removed from the rain collector was to equilibrate an aliquot from the first sample by stirring with electrode inserted for 7 minutes, then replace that with a second aliquot which sat without stirring for 3 minutes before taking a reading. Successive samples were then measured after 3 minutes contact with no stirring.

[3] To be compared with thu Ca/Cl ratio in sea water which is 0.021.

Analysts were G. W. Zellweger and R. J. Avanzino.

Table 4 Composition of sucessive increments (5.3 mm) of rainfall near Honeydew, California, January 18-23, 1972.

Sample Number	Remarks[1]	Specific Conductance (µmho/cm at 25°C)	pH[2]	Constituents in solution (mg/L)						
				Na	Cl	Ca	SO_4	Mg	K	NO_3-N
M1-1	1/18/72, 1745; sampler set up.	7.0	5.20	0.48	0.90	0.13	0.2	0.06	-	0.04
M1-2		17.4	5.03	1.71	3.1	.17	.8	.21	-	.09
M1-3		8.1	5.25	.64	1.15	.09	.3	.08	-	.03
M1-4	On 1/20/72 at 1400 this bottle was 1/3 full.	23.1	4.94	2.39	4.3	.24	1.1	.27	-	.10
M1-5		16.3	5.11	1.58	2.8	.16	.7	.15	-	.04
M1-6		8.5	5.10	.66	1.20	.08	.3	.08	-	.03
M1-7		4.5	5.24	.18	.34	.05	< .2	.02	-	.02
M1-8		3.7	5.24	.07	.15	.04	< .2	.01	-	.02
M1-9		2.6	5.43	.02	.04	.02	< .2	.01	-	.01
M1-10		1.8	5.39	<.01	.02	.03	.2	.00	-	.01
M1-11		1.7	5.46	<.01	.02	.02	.2	.00	-	.02
M1-12		1.7	5.42	<.01	<.02	.02	.2	.00	-	.02
M1-13		1.8	5.54	<.01	<.02	.03	.2	.00	-	.04
M1-14		1.8	5.45	<.01	<.02	.05	.2	.00	-	.03
M1-15		2.4	5.40	<.01	.03	.04	.2	.00	-	.02
M1-16	On 1/21/72 at 1620 this bottle was 1/3 full.	10.2	5.06	1.19	1.55	.11	.4	.11	-	.03
M1-17		11.0	5.14	1.05	1.95	.10	.4	.13	-	.02
M1-18		5.2	5.23	.30	.57	.03	<.2	.04	-	.02
M1-19		4.2	5.24	.16	.27	.03	<.2	.02	-	.03
M1-20		2.7	5.36	.06	.09	.03	<.2	.01	-	.01
M1-21		1.7	5.40	<.01	<.02	.03	<.2	.00	-	.01
M1-22		1.7	5.41	<.01	<.02	.02	<.2	.00	-	.01
M1-23		1.6	5.41	<.01	<.02	.03	<.2	.00	-	.02
M1-24		1.8	5.44	<.01	<.02	.02	<.2	.00	-	.00
M1-25		1.9	5.40	.02	.03	.02	<.2	.00	-	.01
M1-26		1.9	5.42	.01	.03	.02	<.2	.00	-	.01
M1-27		1.7	5.44	<.01	.02	.02	<.2	.00	-	.00
M1-28		2.6	5.37	.04	.06	.03	<.2	.01	-	.01
M1-29		2.4	5.39	.05	.10	.02	<.2	.01	-	.01
M1-30		2.2	5.43	.05	.09	.02	<.2	.01	-	.01
M1-31	On 1/22/72 at 1650 this bottle just completed filling.	2.0	5.41	.04	.05	.02	<.2	.00	-	.01
M1-32		7.0	5.24	.60	1.10	.05	.2	.08	-	.01
M1-33		6.4	5.28	.52	1.00	.05	<.2	.07	-	.01
M1-34		6.8	5.23	.62	1.15	.05	<.2	-	-	.02
M1-35		28.8	5.06	3.07	5.9	.14	.9	.34	.11	.02
M1-36		108	5.12	15.8	28.0	.62	4.5	1.76	.53	.03

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[1] The time of collection of individual samples cannot be shown because there was no suitable recording rain gage at this station.

[2] Because the very low ionic strength precision was only about 0.1 pH unit, pH determinations done were as described for rainfall near Petrolia.

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Many of the rain samples taken during January 1972 were rather low in K concentration, so only those containing higher concentrations of other cations were analyzed for K; however, for 16 samples analyzed from Petrolia containing 0.02 mg/L K or more, r for K and Cl was 0.995 and the ratio K:Cl obtained from the regression line was 0.019 versus 0.021 for seawater.

When hailstorm values were excluded, NO_3 correlation with Na was significant at the 99 percent level at both rain collection sites in the Mattole basin (Petrolia, r=0.63, n=50; Honeydew, r=0.81, n=34). Inclusion of the hailstorm analyses in the correlation, with their high Cl and low NO_3-N concentrations, greatly decreases the correlation coefficient.

Both pH and specific conductance (Sp. Cond.) were measured on unfiltered samples within less than an hour after opening the collection bottles. As expected, the Cl concentration correlates well with Sp. Cond. (r=0.997, N=28 at Honeydew and r=0.999, N=27 at Petrolia), but below 1 mg/L Cl the correlation is poorer, with Sp. Cond. being greater than expected from the Cl concentration. The pH tends to decrease with increasing Sp. Cond. in the conductance range below 30 µmho/cm (25°C). In that conductance range, the correlation coefficients were 0.88 and 0.86 for Sp. Cond. versus H^+ concentration at Honeydew and Petrolia, respectively. The correlations are significant at the 99 percent confidence limit. Such a result is not surprising because H^+ constitutes up to 90 percent of the cation equivalents at very low conductivities.

Sulfate concentrations in most of the rain samples were below the detection limit of 0.2 mg/L; but, in the range 1-4 mg/L Cl, the SO_4 concentrations were readily detectable and tended to be about twice that expected from seawater. In samples containing 6 mg/L Cl or more the SO4:Cl ratio was quite close to that in sea water. The pH of about 5 for rain containing 1-4 mg/L Cl and "excess" sulfate suggests that the observed SO_4 may result from a combination of sulfuric acid and SO_4 from sea salts. The SO_4 concentrations in the 1972 samples are much lower than in the composite rain samples collected in 1967 to 1969 because dry fallout was included in the 1967-69 samples.

The presence of dilute sulfuric acid in rainfall has been reported by several authors (Junge, 1963; Reignam, 1970; Charlson and others, 1974; Likens and Bormann, 1974), especially near highly industrialized areas, where there is an obvious source from combustion of fossil fuels. However, there are no population centers of more than a few families closer than about 50 km to the southeast of the rainfall collection sites (wind direction, as indicated by movement of the lower cloud layers, was from the south-southeast during the early part of the two storms when "excess" sulfate was observed). The nearest potential sources of sulfur oxide gases are lumber mills which burn scrap material, but they lie 30-40 km to the northeast of the collection site. Thus, there are no obvious nearby sources for the sulfuric acid in the rain. However, Likens and Bormann (1974) have pointed out the potential transport of sulfur in the atmosphere for 1000 km or more based on a mean residence of 2 to 4 days (Robinson and Robins, 1968), so a distant source for the sulfuric acid appears feasible.

Alkalinity was not measured in the rainfall, but, for a few of the samples containing 2 to 4 mg/L Cl, it was calculated by difference from the balance of chemical equivalents of anions and cations. In such samples the alkalinity constituted about 5 to 10 percent of the anions. At very low Cl concentrations, all of the analyses were subject to considerable error as analytical detection limits were approached; however, the pH approached that of pure water in equilibrium with CO_2 of the atmosphere (pH= 5.7, Barrett and Brodin, 1955), and it is probable that alkalinity contributed a major fraction of the anions.

Some of the January 1972 rain samples were analyzed for ammonia and for several trace elements in order to determine their approximate concentration range in Mattole rainfall (Table 3a). At the concentration levels found in these samples sorption on the 0.1 µm Millipore membranes by some elements (and contamination by others) is a distinct possibility (Marvin and others, 1970; V. C. Kennedy and G. W. Zellweger, unpub. data, 1975) even though at least two liters of distilled water passed through the filter system before filtration of the rain sample began and 100-200 mL of the rain sample was wasted before taking samples in acid-washed polyethylene bottles. Subsamples were frozen (NH_4 and NO_3 analyses) or acidified to pH 1.5 or less (other constituents). The results indicate mean values in µg/L as follows: NH_4-N=40; Al=3; Cd=0.1; Cu=1; Fe=3; Mn=0.1; Pb=2 (sorptive losses for Pb especially can be large); and Zn=1. The tendency for Al and Fe concentrations to fluctuate together suggests that small amounts of clay may have passed through the 0.1 µm membrane. Because the rain was very low in concentration of suspended solids, little sediment was available to clog the filters and help block the passage of fine clay. As little as 0.2 mg/L suspended clay could contribute the Al and Fe observed in the most concentrated samples. The low ionic strength of the rain would encourage dispersion of the clay and help allow penetration of the filter. If the four samples containing more than 10 µg/L Fe are attributed to clay and excluded, then the mean value for Fe is about 1 µg/L. Similarly, if the four highest Al concentrations are eliminated, the mean value for Al is also 1 µg/L. The standard error of the analyses is 2 µg/L Al and Pb; 0.5 µg/L for Fe; 0.2 µg/L for Cd, Cu, Mn and Zn; and 10 µg/L for NH_3-N.

Discussion

The trace-element concentrations reported herein for rainfall vary in their agreement with data in other studies. Rancitelli and others (1970), using activation analysis, observed Cu in rainfall ranging from 0.4 to 3.4 µg/L, and Fe from 10 to 35 µg/L. Filtered samples were used, but filter pore size was not specified. Turekian (1969), quoting K. Sugawara on rainfall in Japan, reported Cu as 0.8 and Zn as 4.2 µg/L. Fe and Al concentrations were quoted as 230 and 110 µg/L, respectively, which was relatively high and suggest that the samples were unfiltered or passed through filters of rather large pore size. The ratios of Na, Mg and Ca to Cl in the Japanese data also suggest major contributions from continental dust because they greatly exceeded the ratios found in sea water.

Other bulk-precipitation data available for the Pacific coast which were collected under environmental conditions similar to those in the Mattole basin are those obtained by Steele (1968). Steele's estimated average composition of bulk precipitation from November 1966 to April 1967 for the Pescadero Creek area on the relatively undeveloped west side of the peninsula south of San Francisco was 1.0 mg/L Na and 1.8 mg/L Cl. These values are quite close to the 1.0 mg/L Na and 1.9 mg/L Cl found for average bulk precipitation in the Mattole basin the same year. Steele's collecting station nearest the ocean was 10 km inland and ours about 7 km inland. As in the Mattole basin, Steele found that significant deviations from the average were observed in Na and Cl concentrations as well as in Na:Cl ratios in rain samples collected from different sites or at different times.

Whitehead and Feth (1964) studied the chemistry of rain, dry fallout, and bulk precipitation at Menlo Park, California. Their results agree with the present Mattole study in showing increased concentration of dissolved solids in bulk samples over that in rainfall alone and indicate that the soluble salts in dry fallout have a higher proportion of Ca, Mg, and SO_4 than does rain, just as in the Mattole area. The mean Cl content of bulk precipitation observed by Whitehead and Feth (1964) was 12.2 mg/L compared with 1.8 mg/L found by Steele (1968) and 1.9 mg/L reported in this work. This difference may be due in part to the fact that the annual rainfall is about 440 mm in Menlo Park as compared to 1100 mm in the Pescadero Creek basin and 2340 mm in the Mattole River basin, resulting in greater dilution of dry fallout by rainfall in the latter basins.

The NH_4-N and NO_3-N found in Mattole rain is less than that present in rainfall at Menlo Park and also somewhat less than that reported by Feth (1966) in a review of nitrogen compounds in atmospheric precipitation. Presumably, the absence of industrial pollution in the Mattole basin contributes to the lower level of nitrogen compounds in rainfall. It should be pointed out, however, that the Mattole samples covered only one storm period, and it's possible rainfall during that storm was unusually low in nitrogen compounds.

Our sequential rain sampling equipment was tested before taking it to the Mattole River area by obtaining rainfall at two sites in Menlo Park, California. At one site, designated MG, a separate sample was collected for each 1.35 mm of rain and, at the other (Building 3), for each successive 2.65 mm of rain. Both samplers were washed with distilled water just before each storm period in order to reduce collected dry fallout to a minimum.

Information on the chemical characteristics of the rain in Menlo Park is shown in the basic data section at the end of this report. As in the case of the Mattole rain the concentrations of dissolved salts tend to vary inversely with rainfall intensity and Cl concentrations ranged from less than 0.05 to 15 mg/L. Average Cl concentration for all of the rain sampled was a little over 1.0 mg/L, which is reasonably close to the concentration observed in the January 1972 storm in the Mattole basin, and is less than 1.9 mg/L average of bulk precipitation (which includes dry fallout) for the Mattole area.

Pb and Zn dissolved in Menlo Park rain are several times more concentrated than in Mattole rain, and Cu and perhaps Mn are slightly more concentrated. No significant differences were noted for dissolved Cd and Fe. Although Menlo Park is located on a well populated peninsula south of San Francisco, there was no evidence from pH data to indicate that industrial pollutants caused significant decreases in rain pH there compared to the Mattole basin.

Lazrus and others (1970) reported trace metal concentrations in precipitation, excluding dry fallout, at 32 stations in the United States. A 5 µm filter was used to remove coarser solids from monthly composites and the samples were then acidified. Despite potential sorption on polyethylene bottles, the average concentrations found were appreciably higher than those observed in this study, either at Menlo Park or near Petrolia, California. This difference is thought to result mainly from two facts. First, some clay-size solids could penetrate the filter used by Lazrus and others (1970) and be dissolved by the acid. Second, most of the sampling sites were within or near population centers, thus giving results greatly weighted against the rural areas. The ratios of the average dissolved metal concentrations reported by Lazrus and others (1970) for the U. S. compared to average concentrations in rainfall in three storms at Menlo Park, California are as follows: Cu - 15, Mn - 8, Pb - 3.5, and Zn - 16. The ratios of U. S. averages (Lazrus and others, 1970) to those in the Mattole basin for one storm were: Cu - >21, Mn - >12, Pb - >17, and Zn - >75.

Other studies have been made of trace metals in rain. For example, in a study reported in Hales (1974), the trace metal content of rainwater on Lake Superior was, in µg/L, Cd - 1, Cu - 7, Fe - 31, Zn - 55 and Pb - 8. It's not clear whether these analyses are of bulk precipitation or of filtered samples. Schlesinger and others (1974), in a report on bulk precipitation in a montane area of New Hampshire, found a weighted mean concentration of 13.4 µg/L Pb and 0.6 µg/L Cd. These Cd concentrations are appreciably greater than those in Mattole rain, in part, perhaps, because in New Hampshire the samples were unfiltered and there is a greater chance of industrial pollution in the Lake Superior and New Hampshire regions than in the Mattole basin.

STREAM WATER

Composition of Dissolved Solids

Stream water can be conveniently thought of as chemically modified rainwater. The extent of the modification in concentration of each constituent is related to its chemistry; the evapotranspiration rate; characteristics of the vegetation, soils, and rocks which are encountered enroute to the stream; the length of contact period with those soils and rocks; and the individual reaction rates for each dissolved constituent. In effect, then, the chemistry of a stream sample is determined by the path of the water from the time it fell as rain on the vegetation or soil until it was collected and preserved. In order to obtain the most useful information for the purposes of this study, the Mattole River was sampled with a frequency proportional to the expected rate of chemical change, i.e., most often during stream rises and least frequently during slowly declining flow.

Because the Mattole basin has relatively high annual rainfall and the soils and near-surface rocks are well leached, the concentration of dissolved salte in the streams is rather low, even near the end of the dry season. During the 1966-67 rainy season, while discharge changed from 1.9 to 1165 m^3/s (66 to 41, 150 cfs), SO_4 concentration decreased by a factor of 6, Ca and Mg by 5, HCO_3 by 3.5, Na and Cl by 2, and K and SiO_2 showed relatively little change. The variation of each of the different constituents with time and discharge is discussed below using detailed records of concentration changes during several storm periods as well as data obtained less frequently under other flow conditions.

Specific Conductance

The specific conductance of stream water as measured at, or converted to, a standard temperature (25°C in this study) is a useful method of estimating the total concentration of dissolved electrolytes. For many streams specific conductance at 25°C (referred to simply as Sp. Cond. or specific conductance hereafter) decreases as discharge increases because of dilution of terrestrial water by rainfall. Figure 5 shows the relation between log of stream discharge and specific conductance for the Mattole River for the 1967 water year (October 1, 1966 - September 30, 1967). During the long summer dry season, a buildup of soluble salts occurs at the land surface due to atmospheric deposition, evaporation of soil moisture and weathering reactions. These salts can be either carried away in solution by the early rains or washed deeper into the soil profile. That the former occurs is evident from figure 5. The series of points indicated by open circles marks the end of the 1966 low-flow season and the first storm runoff from November 5 to 13 during which about 250 mm of rain fell (an average based upon two U.S. Weather Bureau gages in the basin). The points identified by solid triangles on the figure apparently represent a period after the initial main flushout of salts but before the relationship characteristic of the main rainy season develops. This period extended from November 14 to December 2 and included an additional 550 mm of rainfall. During the period from December 3, 1966 - June 10, 1967 (segment 3) another 1690 mm of rain fell, but the relation between specific conductance and discharge moved along a rather consistent curve suggesting the development of a "steady state" reaction to rainfall. Segment 4 represents the late spring and summer dry period when discharge gradually decreased until the new rainy season began in the autumn.

The lower specific conductance boundary for a specified stream discharge appears to be rather sharply marked and, because Ca + Mg comprise 70-85 percent of the equivalents responsible for the cationic conductance, this implies there is, for a particular runoff rate, a specific minimum release rate from soils for Ca and Mg in the Mattole basin. However, depending upon the length of the dry period preceding the runoff event, this release rate for a set discharge may be exceeded because of a buildup of easily released salts.

The apparent lower specific conductance limit for a particular stream discharge is presumably due to the direct relation between runoff rate and average rainfall rate over the basin during the main rainy season and, in turn, is related to contact time and contact area of the rain with the soil before entering the stream channels. Figure 5, to a significant degree, represents Ca + Mg concentration plotted against the combined effects of reaction time with the soil and variable source area producing runoff.

As pointed out by Luce (1969) for Mg and SiO_2 from serpentine and for Na from albite (using data of Nash and Marshall, 1956) and by Wollast (1967) for SiO_2 from potassium feldspar, the release rate into aqueous solution for these constituents is linear against (time)$^{\frac{1}{2}}$ when solute concentrations are low, which suggests a diffusion controlled process. Kennedy (1971) also noted such a relation for SiO_2 released from composite Mattole soils and sediments. This indicates that as time of contact of the rain with soil decreases, ie. , as the dissolved salt content of the soil-leaching solution decreases, the average rate of release of soluble constituents from the soil increases rapidly. However, the actual release rate also varies with the soil character, terrain, and chemistry of the individual elements. Therefore, the relation of dissolved constituents to discharge will vary from basin to basin and element to element.

Calcium

Calcium is the major cation in Mattole River water, ranging from 57 percent of the cationic chemical equivalents in solution at high flow to about 68 percent at low flow. Thus, it accounts for a major fraction of the specific conductance of the stream water throughout the year. Reference to figure 6, which shows the daily average concentration of Ca against time, demonstrates clearly the abrupt drop in Ca from about 42 mg/L in late October to about 14 mg/L during the first sharp stream rise in early November. However, it is apparent that only superficial leaching occurred during the first storm because of the sharp rebound in Ca concentration prior to the second stream rise in November. By the end of the third storm of the season in early December an average of 1130 mm (44 inches) of precipitation had been recorded by the two rain gauges in the Mattole basin from the beginning of the rainy season, and plenty of opportunity for leaching of surface soils had occurred. The result was a much slower climb in the Ca concentration after the third storm than after each of the first two storms.

Following about a month without significant rainfall during late December and early January a major new storm period occurred in late January and once again a sharp drop in Ca resulted producing a minimum of 9 mg/L Ca (the lowest for the rainy season). This compares to a minimum of 9 mg/L during the major rise in December and minimum of 9.5 mg/L during a somewhat smaller storm in March. During the dry periods ending in mid-January and early March, Ca had managed to increase to about 23 mg/L before more rainfall occurred. However, in both January and March an increase by a factor of 55 in discharge resulted in a drop in Ca concentration of only 60-65 percent, thus indicating the great increase in the rate of release of Ca as rainfall and stream discharge increased.

Although rain continued intermittently from early March until early May (750 mm, or 19 inches, of rain) the average Ca concentration showed no great tendency to change, but simply reflected each small stream rise with a small concentration decrease. Beginning in mid-April Ca concentration began to rise linearly with time, was interrupted by a rain in early May, and rose almost linearly until the end of June. The rate of rise decreased somewhat during July, and then Ca concentration became essentially constant from early August until a slight flushout occurred in late September.

The definite change in rate of Ca increase with time at the end of June is not marked by any obvious break in the discharge curve (it does coincide with a levelling off in pH), but the plateau in Ca concentration coincides with some flattening of the discharge curve at about August 1. It would appear that the river water in August was approaching equilibrium with the rocks from which it came, and that saturation with $CaCO_3$ may have been limiting the Ca concentration. There is some uncertainty about the pH of the water after mid-July, but the available information indicates that the river is slightly super-saturated with calcite.

The ratio of Ca to specific conductance (Ca: Sp. Cond.) is a helpful indication of how the proportion of Ca in the dissolved salts varies with time and discharge. Because Ca is responsible for such a large proportion of the conductance of the water, however, the expected range in the ratio is small. In fact, the general trend during the rainy season is for Ca concentration to decrease slightly as compared to the other constituents, with the greatest decrease observed during large stream rises (figure 6). The range in the ratio is from 0.11 during the largest observed storms to 0.14 at the end of the dry season.

The specific conductance in micromhos is commonly available as part of a water analysis even though all the cations and (or) anions may not have been determined. Hence, comparisons between streams can be made using a cation:Sp. Cond. ratio when only partial water analyses are available. The specific conductance of Mattole River water is numerically very close to 100 times the milliequivalents of cations or anions per liter held in solution and the Ca in mg/L is equal to the Ca in milliequivalents per liter multiplied by the equivalent weight. Therefore, in the case of the Mattole, it is possible to calculate the percent of the total cations present (in milliequivalents) due to a particular cation simply by multiplying the cation:Sp. Cond. ratio by a constant, i.e.

$$\frac{\text{cation (mg/L)}}{\text{Sp. Cond.}} \times \frac{10{,}000}{\text{cation equivalent weight}} = \frac{\text{milliequivalents of individual cation/L}}{\text{total milliequivalents cation/L}} \times 100$$

= milliequivalent percent of a particular cation in solution.

In the case of Ca the constant is $\frac{10{,}000}{20} = 500$.

A similar calculation can be made for the anions. The shape of the cation or anion:Sp. Cond. curves shown in the figures are, for all practical purposes, identical to the shape of milliequivalent percent curve and can be so used in interpretations.

The information above shows the general pattern of Ca variation throughout the year. With this background, some details regarding Ca variation during relatively short time periods is of interest. Such information is available for diurnal variations in Ca concentration at low flow, changes during a moderate stream rise in early fall, and changes occurring with a major storm rise in midwinter. Ca analyses were made on samples collected in early morning (0630) and late afternoon (17-1800) on October 1 and 2, 1968, and at 1730, October 5 and 0800 October 6, 1968. The Ca concentration in late afternoon ranged from 4.6 - 5.3 percent lower than early morning samples (average Ca = 39 mg/L). Such diurnal Ca variations have been observed by others (e.g. Barnes, 1965) and are attributed in part to uptake by organisms involved in photosynthesis and in part to the limiting effects of calcite solubility.

The detailed coverage of a moderate stream rise was done during the period November 7 to 15, 1969. Two small rises preceded the one sampled in detail (see figure 7). The first flushout of the rainy season had occurred during the period October 15-21 when mean daily discharge increased from 1.3 to 22.7 m^3 sec^{-1} (45-622 cfs). The second storm caused a rise which began November 4 at a discharge of 3.1 m^3 sec^{-1}, peaked at 100 m^3 sec^{-1}, and then decreased to 12.6 m^3 sec^{-1} at about midday on November 7, at which time the rise began which is described in detail in this report. Peak discharge on this third rise was 108 m^3 sec^{-1} at 0845 November 8, after which discharge gradually decreased until the next storm on December 8, 1969. Discharge data are from unpublished records of the U.S. Geological Survey.

An attempt was made to sample both the Mattole River near Petrolia and the first significant tributary upstream, Conklin Creek, at approximately one-hour intervals during the first 24 hours of stream rise on November 7-8, then at less frequent intervals thereafter. Ca concentration data versus time are shown for the Mattole River in figure 8 and for Conklin Creek in figure 9. In the Mattole the Ca concentration was increasing slowly early on November 7th as a result of slowly decreasing discharge after the preceding storm. As stream discharge began to increase rapidly with the new storm on November 7, the Ca concentration decreased, reached a minimum at peak discharge, and then increased at a relatively slow rate when compared to its rate of decrease on the stream rise. The Ca concentration on the rise for a specified stream discharge was higher than that on the decline throughout the storm runoff period. As a proportion of the cations in solution Ca apparently (based on Ca:Sp. Cond. ratio) reached a minimum slightly before peak discharge, remained essentially constant over the peak, and then very slowly increased with time and decreasing discharge.

Conklin Creek exhibited a Ca pattern related to discharge much like that observed in the Mattole River, even though the drainage area is only about 15 km^2 as compared to 622 km^2 for the Mattole basin. Because peak discharge on Conklin Creek occurred at about 0215 on November 8 while peak discharge on the Mattole did not occur until 0845, the peak volume of Conklin Creek water entering the river only two miles above the Mattole sampling site arrived during the rising limb of the hydrograph of the main river. The ratio Ca: Sp. Cond. indicated that the proportion of Ca in the electrolytes in Conklin Creek reached a minimum just before and during peak discharge, increased slightly for 1-2 days and then remained at near-constant value significantly below that observed before the rise.

Analyses for Ca are available for samples taken frequently during the major storm of January 20-23, 1972, which followed almost a month of dry weather in the middle of the 1971-72 rainy season (figure 10). Stream discharge was 22 m^3/s before the storm, reached about 290 m^3/s on the first peak on January 21 and a little above 1250 m^3/s on a second peak on January 22 (figure 11). Calcium concentration decreased with discharge as usual and reached minima at or shortly after both peak discharges. Although not plotted, the Ca:Sp. Cond. ratio decreased by almost 13 percent as discharge increased, with the minimum ratio coinciding with minimum measured Ca concentration at or immediately following the second and highest peak stream discharge.

Examination of Ca data from both stream rises described above, and of data from the 1966-67 and 1967-68 rainy seasons, shows that a consistent pattern exists for Ca concentration relative to other cations. The Ca concentration decreases sharply with rising discharge at the beginning of the rainy season and rebounds rapidly after early storms. However, as the rainy season progresses the response to changing discharge becomes more sluggish. The proportion of Ca in the dissolved electrolytes also decreases with increasing discharge, reaching a minimum at or very shortly after peak discharge, but the decrease in the Ca:Sp. Cond. ratio from lowest to highest discharge during the year (<1 to >1000 m^3/s is only about 20 percent. This suggests that Ca could be computed quite accurately from specific conductance modified by a time-discharge-related correction term.

The Sr information presented in figure 11 is discussed later in a section dealing with trace elements.

Magnesium

Approximately 15-18 percent of the cationic chemical equivalents in the Mattole River are composed of Mg, whose concentration ranges from 6.9 mg/L at low flow to 1.5 mg/L at high flow. Like Ca, Mg responds rapidly and inversely to discharge changes. In other respects, Mg resembles Ca in some ways and differs in others (figure 12). The ratio of Mg:Sp. Cond., like Ca:Sp. Cond., decreases during stream rises and increases during declining flow after storms (Mg:Sp. Cond. ratio can be converted to milliequivalent percent Mg by multiplying by 833). However, during the main part of the rainy season there is a tendency for the proportion of Mg in the cations to increase moderately and then decrease during the long spring decline in stream flow before levelling off in late July and increasing slightly again during August and September. The difference between the behavior of Ca and Mg can be seen even better if the Ca:Mg ratio is plotted on a daily basis (figure 12). During the early storms in November and December 1966 the Ca:Mg ratio increased on the stream rises and decreased on the declines for a week or two before turning up again. By late April 1967 there was still some evidence of such a pattern, but the overall trend after the minimum in the ratio in early April, 1969 was for a gradual increase to a peak in late July which exceeded that before the rainy season started. Thereafter, the ratio drifted downward through August and early September until new rainfall caused a renewed increase. The total range in Ca:Mg ratio was from 4.9 in late December to 6.5 in late July.

Diurnal variation of Mg was observed in the samples collected in October of 1968. The average decrease in Mg concentration was about 3 percent from morning until late afternoon at a time when the mean daily Mg concentration was 6 mg/L. No diurnal fluctuation in discharge was detectable from gage height records and no increase in Na or Cl concentration was observed, so evaporative concentration is presumed to have no effect on Mg concentrations.

Figures 13 and 14 show the Mg variation of the Mattole River and Conklin Creek, respectively, during the detailed study of November 7-15, 1969. In the Mattole River, Mg concentration decreased considerably with increasing discharge and the ratio Mg:Sp.Cond. decreased slightly. Both reached a minimum at peak discharge. No significant variation in the Ca:Mg ratio was observed during this relatively small stream rise. For Conklin Creek the pattern is somewhat different from that in the Mattole River. Although Mg concentration decreaeed with increasing discharge the Mg:Sp.Cond. ratio remained constant within the precision of the analyses. The Ca:Mg ratio, on the other hand, decreased on the stream rise and, along with Mg concentration, reached a minimum at or very near peak discharge. The differences between the Mattole River and Conklin Creek in regard to variation of Mg:Sp.Cond. and Ca:Mg ratios may be explained by the higher level of sea salts deposited in the Conklin Creek basin compared to the Mattole basin as a whole. Certainly Na, Cl and Mg concentrations at base flow are significantly higher in Conklin Creek than in the Mattole.

During the major storm of January 20-24, 1972 Mg decreased with increasing discharge of the Mattole River and reached a minimum at peak discharge (figure 15). The ratio of Mg:Sp. Cond., showed a slight increase over base runoff in the first sample taken on the rise and thereafter decreased to about 90 percent of the base runoff value and remained there within about ± 3 percent during the remainder of the storm period.

Sodium

The concentration of Na during the 1966-67 water year ranged from 3.9 to 8.8 mg/L in the Mattole River, as shown in figure 16, which corresponds to about 20 percent of the cationic equivalente at high flow and 12 percent at low flow. As in the case of all the other major dissolved constituents, the first storm of the rainy season caused a sharp concentration decrease in Na, but the percentage decrease for Na in the first major storm in November 1966 was 45 percent as compared to about 67 percent for Ca (fig. 16). A continued inverse relation between discharge and Na concentration was observed for succeeding storms. With gradually decreasing discharge after early May 1967, Na concentration increased through May, June and July before becoming almost constant in August and September.

In contrast to Ca and Mg, the ratio of Na:Sp. Cond. increased during stream rises and fell on the decline (fig. 16, Na:Sp. Cond. ratio can be converted to milliequivalent percent Na by multiplying by 435). However, the ratio, although varying, did not return to the value observed at the end of the summer dry period throughout the rainy season. In fact, it had not returned to the ratio of early November 1966 by September 1967. This may be due in part to the fact that the rainfall during the 1966-67 water year was 25-30 percent greater than that in the 1965-66 water year (based on runoff data; Jorgensen and others, 1971), and hence the stream discharge in September 1967 was somewhat greater than at the same time in 1966.

The increase in the proportion of Na during storms is due, at least in part, to the presence of some sea salt brought in with the rain. The Na:Ca and Na:Mg ratios are much higher in such salt than in the river water, so the proportion of Na in runoff goes up during storms. The greatest increase in the Na:Sp. Cond. ratio occurs during highest flows (and hence follows greatest rainfall). But, according to rain chemistry data in the preceding section, heavy rain probably has a very low Na concentration so some additional source of Na is needed. This suggests increased leachability of Na over Ca and Mg from soil during heavy rainfall, exclusive of the effect of a high proportion of Na in rain salts alone. Possible reasons for this will be discussed later. The ratio of "soil Na" to "sea Na" is also shown in figure 16. The total Na in solution is assumed to represent a combination of Na brought in by precipitation and Na weathered from the soil and rocks. An estimate of the sea Na was made by using the Cl concentration multiplied by 0.556 (the ratio of Na to Cl in sea salts). The difference between total Na and sea Na in solution within the stream was considered to be soil (and rock)-derived Na. Rock-derived Cl was assumed to be negligible in making the calculations.

During the November-December and late January-early February storm periods the ratio of soil Na:sea Na followed a relatively consistent pattern of decreasing on a stream rise and increasing during declining discharge. This pattern seems reasonable because dry fallout and sea salts in the light rain before the main storms would be washed from surficial materials during early runoff and Na from weathered minerals would be included to a greater extent in water draining from the soil after rainfall ceased. In some instances there was a slight increase in the ratio at the very beginning of a stream rise before the decrease occurred.

The storm period beginning in March showed a different pattern in the soil Na:sea Na ratio with variation in stream discharge. The ratio increased with increasing discharge and decreased on the fall. Possible reasons for this change are given later in the report. These short-term changes preceded a longer-term general increase in the ratio beginning in April and continuing until a plateau was reached in early June. Thereafter the ratio remained essentially constant until mid-August when a slow decrease began which accelerated with the early autumn rains.

Figures 17 and 18 show the variations of Na concentration, Na:Sp. Cond. ratio, and soil Na:sea Na ratio for the Mattole River and Conklin Creek, respectively, for the stream rise in November 1969. Na concentration in the Mattole decreased on the rise and was at a minimum at or shortly following peak discharge. Na:Sp. Cond. ratio rose with increasing discharge and fell on the decline. The variation in the soil Na:sea Na ratio with time and discharge was different from that of either Na concentration or the Na:Sp. Cond. ratio. It varied slightly on the initial stream rise then decreased rapidly during the continuing rise and reached a minimum shortly after peak discharge. In Conklin Creek, the soil Na:sea Na ratio apparently increased slightly on the initial rise, decreased rapidly on the further rise to a minimum at or shortly after peak discharge and moved up rapidly on the initial declining discharge. It then increased more slowly until after 7 days it was significantly higher than before the stream rise began. This is not too surprising for these streams inasmuch as the early storms were flushing out sea salts built up during the dry season, especially from tributaries near the coast. The soil Na:sea Na ratio in the Mattole River was larger than in Conklin Creek, showed a smaller percentage decrease during stream rise, rose more slowly than Conklin Creek after peak discharge, and after 7 days the ratio was slightly higher in both streams than before the storm.

The variations in Na concentration, Na:Sp. Cond. ratio, and soil Na:sea Na ratio during the major storm of January 1972 (fig. 19) resembled those of the March-April 1967 period more than those of November 1966-January 1967 or November 1969. Na decreased and Na:Sp. Cond. increased with rising discharge while the soil Na:sea Na ratio, which showed an overall decrease during the storm period, apparently decreased on the initial rise, then may have risen slightly to maxima just before both the first and second peaks in the stream discharge.

During low flow, no evidence could be found for diurnal fluctuations in Na concentration even though Ca and Mg showed such variations.

Potassium

The concentration of K in the Mattole River is the lowest of the major cations and shows the least percentage variation during storm runoff. It ranges from 1 percent of cationic chemical equivalents at low flow to 2.5 percent at high flows. Figure 20 shows the daily mean K concentration for the 1966-67 water year. After the initial decrease in concentration with the first major storm in November 1966, K ranged from about 0.7 - .9 mg/L throughout the remainder of the rainy season, despite variation by a factor of 70 in stream discharge. The declining K concentration during falling discharge in late December 1966 and early January 1967 is the reverse of the trend for the other major cations and is especially notable because the concentration trend is upward following rhe late January-early February 1967 storm period. After the end of April rains the K concentration increases steadily until early July, after which the rate of increase declines sharply. This change in rate of increase around July 1 coincides with a change in the rate of Ca increase and a levelling off in pH. From early December 1966 through March 1967 there appears to be a consistent pattern in K concentration during major storms in which the K decreases initially and then increases again to reach a peak at maximum flow before decreasing again on falling discharge.

As a result of the relative stability of K concentration and variability of specific conductance, the ratio of K to specific conductance (K:Sp. Cond.) increases sharply during storm runoff and almost triples during peak flows (the K:Sp. Cond. ratio can be converted to milliequivalent percent K by multiplying by 256).

Figure 21 shows the K variation in the Mattole River during the period November 7-15, 1969. There is a slight decrease in K concentration during the stream rise but that decrease is less than that for the total electrolytes, as indicated by the increase in the K:Sp. Cond. ratio. Similarly, Conklin Creek (figure 22) shows a decrease in K concentration and an increase in the K:Sp. Cond. ratio during the same storm period.

The K concentration at the beginning of the January 1972 period shown in figure 23, which is only a little more than 0.6 mg/L, suggests that a decrease in K occurred during the month-long dry period just preceding the storm runoff of January 20-24, 1972. This is similar to the K decrease during the December 1966-January 1967 dry period shown in figure 20. After the storm runoff shown in figure 23, the K concentration increased with decreasing discharge just as occurred after the storm in late January 1967. The explanation of the change in the relation between discharge and K concentration before and after the late January storms is not apparent. Presumably, delayed-return flow is responsible for most of the stream flow following the December storms just as in the case of the January storms.

Alkalinity

Bicarbonate, the major anion in Mattole River water, ranged from 134 mg/L at low flow down to 36 mg/L at peak discharge, representing a 77 percent decrease. In terms of milliequivalents the HCO_3 was about 71 percent of the anions at low flow and 66 percent and 77 percent at highest flows in December 1966 and March 1967, respectively. HCO_3 varies inversely with stream discharge (fig. 24). Because HCO_3 constitutes such a high percentage of the anions the ratio of HCO_3 to specific conductance (HCO_3:Sp. Cond.) shows relatively little change during the rainy season except during the first major runoff event following the summer dry season (fig. 24; the HCO_3:Sp. Cond. ratio can be converted to milliequivalent percent HCO_3 by multiplying by 164). At this time the Cl and SO_4 which had accumulated during the summer are flushed from the surface soil and the HCO_3 decreases significantly as a percentage of the total anions. Thereafter, variations in the ratio are relatively minor and, with the exception of the major rise in late January 1967, the ratio tends to decrease on a rise and increase on falling discharge. The stream rise in late January 1967 was relatively slow, after the initial sharp increase, so a higher proportion of interflow as compared to overland flow in the stream may account for the apparently anomalous increase in the ratio during the second, and major, peak in discharge.

Figures 25 and 26 show the variation in HCO_3 and HCO_3:Sp. Cond. ratio for the November 7-11, 1969 period for the Mattole River and Conklin Creek, respectively. Just as in the early storms of the 1966-67 rainy season, both HCO_3 and the HCO_3:Sp. Cond. ratio decreased sharply during the rise and recovered on the decline. In both streams, HCO_3 reached a minimum at or near peak discharge. The minimum in HCO_3:Sp. Cond. ratio, however, appeared to precede peak discharge slightly in the Mattole River while occurring at peak discharge in Conklin creek.

The variations in HCO_3 and HCO_3:Sp. Cond. ratio during the period January 19-24, 1972 are shown in figure 27. Samples are not available for January 20 during the early part of the rise, but it is apparent that both HCO_3 concentration and the HCO_3:Sp. Cond. ratio decreased at that time. Thereafter, the HCO_3 varied inversely with stream discharge but the minimum in HCO_3 may have slightly lagged the second and highest, peak in discharge. The HCO_3:Sp. Cond. ratio apparently showed a brief decrease before the first peak in discharge occurred and then continued to increase very slowly until at least two days after the second and larger discharge peak.

Sulfate

During the 1966-67 water year the concentration of SO_4 ranged from a high of 64 mg/L during the early fall flushout to a low of about 4.5 mg/L just after peak discharge in the storm runoff of late January 1967. This represents a 93 percent decrease from the highest to lowest concentration, the greatest percentage decrease for any of the major anions. Figure 28 shows the daily mean SO_4 concentration for the 1966-67 water year. At the beginning of the first large storm in November 1966 a flushout of SO_4 resulted in an actual increase in SO_4 concentration during rising discharge. Thereafter, SO_4 decreased on rising discharge and, in general, reached minimum concentration within a day after peak discharge occurred. In the dry period of late December 1966 and early January 1967 the SO_4 concentration recovered to about 60 percent of that of early November 1966. Following the storm period of late January-early February discharge again decreased to that of mid-January, but SO_4 concentrations were considerably lower than in January. Presumably much of the SO_4 had been leached from the soil during the first two major storm periods. In mid-April at the end of the main rainy season SO_4 began a gradual, almost linear, increase with time while discharge decreased logarithmically. In late July, the rate of SO_4 increase accelerated briefly and then decreased again until small storms of the 1967-68 rainy season began.

The SO_4:Sp.Cond. (sulfate:specific conductance) ratio showed a large increase during the initial stream rise associated with the first major storm of the 1966-67 rainy season and then decreased rapidly while the stream discharge continued to rise (the SO_4:Sp. Cond. ratio can be converted to milliequivalent percent SO_4 by multiplying by 104). On the second major stream rise associated with that storm, in mid-November, the ratio decreased on rising discharge but recovered somewhat on declining discharge. When the third major storm occurred in early December the ratio decreased sharply on the stream rise and, after a rapid partial rebound as discharge began to fall, it increased slowly toward the ratio observed in early November. As a new storm period began in mid-January 1967 only a slight increase in the SO_4:Sp.Cond. ratio occurred at the beginning of the stream rise. Thereafter, during the storm period, the ratio followed the pattern of SO_4 concentration but with a relatively slow recovery rate. When the last storm period of the rainy season began in early March 1967, the SO_4:Sp.Cond. ratio held almost constant during the initial rise and then decreased during the following major rise. The rebound in the ratio was slight after the major rise and remained almost constant through late March and all of April. Then it began a very slow increase throughout the dry season with a briefly accelerated rate in late July and again in late September.

The SO_4 and SO_4:Sp.Cond. ratio variations observed during the storm runoff of November 7-15, 1969 are similar to those observed in the early part of the 1966-67 rainy season. In the case of the Mattole River (Fig. 29), discharge was still decreasing and SO_4 rising after a prior small stream rise on November 4-5 when renewed storm runoff began on November 7. During the initial rise SO_4 fluctuated sharply before following the normal pattern of decreasing in concentration with increasing discharge. Minimum SO_4 concentration was observed about 10 hours after peak stream discharge; thereafter SO_4 concentration slowly recovered. The SO_4:Sp.Cond. ratio in the Mattole increased slowly at first, then sharply, during rising discharge and reached a maximum before peak discharge. It then declined rapidly to a value which remained almost constant for several days.

Conklin Creek displayed a pattern very similar to the Mattole River in both SO_4 concentration and SO_4:Sp. Cond. ratio (figure 30). However, there was no initial increase in SO_4 concentration with increasing discharge, and minimum SO_4 concentration was observed only about 4 hours after peak discharge.

SO_4 concentrations for the storm runoff period in January 1972 are shown in figure 31. Lack of samples early in the stream rise prevents determination of whether an initial SO_4 flushout occurred. However, the general trend observed during increasing discharge was that of decreasing SO_4 with minima in SO_4 occurring at or shortly after both peaks in discharge. At the SO_4 concentrations shown, the precision of the analyses is probably no better that 1 mg/L and this explains the variation of plotted SO_4 concentrations about a smooth curve.

Chloride

Cl concentration follows a pattern generally similar to that of Na during storm runoff. Figure 32 shows mean daily Cl concentration, the Cl:Sp. Cond. (chloride:specific conductance) ratio and the Na:Cl ratio for the 1966-67 water year (the Cl:Sp. Cond. ratio can be converted to milliequivalent percent Cl by multiplying by 282). Normally, Cl varies inversely with stream discharge, but the percentage change in concentration with extremes in discharge is significantly less than for SO_4 or HCO_3. Minimum Cl concentration in instantaneous samples was 1.9 mg/L representing a 62 percent decrease from the maximum of 5.0 mg/L. After the storm period of late January and early February, 1967, the Cl increased to almost the same concentration in early March as had been observed in mid-January at an equivalent stream discharge. However, after the prolonged period of moderate-sized storms in late March and April the Cl must have been well leached from the surface soils, for it did not reach the concentration of mid-January and early March again until about July 1. At that time the discharge was well below that of early March. Although Cl concentration increased in essentially a linear fashion from mid-May to mid-July, in late July Cl increased more rapidly for a brief period then increased very slowly until the rains of late September 1967.

The only anomalous behavior of Cl was the increase associated with the early part of the major rise at the end of January 1967. This increase in Cl concentration is most easily accounted for by a "high chloride" rain. Unfortunately, only analyses of composite samples of bulk precipitation are available for the last half of January. The occurrence of rainfall averaging 28-38 mg/L Cl associated with a hail storm was documented earlier in this report, so the possibility of such rainfall in this area does exist. Also, during the period of 16 days from January 16 - February 1, 1967 the average Cl content of bulk precipitation collected was 1.9 mg/L which is very high considering that the average rainfall at the two gauges in the basin was 55 cm (22 in.) for the 16-day period and 35 cm of that rain fell in just 5 days. This indicates rather intense rainfall which, based upon the detailed rain sampling of January 1972, suggests that much of the rain would have Cl concentration much less than 1 mg/L. In addition, Na concentrations showed an increase in the river at the same time as the Cl, but the increase was smaller percentagewise. This is to be expected because over 60 percent of the Na apparently is derived from weathering. Another bit of evidence supporting the probable occurrence of high chloride rain is the existence of field notes reporting showers and hail all afternoon on January 24th. The highest anomalous Cl concentration in the river was found in the first sample collected the next morning after the hail storm.

The Cl:Sp. Cond. ratio increased with increasing discharge and normally reached a maximum in less than a day after peak stream discharge. The storm period beginning in mid-March caused less increase in the ratio than the two earlier major storm periods, possibly because the soils were relatively well leached by March. After mid-April the ratio gradually declined along with discharge and reached a minimum in mid-July. Thereafter, the ratio appeared to increase very gradually.

The Na:Cl ratio is to some extent an indication of the leaching of Na due to rock weathering as compared to cyclic Cl from the sea because about two thirds of the Na apparently is derived from rock weathering. During the two major storm periods prior to early March 1967, the Na:Cl ratio tended to increase slightly on the initial stream rise and decline during further increases in discharge. It then rebounded on falling discharge. After early March, the pattern changed and decreases in the Na:Cl ratio during increasing storm runoff did not occur; in fact, there was some increase with high stream discharge. After mid-April the ratio increased until about June 1, then it held relatively constant until the first fall rains, when it decreased as observed in November 1966.

Figure 33 shows the variation in Cl and Cl:Sp. Cond. ratio in Conklin Creek during the period November 7-15, 1969. Cl decreased from a concentration of 7.8 mg/L before the stream rise to a minimum of 6.0 mg/L when the gage height had increased to only one half its maximum. Cl concentration remained constant during the remainder of the rise and increased rather rapidly as discharge began declining. Cl concentration then leveled off while discharge was still declining rapidly and remained essentially constant through November 14. The Cl:Sp. Cond. ratio increased slowly during the first half of the rise then rose rapidly while discharge continued rising, peaked, and began decreasing. Maximum in the ratio occurred approximately 5 hours after peak stream discharge and decreased rapidly at first before declining more slowly.

A different pattern of Cl and Cl:Sp. Cond. was observed for the Mattole River (Figure 34) than in Conklin Creek. After a slight decrease at the very beginning of the rise, Cl increased to a maximum 2-3 hours before peak discharge and then decreased to a minimum value slightly below the original concentration before increasing again slowly. The Cl:Sp. Cond. ratio rose with increasing discharge, reached a maximum at peak stream discharge and declined very slowly thereafter.

The increase in Cl concentration with rising discharge of the Mattole can be attributed at least in part to flushing out of Cl from the high-chloride tributaries of Conklin Creek and McGinnis Creek, which enter the Mattole a couple of miles above the sampling site. It should be noted that the Cl concentration in the Mattole was about 3.9 mg/L before the stream rise, whereas the minimum concentration reached in Conklin Creek near peak discharge was 6.0 mg/L. Furthermore, the time of maximum discharge of Conklin Creek coincides well with the Cl increase in the Mattole River observed during increasing discharge. This would be anticipated, for the travel time from the mouth of Conklin Creek to the sampling site on the Mattole is estimated to be an hour or less. The Cl flushout from Conklin and McGinnis Creeks affects the Cl:Sp. Cond. ratio also by shifting the peak in the ratio forward in time. Without such an input it seems probable that the peak in the ratio would have lagged peak stream discharge, much as it did in Conklin Creek.

The variations in Cl and Cl:Sp. Cond. ratio during the period January 19-24, 1972 are shown in figure 35. Cl concentration is reduced relatively little during the initial rise, increases after the first peak in discharge, then decreases to a minimum at or shortly before the second peak in discharge. It is interesting to note that, despite an increase in stream discharge by a factor of almost 60, Cl decreases in concentration by only one third. The ratio Cl:Sp. Cond. showed a general overall increase during the full storm period. This increase was interrupted by a decrease during the early part of the second rise but then the ratio increased again to a maximum after peak stream discharge.

Silica

The variation in silica with time and discharge in the Mattole River has been previously discussed by Kennedy (1971) in a separate report, but the daily mean variations in silica are summarized in figure 36. Silica characteristically decreases in concentration during a sharp increase in stream discharge and then, in the latter part of the rise, increases rapidly until it reaches a maximum within about a day after peak discharge. The concentration then slowly decreases until the next stream rise, when the cycle begins again. With each succeeding storm period during the 1966-67 rainy season the peak silica concentration after a rise was slightly higher than for the preceding peak and reached a seasonal maximum at the end of April. Although the silica concentration decreased somewhat in May and June, a relatively rapid decrease did not occur until late July. After that the silica decreased slowly until early rains in mid-September caused a slight increase again.

The ratio of silica to specific conductance (SiO_2:Sp.Cond.) increased during individual storm periods and for the rainy season as a whole when compared to low-flow periods. Although stream discharge was briefly somewhat higher in early December than in the late January storm period, leaching of electrolytes from the soil was not as complete in December as in January and that, combined with the seasonal increase in silica concentration, caused a significantly higher SiO_2:Sp.Cond. ratio in January than in December. During periods of falling discharge the silica generally decreased or held constant while the electrolyte concentration increased so the SiO_2:Sp.Cond. ratio decreased relatively rapidly compared to silica concentration.

pH

The soils in the Mattole basin are commonly in the pH range 4.5-6.0 (McLaughlin and Harradine, 1965), and hence might be expected to yield moderately acid waters to the streams during periods of storm runoff. Although there is a definite decrease in pH during storm runoff (Kennedy, 1971), the lowest pH observed was 6.9 during high flow in March 1967. In general, for the 1966-67 water year the pH of Mattole waters was about 8.3 during the summer, decreased to 7.5-8.0 during the fall storm periods and decreased further to 7.0-7.5 during early spring storms. It then slowly increased again to about 8.3 by early July (figure 37).

Minor Constituents

The determination of minor constituents in clean streams can and does present major analytical problems. One of the problems is that of removing particulate material from the water samples without affecting the content of dissolved minor constituents. In a separate report (Kennedy and others, 1974) it has been shown that Al, Fe, Ti and, to a lesser extent, Mn are present in particulate form in sediment-laden Mattole water after it has passed through a 0.45 µm membrane filter. When the sample is acidified for preservation, these particulates passing through the filter are at least partly dissolved and the analyses of dissolved materials (reported for the original sample) can be in error by as much as several hundred percent in the case of Al, Fe and Ti. The use of 0.1 µm filters appears to largely--but not completely--eliminate this specific problem.

Another problem, which was pointed out by Sandell (1944), and also by Marvin and others (1970), is the possible alteration in the concentration of trace metals by contact with a filter. A similar problem for nutrients was described by Jenkins (1968) and by Marvin and others (1972). If the minor constituent level is above a certain value, uptake by the filter can occur and, if below that value, the filter can release the constituent. Release of Zn and Cu into solution from 0.45 µm Millipore filters has been observed and uptake by the filter of several other trace metals (concentration in the 1-10 µg/L range) has also been found (unpublished data, Kennedy, V. C. and Zellweger, G. W.). At the time of writing (1977) no method of completely eliminating this problem is available. Therefore, the trace element concentrations reported must be considered as approximate. A standard procedure used in this study to reduce contamination from, or uptake by, the filters was to discard the first 1-1.5 liters of water passing through a 102 mm filter and the first 2-3 liters through a 142 mm filter.

Spectrographic analyses [1/] of 10 freeze-dried residues (preparation begun as soon as filtration was completed in the field) are presented in table 4. Al, Fe and Ti concentrations are not shown because they are believed to be largely derived from particulates passing through the 0.45 µm filter (Kennedy and others, 1974). Mn does not show significant correlation with Al or Fe in these samples and is included because the Mn contribution from particulate material is believed to be small.

[1/] Analyses under the supervision of P. R. Barnett.

Table 4 Trace element content of Mattole River waters (mg/L) from spectographic analysis of freeze-dried residues.[1/]

Element	DATE									
	11-10-66	11-11-66	11-12-66	1-14-67	1-27-67	2-3-67	3-6-67	6-4-67	9-17-67	9-30-68
	DISCHARGE AT TIME OF SAMPLING (m^3/s)									
	1.2	1.9	26.6	10.9	789	110	9.4*	8.6	1.1	1.0
Ba	0.05	0.05	0.03	0.03	0.01	0.02	0.03	0.03	0.04	0.05
Be	<.0009	<.0009	<.0009	<.0005	<.0003	<.0004	<.0005	<.0005	<.0007	<.0007
Bi	-	<.004	<.004	-	<.0015	<.002	<.003	-	<.004	<.004
B	.14	.12	.12	.09	.026	.05	.03	.08	.11	.16
Cr	<.006	<.004	<.004	<.003	<.0015	<.002	<.003	<.003	<.004	<.004
Co	<.008	<.003	<.003	<.003	<.001	<.0015	<.002	<.001	<.003	<.003
Ga	<.002	-	-	<.001	-	-	-	<.001	-	-
Ge	<.008	-	-	<.005	-	-	-	<.005	-	-
Pb	<.004	<.006	<.006	<.002	<.002	.004	<.003	<.002	<.006	<.006
Mn	.016	.009	.002	.007	.002	.008	.005	.003	.006	.006
Mo	.002	.002	.003	.001	.0008	.0007	.001	.001	.001	.001
Ni	<.004	-	-	<.002	-	-	-	<.002	-	-
Ag	<.0004	<.0004	<.0004	<.0002	<.00015	<.0002	<.0003	<.0002	<.0004	<.0004
Sr	.34	.32	.33	.18	.09	.14	.20	.17	.28	.34
Sn	<.008	<.00[illegible]	<.004	<.005	<.0015	<.002	<.003	<.005	<.004	<.004
V	<.006	<.004	<.004	.004	<.0015	<.002	<.003	<.003	<.004	<.004
Zr	<.008	-	-	<.005	-	-	-	<.005	-	-

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* Interstitial water from gravel river bar.

[1/] Analysts were P. R. Barnett and D. Golden.

"Less than" values are shown in table 4 for many elements because such information is believed to be useful. The sensitivity of the spectrographic method increases with decreasing dissolved solids content of the orginal water sample and, hence, with increasing discharge in the case of Mattole River samples.

Because it is known that 0.45 μm membranes are only moderately effective in removing particulate matter from stream waters (Kennedy and others, 1974), a series of samples was collected from the Mattole River during a stream rise in January 1972, passed through a 0.1 μm filter and analyzed for several trace metals. Al, Fe and Mn concentrations and stream discharge are plotted against time in figure 38. Al increased from about 4 to 13 μg/L during the rise. Fe increased from less than 1 to about 2 μg/L and Mn increased slightly from about 2 to perhaps 3 μg/L. As the discharge decreased after the rise, Al decreased somewhat and Mn showed no consistent trend. However, Fe showed a pronounced decrease to 0.2 μg/L or less. Extractions for these metals were done in the field at a pH of 8.6, so it appears unlikely that leaching of metals from solids passing the 0.1 μm filter contributed a significant fraction of metals determined. Other trace elements extracted in the field and analyzed later in the laboratory were Cd (<0.1 μg/L), Cu (0.1-0.6 μg/L), Pb (<0.3 μg/L) and Zn (<0.1-1 μg/L) with no trends in the data evident. Apparently a precision on the order of at least 0.05 μg/L for Zn and Cu and 0.01 for Cd and Pb would be needed to detect trends in these metals with discharge of the Mattole. Such precision was not obtained in this study. Although Ti determinations by atomic absorption spectrophotometry are not sensitive enough to detect directly the concentrations found in the Mattole, positive correlation between Al and Ti in spectrographic analyses of residues from <0.45 μm filtrates extends down to a Ti level of 1-2 μg/L (Kennedy and others, 1974) suggesting that the dissolved Ti is less than 1 μg/L.

Nutrient levels in the Mattole River were, as anticipated for a rather clean stream, relatively low. Scattered samples were available for NO_3-N (nitrogen as nitrate) analyses during the 1966-67 sampling period but not in sufficient quantity to permit detailed concentration-vs-time curves of the type shown for major constituents. However, a general seasonal trend is shown in figure 39. At the end of the 1966 dry season and during the summer of 1967, NO_3-N was less than 10 μg/L. During storm runoff in the early part of the 1966-67 rainy season, NO_3-N was in the range 200-600 μg/L. By the end of about 5 weeks of relatively dry weather in late December 1966 and early January 1967 NO_3-N had decreased to approximately 40 μg/L. With new storm runoff in late January, NO_3-N increased to a little more than 100 μg/L and then decreased with declining discharge to <10 in early March. Again, storm runoff of mid to late March caused NO_3-N to increase to about 100 μg/L and then a steady decline in NO_3-N began until it was less than 50 μg/L by mid-April and about 10 μg/L in late May.

In figures 40 and 41 respectively, the variation in concentration of NO_3-N (nitrogen as nitrate) and PO_4-P (phosphorus as orthophosphate) in the Mattole River and Conklin Creek are shown for a stream rise in early November 1969. Nitrate concentrations in the Mattole were decreasing on November 7 after a small rise which began on November 4 and had peaked early on November 5. Nitrate concentration decreased at first then increased with increasing discharge on the 7th and maximum concentration was attained 2-3 hours after peak discharge on November 8 after which the nitrate concentration decreased rapidly as discharge decreased. Similarly, in Conklin Creek, nitrate continued to decrease during the first few hours of the stream rise, increased rapidly while the stream was still rising, peaked about 8 hours after maximum stream discharge, then decreased with decreasing discharge.

PO_4-P behaved somewhat differently from nitrate (figure 40). Five samples collected from the Mattole on November 4 and 5 before the intensive study of the rise on the 7 and 8th, indicated that PO_4-P decreased from 12 µg/L to 10 µg/L early in the rise on the 4th, rose rapidly as discharge increased, peaked at about 29 µg/L a few hours after peak discharge, and then decreased to the 26-28 µg/L range and held that concentration from November 5 through November 10 with no evidence of a decrease in concentration similar to that observed in the case of nitrate. In Conklin Creek the PO_4-P level was 24 µg/L before the November 4th rise and increased to at least 33 µg/L on that rise. After peak discharge on the 5th, it decreased again to 24 µg/L before the November 7-8 rise. Although analyses are not available to document the PO_4-P increase with increasing discharge in detail on November 7 (fig. 41), 6 hours after the rise started, ie. 4-5 hours before peak discharge, PO_4-P had reached the 38-40 µg/L concentration level and held there until about 2 hours after peak discharge. It then began a slow decrease to 25 µg/L by November 14.

The data for early November 1969 represent the third small runoff event following a long summer dry season. These data may be contrasted with the data obtained from the Mattole River in late January 1972 at the end of almost a month of dry weather during the middle of the rainy season. NO_3-N and PO_4-P data are plotted in figure 42 and show lower concentrations and a rather different pattern than seen in the early fall runoff. NO_3-N and PO_4-P were relatively low on the 18th and 19th as flow remained almost constant. On the morning of the 21st the river was rising rapidly and both NO_3-N and PO_4-P had increased over the levels on the 19th. NO_3-N increased very slowly with rising discharge and continued to increase during the period of temporary falling discharge late on the 21st and beginning of the new rise early on the 22nd. As discharge increased rapidly on the 22nd, NO_3-N gradually decreased to a minimum shortly after peak discharge and increased as discharge decreased. PO_4 behaved much like NO_3-N with an increase during rising discharge on the 21st, but then it decreased to a relatively constant value (within the precision of the method) until just before the discharge peak on the 22nd, at which time it began another decrease. Shortly after peak discharge, PO_4 levelled off and remained constant through the 24th.

Phosphate analyses for the 1966-67 water year are not available for comparison with NO_3 analyses.

Variations in Dissolved Load

Some dissolved constituents increase in concentration with increasing discharge and others decrease, as shown in the preceding section. Hence, discharge of specific dissolved constituents (product of concentration and stream-water discharge) can vary percentagewise to a greater or lesser degree than stream discharge itself. In table 5, monthly loads of the major dissolved constituents are presented along with the discharge of stream water. No water samples were collected during October 1966 and, hence, the concentrations of the various dissolved constituents were estimated on the basis of data from samples in November 1966 and September 1967 and the fact that rainfall and runoff were greater during the 1966-67 water year than in the 1965-66 water year.

Comparison of percent-of-annual load data for various dissolved constituents with percent of water discharge in table 5 is indicative of the relative degree to which certain constituents are flushed from the basin on a seasonal basis. Cl is flushed out early, while the SiO_2 load is relatively high during the latter part of the rainy season. Ca, Mg and HCO_3 are relatively high from the latter part of the rainy season through September. SO_4 is relatively high during the very early fall flushout, relatively low during the middle of the rainy season and again relatively high during the summer low-flow period.

Table 5. Monthly discharge of stream water and dissolved constituents in the Mattole River, 1966-67 water year, and percent of annual load.

1966	Water		Ca		Mg		Na		K		HCO_3		SO_4		Cl		SiO_2	
	Discharge $m^3 \times 10^6$	% [1]	Metric tons	%	Metric tons	%	Metric tons	%	Metric tons	%	Metric tons	%	Metric tons	%	Metric tons	%	Metric tons	%
October	2	0.2	85	.45	15	0.45	20	.3	2.8	.3	300	.45	70	.5	11	.3	18	0.1
November	198	14.3	2990	16.0	505	14.6	1020	14.8	176	15.9	9315	13.5	3100	21.9	605	21.9	1970	13.0
December	319	23.2	3960	21.3	740	21.4	1530	22.2	270	24.4	15540	22.6	2950	20.8	955	24.1	3460	22.9
1967																		
January	314	22.7	3310	17.7	630	18.2	1400	20.3	241	21.8	13300	19.3	2300	16.2	875	22.1	3280	21.7
February	109	7.9	1630	8.7	325	9.4	590	8.6	84	7.6	6240	9.1	1170	8.2	335	8.4	1300	8.6
March	190	13.8	2430	13.0	465	13.4	940	13.7	144	13.0	9200	13.4	1710	12.1	490	12.4	2080	13.7
April	160	11.7	2310	12.4	445	12.9	830	12.1	108	9.8	8260	12.0	1530	10.8	435	11.0	1980	13.1
May	56	4.1	1080	5.8	195	5.65	335	4.9	45	4.1	3800	5.5	735	5.2	160	4.0	710	4.7
June	16	1.1	410	2.2	65	1.9	110	1.6	16	1.5	1380	2.0	275	1.9	50	1.2	190	1.3
July	7	.5	220	1.2	35	1.0	50	.7	8.7	.8	705	1.0	150	1.1	24	.6	78	.5
August	4	.3	130	.7	21	.6	30	.4	4.7	.4	435	.65	95	.6	14	.4	33	.2
September	3	.2	105	.55	18	.5	25	.4	3.8	.4	355	.50	80	.6	12	.3	26	.2
Totals	1378		18680		3459		6880		1104		68830		14165		3966		15125	

[1] Percent of annual water discharge, or, in the case of a particular dissolved constituent, percent of annual dissolved load.

Suspended Sediment

Concentration and Load Variation

There has been extensive disturbance of surface soils by logging activity in the Mattole basin over the last 20-30 years and this, plus the occasional burning to remove brush and encourage the growth of grass for livestock, has contributed to the high sediment loads transported by the Mattole River. According to local residents, the Mattole River has become much shallower since about 1955 and has been eroding its banks. This is characteristic of aggrading streams carrying high sediment loads.

Suspended-sediment samples were collected at approximately the same time as water samples and, in most instances, represent the water column from about 9 cm (0.3 ft) above the stream bed to the water surface (See Methods Section, p. 24 for details). Very sharp increases in suspended-sediment concentration occurred during stream rises with the maximum commonly occurring at or just before peak stream discharge. Figure 43 shows the changes in sediment concentration with time and discharge during November 1966. Both stream discharge and sediment concentration are plotted on a logarithmic scale. It is evident that during storm runoff sediment concentration shows even greater percentage changes with time than does discharge. Sediment concentration variations during the late November-early December 1966 rainy period and that of January-early February 1967 were presented elsewhere (Kennedy, 1971). The maximum sediment concentration was about 14,000 mg/L in samples collected from the upper 0.7 m of flow during the very high discharge on December 4, 1966. At that time flow velocity and water depth were too great to sample throughout the water column

with the available equipment. If this had been done, it is probable that average suspended sediment concentrations exceeding 15,000 mg/L (1.5 percent solids in the suspension) would have been measured.

Figure 44 shows the relation between stream discharge and suspended-sediment concentration in the Mattole River during the 1966-67 water year. The samples collected during November 11-13, 1966 contain above-normal sediment concentrations for a specified stream discharge, but by the 14th concentrations were back to the normal for the year. The samples taken on January 19-20 1967 were obtained early on a major stream rise following 4-5 weeks of almost no rain. The pattern of increased sediment concentrations for a given discharge after dry periods is consistent for the Mattole and is similar to the relation found in many other streams.

Much of the annual sediment load in the Mattole River is carried in a short time span; in fact, during the 1966-67 water year about 54 percent of that load was carried during the 6 days of highest stream flow. Table 6 shows the monthly suspended-sediment discharge for the Mattole basin and the percent of the total annual suspended load carried during each month. The total suspended sediment discharge for the year was 3,565,000 metric tons.

Table 6 . Suspended sediment transported by the Mattole River at Petrolia during the 1966-67 water year.

	TIME PERIOD											
	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Metric tons	11	566,000	1,140,000	1,220,000	50,000	512,000	74,000	2,800	170	47	18	14
Percent of annual load	0.0003	15.9	32.0	34.2	1.4	14.3	2.1	0.08	0.005	0.001	0.0005	0.0004

The average suspended sediment yield from the 622 sq km (240 sq mi) Mattole basin was approximately 0.5 gm/sq cm (16,370 tons/sq mi) which, if one assumes an average soil bulk density of 1.4, corresponds to erosion of 3.5 mm (.15 in) of soil from the whole basin in just one year. This annual sediment yield compares with an average of 157 tons/sq mi. for United States streams tributary to the Pacific Ocean and 9,426 tons/sq mi. for the Eel River in northern California (Curtis and others, 1973).

Chemical and Mineralogical Composition

Stream sediments are known to adsorb heavy metals from surface waters, and many published analyses of stream sediments are from moderately to highly polluted environments. The Mattole River study offered an opportunity to determine the composition of stream sediments from a relatively unpolluted area and, hence, to help establish background values. Shales commonly contain higher concentrations of many of the trace elements than sandstones (e.g. Rankama and Sahama, 1950; Turekian and Wedepohl, 1961) so it was anticipated that there would be marked changes in the composition of Mattole suspended sediment with grain size. Separate composite suspended-sediment samples were prepared from a series of samples collected during a rising river stage on January 22-23, 1970, and during a falling stage on January 28-30, 1970. Each composite sample was size fractionated by settling in distilled water, and the sand-size materials were sieved through plastic screens. Semi-quantitative spectrographic (analyst , Chris Heropoulos) and rapid silicate (analyst , Lowell Artis) methods of analysis were used for these size fractions as well as for a series of suspended-sediment samples collected from the Mattole River. The results of the analyses of various size fractions are presented in table 7.

Table 7. Composition of various size fractions of suspended sediment from the Mattole River of northern California.[1]

Size fraction	<2 um		2-8 um		8-32 um		32-62 um		62-125 um		125-250 um	
Flow Conditions [2]	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing
	Percent											
SiO_2	50.0	50.9	59.2	58.5	65.4	64.6	70.6	70.5	69.6	71.2	72.9	71.9
Al_2O_3	19.6	20.1	16.7	16.8	15.3	15.1	13.8	14.3	13.9	13.8	12.9	13.1
Fe_2O_3	6.2	6.8	4.3	4.2	3.0	2.8	2.0	2.3	2.3	3.8	1.9	3.5
FeO	3.2	3.4	2.7	2.8	2.0	2.1	1.5	1.5	1.5	-	1.5	-
MgO	3.6	3.9	2.7	2.7	2.0	2.0	1.5	1.5	1.4	1.5	1.4	1.4
CaO	1.4	1.4	1.2	1.2	1.4	1.5	1.7	1.5	1.2	1.3	1.3	1.2
Na_2O	.96	1.1	2.2	2.4	3.0	3.0	3.4	3.3	3.0	3.0	2.7	3.0
K_2O	2.7	2.8	2.1	2.1	1.8	1.9	1.8	1.9	1.8	1.9	1.8	1.9
H_2O+	5.9	3.1	4.5	4.5	3.2	3.0	2.2	1.8	2.5	2.1	2.6	-
H_2O-	4.3	3.8	2.6	2.3	1.6	1.6	1.1	1.1	1.1	1.1	1.0	.90
TiO_2	.96	.96	.93	.93	.73	.70	.57	.51	.46	.48	.43	.41
P_2O_5	.21	.29	.23	.24	.21	.20	.16	.15	.13	.13	.13	.13
MnO	.11	.14	.11	.11	.07	.07	.03	.07	.05	.07	.03	.07
CO_2	.04	.02	.02	.04	.02	.02	.02	.06	.02	.02	.04	.02

[1] Analyst was Lowell Artis, under the supervision of Leonard Shapiro.

[2] "Increasing flow" and "decreasing flow" refer to composite samples taken, respectively, during rising discharge on January 22-23, 1970 and during falling discharge on January 28-30, 1970.

Table 7. Composition of various size fractions of suspended sediment from the Mattole River of northern California (continued).

Size fraction	<2 um		2-8 um		8-32 um		32-62 um		62-125 um		125-250 um	
Flow Conditions	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing	Decreasing
						Mg per Kg[3]						
As	--	10	--	10	--	10	--	10	--	--	--	--
B	50	50	30	30	50	20	20	20	20	30	30	30
Ba	500	700	700	700	700	700	700	700	1000	1000	1000	1000
Cd	--	1.4	--	1.4	--	1	--	0.8	--	--	--	--
Co	20	20	15	15	10	10	7	7	10	10	7	7
Cr	150	150	150	100	100	150	100	100	100	70	70	70
Cu	100	100(70)	50	70(50)	30	50(35)	20	30(20)	20	30	20	30
Ga	20	30	15	15	15	15	10	10	10	10	15	10
Hg	0.36	0.31	0.18	0.23	0.08	0.10	0.07	0.12	0.07	-	0.07	-
La	30	<20	<20	30	<20	<20	<20	<20	<20	<20	<20	<20
Nb	10	15	10	10	<10	10	<10	7	<10	7	<10	<10
Ni	70	70	70	50	50	30	30	20	30	30	30	30
Pb	20	70(40)	100	15(25)	10	15(20)	70	30(80)	100	30	70	30
Sc	30	30	20	20	15	15	10	10	10	10	7	10
Sr	70	100	200	300	300	300	300	300	300	300	300	300
V	200	200	150	150	100	100	70	70	70	70	70	70
Y	30	30	20	20	15	15	15	10	10	10	15	10
Yb	3	3	2	2	1.5		1.5		1		1	
Zn	--	70	--	60	--	45	--	35	--	--	--	--
Zr	100	70	70	70	100	100	150	100	100	50	70	70

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[3] Spectrographic analyses by Chris Heropoulos. Cu and Pb concentrations in parens and As, Cd, Zn and Hg analyses by K.W. Leong.

The rapid-silicate analyses show trends in the concentration of major constituents. Silica increases with increasing grain size and Fe, Al, Mg, K, P, Ti and Mn decrease. Ca is essentially uniform in concentration for the silt and clay sizes but decreases somewhat in the fine sand fraction. Na is lowest in the clay fraction, increases with grain size in the silt fraction, and decreases again slightly in the sand sizes.

The percentage variations in many of the minor elements are great enough that they can be detected with semiquantitative spectrographic methods. Co, Cu, Hg, Sc, V, Y and Yb show at least a factor of 3 decrease in concentration with increasing grain size, whereas B, Cr, Ga, La, Nb and Ni decrease to a lesser extent. Ba and Sr increase with increasing grain size and Zr is at a maximum in the coarse silt sizes. Pb shows no obvious relation to grain size, but, the large differences in concentration between composite samples of equivalent grain size suggests possible contamination.

With knowledge of the variation in chemical composition of suspended sediment with grain size, one can examine analyses of suspended sediment collected under various flow conditions to see whether there are any systematic trends in composition. In table 8 analyses of suspended sediments are presented along with the stream discharge at the time of sample collection. Samples collected from 1630 on December 4 to 0915 December 6, 1966 were obtained from only the top 0.6 m (2 ft. approx.) of stream water because of the great turbulence and velocity of the river and the floating debris. Such samples would contain less sand than ones that were depth-integrated. However, the vigorous vertical mixing which existed would have helped to reduce such sorting.

Examination of the data in table 8 shows that the SiO_2 range is from 60 to 65.1 percent and the Al_2O_3 range is from 15.2 to 17.4 percent. Such a compositional range corresponds to that of the 2-32 μm size range of Mattole suspended sediment (Table 10). If one compares the concentration of other elements in the suspended sediment with that of the various size fractions, it is found that Co, Ga, Sc, Ti and Y, which vary appreciably with grain size, also indicate a mean size range for the suspended sediments of 2-32 μm. There is a tendency for suspended sediments collected at high stream flows to have a somewhat higher SiO_2 content and lower Al_2O_3 than those at moderate flows, and this is presumed to be due to the greater proportion of fine sediment in the lower flow samples.

Table 8 Composition of suspended-sediment samples from the Mattole River of northern California.

Collection time	12-3-66 2130	12-4-66 0900	12-4-66 1630	12-4-66 2130	12-5-66 0130	12-5-66 1030	12-5-66 1530	12-5-66 2300	12-6-66 0915	12-8-66 1800
Stream discharge (m^3/s)	263	364	646	1165	1048	533	421	331	222	110
					Percent[1]					
SiO_2	64.6	65.1	62.5	61.1	60.5	60.8	61.7	62.5	62.8	62.2
Al_2O_3	15.6	15.4	15.8	16.5	16.5	16.1	16.3	16.2	15.8	16.2
Total Fe as Fe_2O_3	5.8	5.4	-	-	-	-	6.4	6.2	6.1	6.5
Fe_2O_3	-	-	3.6	4.1	4.2	3.9	-	-	-	-
FeO	-	-	2.2	2.1	2.1	2.2	-	-	-	-
MgO	2.2	2.2	2.3	2.4	2.4	2.3	2.3	2.3	2.3	2.4
CaO	1.4	1.4	1.3	1.5	1.3	1.4	1.5	1.3	1.4	1.5
Na_2O	2.6	2.5	2.4	2.3	2.3	2.3	2.3	2.6	2.4	2.4
K_2O	2.0	2.0	2.0	2.1	2.1	2.1	2.1	2.1	2.1	2.1
H_2O+	-	3.7	4.1	4.5	4.6	4.3	4.4	-	4.2	-
H_2O-	-	1.8	2.1	2.4	2.5	2.2	2.1	-	1.9	-
TiO_2	.70	.64	.70	.74	.76	.78	.74	.73	.73	.72
P_2O_5	.21	.20	.21	.23	.22	.22	.22	.21	.21	.22
MnO	.14	.07	.07	.11	.09	.07	.09	.11	.07	.11
CO_2	.08	.06	.02	.04	.06	.04	.06	.02	.02	.06

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[1] Analyst was Lowell Artis, under the supervision of Leonard Shapiro.

Table 8 Composition of suspended-sediment samples from the Mattole River of northern California (continued).

Collection time	12-9-66 0845	12-9-66 1800	12-16-66 1300	1-26-67 1000	1-26-67 1415	1-27-67 1530	1-31-67 2100	2-8-67 1045	3-16-67 0930	3-18-67 1055
Stream discharge (m^3/s)	94	87	82	252	313	633	255	49	529	116
					Percent[1/]					
SiO_2	62.8	61.4	61.4	64.7	62.3	63.4	63.9	58.6	61.4	60.0
Al_2O_3	16.4	16.4	16.6	15.2	16.0	15.9	15.9	17.4	16.3	16.7
Total Fe as Fe_2O_3	6.4	6.5	6.8	5.4	-	-	6.1	7.2	6.4	-
Fe_2O_3	-	-	-	-	3.9	3.7	-	-	-	4.1
FeO	-	-	-	-	2.2	2.2	-	-	-	2.9
MgO	2.5	2.5	2.5	2.1	2.5	2.3	2.4	2.7	2.5	2.7
CaO	1.7	1.5	1.4	1.5	1.6	1.2	1.4	1.5	1.5	1.3
Na_2O	2.5	2.5	2.5	2.6	2.4	2.4	2.6	2.3	2.5	2.2
K_2O	2.1	2.1	2.1	2.1	2.0	2.1	2.1	2.2	2.1	2.2
H_2O+	-	-	-	-	4.3	4.2	-	-	-	5.0
H_2O-	-	-	-	1.7	2.1	2.0	-	-	-	2.2
TiO_2	.72	.74	.76	.55	.74	.70	.68	.82	.74	.78
P_2O_5	.21	.22	.24	-	.22	.21	.21	.25	.23	.25
MnO	.11	.07	.07	.08	.07	.07	.07	.11	.11	.07
CO_2	.06	.08	.08	-	.08	.06	.08	.04	.04	.08

[1/] Analyst was Lowell Artis, under the supervision of Leonard Shapiro.

Table 8 Composition of suspended-sediment samples from the Mattole River of northern California (continued).

Collection time	12-3-66 2130	12-4-66 0900	12-4-66 1630	12-4-66 2130	12-5-66 0130	12-5-66 1030	12-5-66 1530	12-5-66 2300	12-6-66 0915	12-8-66 1800
Stream discharge (m^3/s)	263	364	646	1165	1048	533	421	331	222	110
					mg per Kg[2]					
As	--	10	10	10	10	--	--	--	--	--
B	50	30	30	30	20	30	20	30	30	30
Ba	1000	700	1000	1000	700	1000	1000	1000	1000	1000
Cd	--	0.7	0.8	1.5	0.7	--	--	--	--	--
Co	10	10	15	15	15	10	15	10	10	10
Cr	150	100	150	150	150	150	100	150	150	150
Cu	100	150(95)	70(45)	70(50)	70(45)	70	70	70	70	70
Ga	15	15	15	15	15	15	15	15	15	15
Hg	--	0.14	0.13	0.15	0.08	--	--	--	--	--
La	<20	<20	<20	<20	30	<20	<20	<20	30	<20
Nb	10	7	7	10	10	7	7	7	10	7
Ni	70	50	50	70	50	50	50	50	50	70
Pb	20	30(75)	<10(20)	10(20)	10(20)	20	15	20	10	30
Sc	15	15	20	20	20	20	15	15	15	20
Sr	300	200	300	300	300	300	300	300	300	300
V	150	100	150	150	150	150	100	150	100	150
Y	15	15	20	20	20	20	20	30	20	20
Yb	2	2	2	2	2	2	2	3	2	2
Zn	--	55	50	50	50	--	--	--	--	--
Zr	100	150	100	70	100	70	100	100	100	100

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[2] Spectrographic analyses by Chris Heropoulos. Cu and Pb concentrations in parens and As, Cd, Zn and Hg analyses by K.W. Leong.

Table 8. Composition of suspended-sediment samples from the Mattole River of northern California (continued).

Collection time	12-9-66 0845	12-9-66 1800	12-16-66 1300	1-26-66 1000	1-26-67 1415	1-27-67 1530	1-31-67 2100	2-8-67 1045	3-16-67 0930	3-18-67 1055
Stream discharge (m^3/s)	94	87	82	252	313	633	255	49	529	116
					mg per Kg[2]					
As	--	--	--	--	10	10	--	--	--	--
B	50	30	50	30	30	30	20	30	30	20
Ba	1000	1000	1000	1500	1000	700	1000	700	700	700
Cd	--	--	--	--	0.7	0.8	--	--	0.8	--
Co	10	10	10	15	10	10	7	15	10	10
Cr	150	100	100	100	150	150	150	150	150	150
Cu	100	70	100	50	70(45)	70(55)	70	100	70(45)	70
Ga	15	20	20	20	15	15	15	20	10	15
La	30	<20	<20	<20	<20	30	<20	<20	<20	<20
Nb	10	7	7	7	7	7	10	7	7	<10
Ni	50	50	70	70	70	70	50	70	50	50
Pb	150	30	15	10	10(20)	10(15)	10	20	15(20)	30
Sc	15	15	20	15	20	15	15	20	15	20
Sr	200	200	200	300	200	200	300	200	200	200
V	150	100	100	100	100	100	150	150	100	150
Y	20	20	20	30	20	20	20	20	15	20
Yb	2	2	2	2	2	2	2	2	2	2
Zn	--	--	--	--	50	45	--	--	50	--
Zr	70	150	100	100	100	100	100	100	100	70

[2] Spectrographic analyses by Chris Heropoulos. Cu and Pb concentrations in parens and As, Cd, Zn and Hg analyses by K. W. Leong.

If one wishes to determine the composition of various size fractions of stream sediment, it is much easier to collect a bed sample at low flow than to attempt to composite enough suspended sediment at higher flows to permit size separations and chemical analyses. However, the possibility of selective enrichment of heavy minerals in the bed sediment exists, and this could result in erroneous estimates of the chemical composition of the stream-sediment load. To determine whether this is a serious problem in the case of the Mattole sediments, spectrographic analyses of 0.125-0.25, 0.062-0.125 and <0.062 mm size fractions of bed sediment were compared with analyses of suspended sediment in the same size ranges (Table 9). Analyses of a composite of the <0.062 mm fraction of the suspended sediments were not available, so the comparison was made with the 2-8 μm size fraction of suspended sediment. Co and Sc contents of the <0.062 mm bed sediment are approximately equal to corresponding concentrations in the 2-8 μm fraction of the suspended sediment. Fe, Ti, Cr, Ni, Sr, V, Yb and Zr are somewhat more concentrated in the 0.125-0.25 and 0.062-0.125 mm sizes of bed sediment, with Cr and Zr showing the greatest concentration factor. In the <0.062 mm size fraction of bed sediment only Cr and Zr show a factor of 2 or more increase in concentration in bed sediments compared with the 2-8 μm suspended sediment. Thus, it would appear that for Mattole sediments there are relatively few elements enriched in the fines mixed with coarse sand and gravel on the stream bed as compared to the equivalent size fractions in suspension.

Table 9. Semiquantitative spectrographic analyses of suspended-sediment and bed sediment of the same grain size.

Grain size	0.125-25 mm					0.062-.125 mm					<0.062 mm				
Matrix character	Cobbles	Pebbles	Pebbles	Bed sand	Suspended sediment	Cobbles	Pebbles	Pebbles	Bed sand	Suspended sediment	Cobbles	Pebbles	Pebbles	Bed sand	Suspended sediment
								Percent 1/							
Al	10	10	10	10	7	10	10	10	10	7	>10	10	10	10	10
Ca	1	1	1	1	1	1	1.5	1.5	1.5	1	1.5	1.5	1	1.5	1
Fe	5	5	5	5	3	5	5	5	5	3	5	5	5	5	5
Mg	.7	.7	.7	.7	.8	.7	.7	.7	.7	.8	1	1	1	1	1.5
Na	2	2	2	2	2	3	3	3	3	2	3	2	2	2	1.5
K	2	2	2	2	1.5	2	2	2	2	1.5	2	2	2	2	1.5
Ti	.5	.5	.5	.5	.3	.5	.5	.5	.5	.3	.5	.5	.5	.5	.5
								mg per kg 1/							
B	20	20	20	20	30	20	20	20	20	20	30	30	30	30	30
Ba	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	700
Co	7	7	7	10	7	7	10	10	10	10	15	15	15	15	15
Cr	300	300	300	200	70	200	200	500	300	100	300	300	300	500	150
Cu	30	50	50	50	30	30	50	50	50	30	70	70	70	50	70
Ga	15	15	15	15	15	15	15	15	15	10	20	20	20	20	15
Mn	500	500	500	500	400	500	500	500	500	500	700	1000	700	700	700
Nb	7	10	7	7	10	7	7	10	10	7	7	10	7	7	10
Ni	50	50	50	50	30	50	50	70	50	30	70	70	70	70	70

1/ Analyst was Chris Heropoulos.

Table 9. Semiquantitative spectrographic analyses of suspended-sediment and bed sediment of the same grain size (continued)

Grain size	0.125-25 mm					0.062-.125 mm					<0.062 mm				
Matrix character	Cobbles	Pebbles	Pebbles	Bed sand	Suspended sediment	Cobbles	Pebbles	Pebbles	Bed sand	Suspended sediment	Cobbles	Pebbles	Pebbles	Bed sand	Suspended Sediment
	mg per kg[1/]														
Pb	10	15	10	10	50	20	10	20	15	60	10	10	10	10	15
Sc	10	10	10	10	10	10	10	10	15	10	20	20	20	20	20
Sr	500	500	500	500	300	500	500	500	500	300	500	500	500	500	300
V	100	100	100	100	70	100	100	100	100	70	100	100	100	100	150
Y	15	15	15	10	10	15	15	15	15	15	20	20	20	20	20
Yb	1.5	1.5	1.5	1.5	1	1.5	1.5	2	2	1	2	2	2	2	2
Zr	150	150	150	100	70	200	100	500	150	70	150	150	200	200	70

[1/] Analyst was Chris Heropoulos.

Many trace elements were sought and not found in the spectrographic analyses of Mattole sediments. For those elements which are detectable at low concentrations by the spectrographic method, the information that a particular element is below the detection limit can provide useful geochemical information. All Mattole sediments analyzed contained, in mg/kg, <1 Be, <10 Ge, <5 Mo, and <10 Sn. In addition to the spectrographic analyses, Au determinations were made by a wet-digestion atomic-absorption method (Thompson and others, 1968; analtyst K. W. Leong) on the 0.062-0.125 mm and <0.062 mm sizes from the bed sediments and these size fractions were found to contain <0.02 mg/kg Au.

The mineralogy of Mattole sediments is related to the lithology of the rocks in the area as modified by weathering factors. Because much of the Mattole basin is underlain by folded and faulted, well-indurated, fine-grained clastic sediments, sand-size and coarser stream sediments commonly contain major amounts of siltstone and mudstone aggregates. This is demonstrated by the data in table 10, which shows the composition of various sizes of sand from the Mattole River.

Table 10. Composition of Mattole River sand

Size fraction (μm)	Mineralogy (Volume Percent) [1]						
	Quartz	Chert	Feldspar	Quartz + Feldspar aggregates	Quartz + Feldspar & silt aggregates	Siltstone mudstone fragments	Miscellaneous grains
62-125	17	1	19	1	14	45	3
125-250	20	2	16	3	9	46	4
250-500	18	4	16	6	4	47	5
500-1000	2	1	1	2	13	80	1

[1] Analyses made by determining the area occupied by each type of sand grain in a grain-mount thin section.

In the size range 62-500 μm almost half of the grains are siltstone or mudstone fragments and most of the rest are composed of quartz, feldspar or quartz-feldspar aggregates. At least one carbonate grain was observed in each size fraction, but the average carbonate content was well under one-half percent in all sizes examined. Most of the "miscellaneous" grains reported in table 10 were iron stained to the point where identification was not feasible. In the 500-1000 μm size fraction the siltstone-mudstone fragments made up 80 percent of the grains examined. This trend toward an increasing percentage of such aggregates with increasing grain size would be expected to continue into the >1 mm sediment particles, and examination of coarser sediment in hand specimens demonstrates this to be true.

Although staining tests were not used to identify K-feldspars in thin section, chemical analyses of the 62-125 and 125-250 μm size fractions (Table 9) show the K content averaged about 1.85 percent. Assuming the K content of K-feldspar is 15 percent [theoretically, 16.9 percent but some Na is normally present (Wahlstorm, 1955)], the maximum K-feldspar content would be about 12 percent if K were present only as feldspar. Examination of table 10 suggests that about 20 percent feldspar is present in 62-250 μm grains exclusive of that in siltstone-mudstone fragments. Therefore, at least 40 percent of the feldspar may be plagioclase. However, considering that a significant fraction of the K probably is tied up in the siltstone fragments, it is likely more than 50 percent of the feldspar is indeed plagioclase.

The presence of considerable quantities of plagioclase in the stream sediments would not be expected if only extensively weathered surface soil were being eroded because plagioclase feldspars are known to weather rather easily (Ollier, 1969). However, road construction and extensive erosion associated with logging operations as well as other cultural activities have apparently exposed less-weathered C horizon material deep in the soil to erosion, thus resulting in large quantities of such material being transported by the Mattole River.

Kaolinite, vermiculite, aluminum-interlayered vermiculite, and mixed-layered minerals are the major clay minerals of the Mattole River sediment, but much lesser amounts of illite, montmorillonite, and chlorite also occur. Such a clay mineral assemblage is characteristic of extensive weathering and soil development under good drainage conditions in an acid environment (Bear, 1964). The cation-exchange capacity of the clay-size fraction of the Mattole River sediments is about 35 meq/100 g (milliequivalents per 100 grams) (Malcolm and Kennedy, 1970). This indicates that the clay fraction present cannot contain more than 30 percent true vermiculite, which has a cation-exchange capacity of 100-150 meq/100 gm (Grim, 1968). In fact, allowing for the exchange capacity of kaolinite, aluminum-interlayered vermiculite, and mixed layered minerals present, a better estimate is only 10-15 percent true vermiculite.

Exchangeable Cations

A significant fraction of the cations carried by rivers can be transported as exchangeable cations held on the stream sediments (Kennedy, 1965). Because the rate of sediment transport increases drastically with increasing stream discharge, the adsorbed cation load also increases greatly. The cation-exchange capacity (CEC) of Mattole River sediments as measured by saturation with 0.5 N NaCl was determined for 51 suspended sediment samples collected between November 11, 1966 and January 24, 1967. The CEC ranged from 29 milliequivalents per 100 grams (meq/100 g) for the fine sediment transported near the beginning of the first storm rise to as little as 16 meq/100 g during high flow periods. Many of the sediments were in the range 17 to 20 meq/100 g with the average during moderate to high flow - when more than 80 percent of the annual sediment load was transported - being about 18 meq/100 g. This CEC corresponds to that reported by Malcolm and Kennedy (1970) for the 2-10 μm size fraction of Mattole sediment. If one uses the average Al_2O_3 content of suspended-sediment samples (Table 8) as 16.2 percent, this corresponds to an equivalent grain size slightly coarser than the 2-8 μm size range, whose composition was reported in table 7. A similar calculation with SiO_2 shows an average equivalent grain size for Mattole suspended sediment midway between the 2-8 μm and 8-32 μm size fractions of table 7. It would appear that the CEC measurements indicate a somewhat smaller effective grain size for Mattole River suspended sediment than that calculated from chemical analyses of the sediments.

In order to calculate annual adsorbed loads of exchangeable cations, average CEC, annual sediment discharge and the composition of the exchangeable cations must be known. The composition of the exchangeable cations determined will depend to some degree upon the character of the desorbing solution, so subsamples of a suspended sediment collected November 15, 1966 were desorbed using 1 N ammonium acetate (NH_4OAc), 0.5 N NaCl and 1 N $SrCl_2$. Results are shown in table 11. Exchangeable Ca and Mg were essentially the same for all three desorbents, but K released by NH_4OAc was somewhat less than for NaCl and $SrCl_2$. Additional desorptions were made using NH_4OAc on two samples collected in early December 1967, and 10 samples collected in January 1972 were desorbed with 0.5 N NaCl.

The data, when taken as a whole, indicated that in terms of milliequivalents approximately 84, 12.6, 0.3, 2.3, 0.8 and 0.04 percent of the exchangeable cations, are Ca, Mg, Sr, K, Na and Mn, respectively, on Mattole River sediments.

Table 11 Exchangeable cations on suspended sediment from the Mattole River

Collection Date	Desorption Method	Reporting Method	Percent of exchangeable cations[1]						
			Ca	Mg	Sr	K	Na	Mn	Cation-exchange capacity(meg/100g)
11-15-66	1N NH_4OAc	By Milliequiv.	86.3	10.4	.4	1.8	1.1	-	17.5
		By Weight	87.8	6.4	.9	3.6	1.3	-	
	0.5N NaCl	By Milliequiv.	86.8	10.4	.4	2.1	-	-	16.0
		By Weight	88.5	6.4	.9	4.2	-	-	
	1N $SrCl_2$	By Milliequiv.	84.6	10.9		2.8	1.3		16.2
		By Weight	86.2	6.7		5.6	1.5		
12-2-67	1N NH_4OAc	By Milliequiv.	84.1	13.6	-	1.5	.75		21.3
		By Weight	87.5	8.6	-	3.0	.9		
12-4-67	1N NH_4OAc	By Milliequiv.	85.3	12.4	-	1.7	0.6	-	20.0
		By Weight	88.1	7.8	-	3.4	0.7	-	
1-22 to 24-72 Average and range of 10 samples	0.5 N NaCl	By Milliequiv. Average	82	14.4	.25	2.9	.75[2]	0.04	20.0
		Range	81-84	13.2-15.4	0.20-0.35	2.0-3.4		0.01-.05	
		By Weight Average	83.8	8.9	.56	5.8	.87	0.06	

[1] Analysts were R. J. Avanzino and G. W. Zellweger. [2] One sample was also desorbed by NH_4OAc to determine adsorbed Na.

Table 6 shows that there were about 3.6×10^6 metric tons of suspended sediment transported by the Mattole River during the 1966-67 water year. Assuming an average cation-exchange capacity of 18 meq/100 g for that sediment, the total annual absorbed load was 65×10^6 equivalents. In terms of weight this amounts to 10,900 metric tons, of Ca, 1000 tons of Mg, 85 tons of Sr, 585 tons of K, 120 tons of Na and 27 tons of Mn. Comparison of these figures with data in table 5, which shows total annual dissolved loads of various ions, indicates that 37 percent of the Ca, 22 percent of the Mg, 35 percent of the K and 1.7 percent of the Na transported to the ocean in easily available form is in exchangeable position on suspended sediment. Although data on Mn are limited both for the dissolved and absorbed forms, a very rough estimate of the proportion of Mn annually carried adsorbed and in solution can be made using a value of 3 μg/L in solution and the figure for absorbed Mn given above. During the 1966-67 water year about 1.38×10^{12} liters of water was discharged by the Mattole River near Petrolia (U. S. Geological Survey, 1968) and, at 3 μg/L this is a little more than 4 metric tons of dissolved Mn. Therefore, 80-90 percent of the readily available Mn is carried absorbed on the suspended sediment.

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Components of Stream Flow as Related to Stream Chemistry

The Mattole basin contains soils of widely varying slope and permeability, and it is probable that most of the runoff generating mechanisms described in the literature are represented to some degree in the basin. Much of the work done elsewhere in attempting to understand rainfall-runoff paths has been concerned with the physical aspects of the various processes. It is evident, however, that information on variations in chemical composition of storm runoff can contribute important evidence in determining the source and pathways of the waters making up storm runoff.

Most chemical studies of storm runoff devote little or no attention to the rapid dissolution of soil solids which occurs when rain comes in intimate contact with the soil. It has been common to attribute the increased load of dissolved solids in storm runoff to increased groundwater flow, but this can require movement of large volumes of ground water out of storage in a very short time if runoff during an individual storm is large. Such displacement may be feasible in specific instances, but it seems unlikely for the general case.

Some of the mechanisms proposed for generating storm runoff are discussed below in terms of their applicability to the Mattole River basin. Because only 1-2 percent of the basin area is composed of stream channels, rain falling directly on stream water will result in only perhaps 2 percent of the rainfall being translated immediately into increased stream discharge.

Stream channels are incised in all except the very uppermost reaches of the streams, so there are essentially no areas of shallow water table near the streams to be raised to the surface by rapidly infiltrating rainfall. Thus, storm runoff greater than about 2 percent of the rainfall must be generated by flow from areas in which the water table can reasonably be expected to lie 3 or more feet beneath the land surface.

Visual observation confirms that surface runoff occurs from hillsides covered with a thin, and frequently discontinuous, stand of grass. During heavy rainfall such areas exhibit a myriad of rivulets draining away the sheet of water on the soil surface. At these times there is little doubt that true surface runoff is occurring. What is not clear from visual observation is the extent to which the surface runoff is mixed with water that has had enough contact with the soil to be considered quick-return flow.

Rainfall heavy enough to cause such obvious surface runoff on well grazed grassy slopes will cause no rapid outflow at all from the most permeable forest soils, and outflow from the soils of intermediate permeability will occur with a delay corresponding to the time required for rainfall to infiltrate the uppermost layers of the soil and return to the land surface. The subsurface flow from the permeable forest soils continues for weeks after the rainfall ends and can be observed in road cuts draining from the contact zone between porous surface soils and more compact subsoils.

Early in the rainy season before the soils have a high moisture content, 30 percent or less of the rain falling on the Mattole basin appears as storm runoff during the period of rain and the following 24 hours (see figure 45). However, after 1000 mm or more of rain have fallen, storm runoff can equal 60 to 80 percent of the rain falling on the basin. This indicates that many areas far from any stream channel must be contributing to storm runoff during the latter part of the rainy season.

Despite the large volumes of storm runoff when rainfall exceeds 20 mm per day, the dissolved SiO_2 content does not decrease to less than about 60 percent (8 mg/L SiO_2) of that of delayed-return flow, which has had several days to react with the soil (Kennedy, 1971). Reaction with suspended sediment in the stream channel appears to be an unlikely source for more than about 1 mg/L SiO_2 in the contact time available (Kennedy, 1971). Therefore, at least 50 percent of the storm runoff at peak stream discharge may have had intimate enough contact with the soil to be considered quick-return flow, assuming that subsurface runoff equilibrated with the soil contained 13-14 mg/L SiO_2 (the highest SiO_2 value observed in the Mattole when flow was essentially all quick-return flow). If one assumes a lower SiO_2 concentration in equilibrated quick-return flow, a correspondingly greater percent of the storm runoff must have been quick-return flow.

If, as seems probable, at least 50 percent of the storm runoff is quick-return flow at peak discharge, the question remains as to how such close contact with the soil could occur during the first few hours time available before much of the storm runoff has left the hillslopes.

The explanation is believed due in part at least to interflow on a scale not usually considered. Selim and others (1972, 1974) have shown that subsurface runoff can occur on hillslopes of irregular surface if a thin layer of free water covers a saturated, more permeable layer of soil overlying a much less permeable zone. If the irregularities on such slopes have dimensions of a few centimeters, and the saturated layer has a thickness on the order of a centimeter or two, the percolation distances for quick-return flow can be quite short and travel times much less than that required if subsurface runoff distances are on the order of several meters. A similar process was discussed by Zaslavsky (1970), Zaslavsky and Sinai (1977), Sinai and Zaslavsky (1977), and used by Kennedy (1977) to explain pickup of dissolved salts by storm runoff.

In addition to the actual subsurface flow on the hillslopes, there is an opportunity for diffusion of dissolved solids over a very short distance from the interstices of the saturated surface soil into the thin film of surface runoff moving toward nearby rills. The relative importance of these processes in controlling the composition of quick-return flow is not known but undoubtedly would vary from place to place in the basin.

In the Mattole basin, the well grazed grassy hillsides are the major sources of storm runoff during storms of moderate intensity and, in that sense, they constitute the partial area of contribution described by Betson (1964) and Ragan (1968). However, as rainfall intensity increases, rivulets extend further upslope and fan out over the hillside from well marked drainage lines in a manner typical of the variable-source-area concept (Hewlett and Nutter, 1970). Rain falling on these rivulets and rills will add greatly to the surface runoff component of storm runoff. One would, therefore, expect an exponential increase in storm runoff as rainfall increased linearly.

In both the Mattole area and in Menlo Park, as well as elsewhere, rather short (1-10 minutes) periods of intense rainfall commonly are interspersed with longer periods of less intense rainfall, all within the same general storm period. This means that, although the rainfall rate averaged perhaps 1-2 mm per hour during the storm, most storm runoff may very well have occurred

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In both the Mattole area and in Menlo Park, as well as elsewhere, rather short (1-10 minutes) periods of intense rainfall commonly are interspersed with longer periods of less intense rainfall, all within the same general storm period. This means that, although the rainfall rate averaged perhaps 1-2 mm per hour during the storm, most storm runoff may very well have occurred during short periods when the rainfall rate considerably exceeded 2 mm per hour. Following such short intense bursts many rivulets concentrate the resulting storm runoff, and the following less intense rain falls on a greatly expanded area of water surface. Thus, more surface runoff is produced by the following lower intensity rain than if the high intensity rain had not occurred.

In the Mattole basin, then, during peak storm runoff less than 50 percent of the stream flow is surface runoff, perhaps 2 percent is direct rainfall on stream channels, a few percent at most is base runoff and the rest is subsurface runoff. Solution of soil solids on the hillslopes is the major source of dissolved constituents in storm runoff. Outside of storm periods, stream discharge is sustained by delayed-return flow containing solutes from soil and rocks above the water table and by ground water some of whose solutes are in near equilibrium with minerals below the water table.

It is reasonable to assume that the added soil-contact time of runoff from forested and the more organic soils compared to that from the less permeable soils on grassy slopes should be reflected in the stream chemistry. As rainfall increases in time and/or intensity and runoff from increasingly permeable and organic soil reaches the stream, the elements concentrated in, and easily leached from, vegetation will be contributed to the stream in much greater amounts, Such additional contribution could counteract or even override the tendency toward dilution due to water coming from less permeable sparsely covered grassy slopes. As rainfall continues, causing the more permeable soils to contribute to storm runoff, there will be greater opportunity for quick-return flow from even the less permeable soils. As some surface soils become saturated and ponding and runoff begins, the rivulets developing on the slopes may permit drainage from the uppermost soil layers with relatively little head difference because surface-tension effects restraining such outflow from the soil would be reduced. The quick-return flow observed in the Mattole basin, therefore, is probably a mixture of rainfall that has entered and seeped from both the thicker more permeable soils and from thin layers of the less permeable soils.

In addition to the changes in stream chemistry due to water coming from various soil horizons during storm runoff are the changes resulting from channel travel-time effects, geologic variations within the basin, and differences in the amount of airborne sea salts deposited at various distances upstream. Comparison of chemical changes in Conklin Creek (10-15 km^2 basin) with those in the Mattole River (620 km^2 basin) during storm-runoff periods helps to separate travel-time and aerosol effects from the soil-source effects. The photographs in figures 45 and 46 show the upper and lower parts of the Mattole basin. It is apparent that the lower part of the Mattole basin has a higher proportion of grasslands than does the upper basin. Thus, one would anticipate that much of the rapid storm runoff would come from the lower basin, with flow from the upper basin delayed in part due to longer travel times in the stream channel and in part due to delays in the soil.

Travel-time Effects on Stream Chemistry

No time-of-travel studies using dyes or other tracers were conducted in the Mattole basin, so inferences regarding travel-time effects on stream chemistry must be drawn from such studies on other streams and from available velocity data at the U. S. Geological Survey gaging station at Petrolia. Figure 47 shows the mean velocity of the Mattole River at the bridge near Petrolia plotted against stream discharge.

Leopold and Maddock (1953) have shown how increase in stream gradient, as one goes upstream, tends to oppose a reduction in stream velocity expected because of decreased water depth. The result is that the mean stream velocity decreases only moderately in a headward direction. In the case of the Mattole River, average discharge decreases perhaps 50 percent between the sampling site and the center of the basin (based upon the area and rainfall rate above and below the basin center). Leopold and Maddock's data (1953) indicate a decrease in average velocity of about 10 percent for such a decrease in discharge. Outside the stream-channel system flow velocity on the hill slopes is probably much less than in the channels. Emmett (1970) observed surface runoff increasing from an initial velocity in the range 0.003-.02 to a final velocity range of 0.09-.5 m/s at 30 m for hillsides with slopes ranging from 0.029 to 0.33. Time to travel the first 30 m ranged from about 5 to 8 minutes and an additional 120 m was traversed in less than 16 minutes. Thus, applying these figures to the Mattole basin, one could estimate that in less than 1/2 hour surface runoff might reach a rill or small channel during active storm runoff.

If, as a first approximation, the mean velocity in the stream cross section for the Mattole near Petrolia at peak discharge is indicative of maximum velocities in water channels throughout the basin for a particular storm, an estimate of the travel times from different parts of the basin can be made for various flow conditions. The results of such an estimate are shown in Table 12. It can be seen from the

Table 12 - Channel distance to runoff-contributing areas within the Mattole River basin and estimated time of travel for various stream discharges 1/

Distance from sampling site (km)	Percent of basin contributing	Cumulative percent of basin contributing	Discharge (m^3/s)						
			1	5	10	50	100	500	1000
			Mean Travel Time (hours) 2/						
<10	0-6.3	0-6.3	<2.5	<2.1	<1.9	<1.4	<1.1	<0.6	<0.5
10-20	4.7	11.0	7.5	6.3	5.6	4.2	3.4	1.9	1.5
20-30	8.9	19.9	12	10	9.4	6.9	5.7	3.1	2.5
30-40	11.0	30.9	18	15	13	9.7	8.0	4.4	3.5
40-50	21.7	52.7	22	19	17	12	10	5.6	4.5
50-60	8.4	61.0	28	23	21	15	12	6.8	5.5
60-70	10.5	71.5	32	27	24	18	15	8.1	6.5
70-80	10.6	82.1	38	32	28	21	17	9.4	7.5
80-90	9.7	91.8	42	36	32	24	19	11	8.5
90-100	7.7	99.5	48	40	36	26	22	12	9.5
>100	0.5	100	52	44	39	29	24	13	10

1/ Channel distance upstream from sampling site near Petrolia.

2/ Estimated from mean velocities measured in the stream cross section near Petrolia by U. S. Geol. Survey personnel.

table that about 40 percent of the basin area is in the range 30-60 km distant from the sampling site near Petrolia, 20 percent is less than 30 km and 30 percent is 60-90 km distant. The area 30-60 km distant probably has a higher average rainfall than the basin as a whole (Rantz and Thompson, 1967) and contains extensive grassy slopes; thus, it seems probable that runoff should arrive from this area at about the time of peak discharge during storm periods. Comparison of peak rainfall occurrence from a U. S. Weather Service recording rain gage near Honeydew (which lies about 35 river kilometers from the sampling site) with the time of arrival of peak discharge at the sampling site permits some evaluation of the accuracy of such an estimate. The Mattole peaked at 320 m^3/s on January 21, 1972, and calculation of the time to travel 45 km from data in table 12 indicated that approximately 7 hours (6.5 + 1/2 hour surface runoff) should have elapsed between peak rainfall and arrival of the peak. Actual observed time was 6.5 ± 1 hours. The higher peak discharge on January 22 (1100 m^3/s) arrived about 5 hours after peak rainfall at Honeydew and the calculated time was 5 hours (4.5 + 1/2 hour surface runoff). On February 28, 1972 actual arrival time of the peak was about 7.5 ± 1 hours after intense rainfall and calculated time was 6.5 hours. In each of the cases referred to there was a well defined 1-3 hour period of high-intensity rainfall. At lower peak discharges and with longer periods of low-intensity rain the relation between calculated and actual arrival times of peak discharges is less consistent and the differences can be as much as 6 hours, although it is usually less. In the case of the November 7-15, 1969 study, incomplete rainfall records at Honeydew indicate that maximum rainfall intensity occurred at 2200 ± 1 hour on November 7th, which resulted in a peak discharge at the sampling site about 9.5 hours later. This compares with a calculated time of travel of 10.5 hours (10 + 0.5 surface runoff). Using a similar calculation for Conklin Creek, the estimated travel time of peak discharge from the headwaters to the creek mouth was 1-1.5 hours, and observed travel time was 3 ± 1 hours, which suggests that flow velocities in headwater streams are slower than allowed for in table 12. It is possible that peak rainfall occurred later at Conklin Creek than near Honeydew, where the rainfall records were obtained, but storms normally move into the Mattole area from the northwest with storm-front velocities on the order of 50-75 km/h (H. G. Draencke, U. S. Weather Service, personal comm., 1975). Inasmuch as the airline distance from the Conklin Creek drainage to Honeydew is only about 12 km there should be, on the average, only 10-15 m delay between heaviest rainfall at Conklin Creek and at Honeydew. Thus, although the travel times shown in table 12 are approximate, they do permit a useful estimate of the time required for runoff to travel from various parts of the drainage basin to the sampling site.

The chemical composition of the tributaries to the Mattole River displays readily detectable changes between the lower basin and the headwaters. Figure 48 shows the location of tributaries sampled during three different moderate to low flow periods in 1967. Analyses of these tributaries and of the main stream at several points in the basin are presented in table 13.

The effect of travel time is shown perhaps most clearly in the case of Cl during the November 1969 detailed study. The McGinnis Creek and Conklin Creek basins, labeled No's. 14 and 15, respectively, in figure 48, are at the northwest end of the drainage basin just upstream from the Mattole sampling site and must receive sea salts as dry fallout swept in from the northwest by the prevailing winds. It is apparent that the Cl concentration in Conklin Creek and McGinnis Creek is higher than in other tributaries further upstream. Although the Indian Creek basin is closer to the ocean than Conklin and McGinnis Creeks, a 450-m hill between it and the ocean may act to shunt near-surface winds away from the basin. In the picture shown as figure 2, the Conklin and McGinnis Creek basins lie on the left in front of the distant skyline, whereas Indian Creek is protected by the hill shown on the right side of the picture. When runoff from Conklin and McGinnis Creeks arrived at the Mattole River sampling point, the higher Cl concentration in the tributary water was observed (Figure 34) as about a 0.2 mg/L increase in Cl concentration in the main stream. The timing of the Cl rise at the Mattole sampling site coincided well with the estimated time of travel from the tributaries' mouth.

Table 13 Chemical composition of streams in the Mattole River basin[1].

Stream identification	Distance upstream (River km)[2]	Concentration in mg/L																				
		January 14-17, 1967							June 3-5, 1967							September 16-17, 1967						
		Ca	Mg	Na	K	Cl	SO_4	SiO_2	Ca	Mg	Na	K	Cl	SO_4	SiO_2	Ca	Mg	Na	K	Cl	SO_4	SiO_2
1 Mattole R. above Thorn	95	4.7	1.5	4.7	0.4	-	1.2	12.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2 Mattole R. above Bridge Cr.	83	-	-	-	-	-	-	-	4.9	1.7	4.9	0.7	3.4	2.0	14.7	-	-	-	-	-	-	-
3 Bridge Cr.	83	-	-	-	-	-	-	-	6.5	1.9	5.1	0.7	3.2	3.2	14.5	-	-	-	-	-	-	-
4 Mattole R. above Bear Cr.	66.	10	2.3	5.3	0.5	-	8.0	12.4	8.5	2.0	5.1	0.7	3.1	5.4	14.1	16	3.1	7.0	1.1	3.8	10	10.7
5 Bear Cr.	66	14	2.8	5.3	0.4	3.1	11.8	12.0	14.9	2.9	5.4	0.6	3.0	8.8	13.5	22	3.7	7.0	0.9	3.6	15	10.7
6 Blue Slide Cr.	64	12	4.4	7.1	0.8	4.1	3.8	12.0	13.1	4.7	7.8	1.1	3.7	3.0	14.1	25	7.3	10.8	1.7	7.1	6	12.0
7 Mattole R. above Honeydew Cr.	37	-	-	-	-	-	-	-	-	-	-	-	-	-	-	38	5.7	0.3	1.5	4.8	19	10.1
8 Honeydew Cr.	37.	23	3.5	5.7	0.6	2.3	22.4	8.4	23	3.6	5.5	0.8	2.2	21	9.5	36	4.8	7.1	1.2	2.8	32	9.2
9 Mattole R. at Honeydew	34	18	3.6	5.7	0.7	3.1	13.4	10.1	18.3	3.6	6.2	1.0	3.0	13	12.2	-	-	-	-	-	-	-
10 Upper North Fork Mattole R.	33	28	4.7	7.5	0.9	3.7	26.6	9.1	28	4.7	7.5	1.1	3.3	23	10.3	44	6.7	9.6	1.8	5.1	31	11.1
11 Pritchett Cr.	24	24	4.8	8.8	0.7	4.0	16	13.1	25	4.8	8.6	0.9	3.7	15	13.9	-	-	-	-	-	-	-
12 Squaw Cr.	17	25	4.1	7.5	0.8	3.7	26	9.3	26	4.0	7.1	1.0	3.2	23	10.5	42	5.6	9.6	1.4	4.8	33	9.9
13 Indian Cr.	11	15	3.3	6.4	0.5	3.8	13	13.9	15	3.2	6.3	0.6	3.6	12	13.5	28	3.9	7.6	0.7	4.2	9	14.5
14 McGinnis Cr.	5	35	6.3	9.9	0.9	4.6	33	11.6	34	6.2	9.8	1.1	-	27	12.6	44	7.0	12.5	1.6	6.5	31	13.4
15 Conklin Cr.	4	24	4.8	9.5	0.8	5.1	20	11.5	24	4.9	8.9	0.8	4.2	19	13.0	31	6.0	12.0	1.3	7.1	26	12.4
16 Mattole R. nr Petrolia	0	23	4.2	6.3	0.8	3.4	18	10.4	24	4.0	6.8	0.9	3.1	16	12.2	36	5.9	0.6	1.3	4.2	28	9.2

[1] Listed in downstream order. Analyses under the supervision of J. W. Helms.

[2] Distance upstream is measured from the sampling site on the Mattole River near Petrolia.

The relatively high SO_4 content of tributaries downstream from the town of Honeydew may cause SO_4 to remain moderately high during the early phases of a stream rise because such waters arrive at the sampling site before upper basin waters. However, the actual concentration of SO_4 during rising discharge near the beginning of the rainy season significantly exceeded that observed in any of the tributaries to the Mattole. Therefore, at least part of the SO_4 carried must have been leached from surface soils. The major cations, Ca, Mg, and Na are generally higher in concentration in the downstream tributarie and this is reflected in the concentrations of these elements during earl phases of a stream rise, just as for SO_4 and Cl.

Glover and Johnson (1974) demonstrated the increasing lag of the minimum in dissolved solids concentration behind peak stream discharge as water moves downstream and attributed it to the fact that the velocity of the kinematic wave is always greater than the mean water velocity. Walling and Foster (1975) observed a similar lag which was attributed in part to processes outside the stream channel. In the case of the Mattole River, coincidence of the Ca and Mg concentration minima with maximum discharge would appear to show either there has been no significant shift in time of travel of the peak flood wave compared to the actual water coming from the slopes during Ca and Mg minima or, if there is such a shift, that the Ca and Mg minima precede peak runoff and the flood wave catches up to the minima during passage down the stream channel. Reasons for the minima preceding maximum discharge are presented later in the report section concerned with soil-source effects. The fact that the Ca and Mg minima occur at or very near peak stream discharge in Conklin Creek where travel distances are relatively short, as well as in the Mattole River, would argue either that there is no significant difference in travel time between the flood wave and movement of the water mass in the distances characteristic of the Mattole basin or, if there is such a difference, its effects are not detectable by the time the water arrives at the sampling site near Petrolia. In the following discussion it will be assumed there is no appreciable time difference between peak discharge and minimum in Ca and Mg, although the Mattole basin is large enough that the peak is rather broad and sampling frequency was usually such that a 1 to 2 hour lead or lag in the dissolved solids minimum with respect to peak stream discharge could go undetected.

Soil-source Effects on Stream Chemistry

During storm runoff many streams show decreasing dissolved solids concentrations with rising discharge, and the Mattole River and its tributaries are not exceptions. This dilution during rainfall makes it difficult to recognize the relative increases or decreases of the various dissolved constituents during changing discharge. However, the effect of dilution can be essentially eliminated by using the ratio of a particular constituent to specific conductance, which is a measure of the total electrolytes present. Variations in this ratio indicate changes in the concentration of a particular constituent relative to the total dissolved electrolytes.

As described elsewhere (Kennedy, 1971), the observed variations in the proportions of the various electrolytes during changing stream discharge can probably be best understood by visualizing the distribution of these materials at the land surface prior to rainfall and then, with some knowledge of their chemical properties, making some reasonable hypotheses regarding their movement during rainfall. The resulting hypotheses can be tested by field data and observations.

Conceptual Model of Streamflow Components

At the end of the summer dry season, sea salts have been deposited on vegetation and the soil surface in decreasing amounts as one goes upstream in the Mattole basin because prevailing winds are from the northwest and perhaps because mountains 600 to 1200 m high lie to the west between the ocean and the middle and upper part of the Mattole River basin (Elford, 1970). Also, decomposition of organic matter at or near the land surface has released water-soluble K, NO_3, PO_4, SO_4, other inorganic materials, and various organic substances. Vadose water has largely drained to the water table and evapotranspiration has left surface soils thoroughly dried.

When light rains occur before the beginning of the main winter rainy season, highly soluble materials such as Na, Cl, K, and NO_3 are washed from vegetation and the surface litter down into the upper few inches of soil. Similar, but less effective, leaching probably occurs for less mobile constituents such as sulfates. As rainfall becomes more intense, downward leaching of soluble salts continues while the uppermost soil horizons become wet and storm runoff begins. This initial storm runoff is on just-leached surface soil and, hence, would be expected to be relatively low in dissolved salts. However, as rainfall continues and there is time for some of the infiltrated rainfall to seep laterally downslope, some quick-return flow occurs which carries higher concentrations of dissolved salts than the initial storm runoff. This quick-return flow (which is identified chemically by relatively high dissolved salt content and which may be in part water that has simply had very intimate and thorough contact with the irregular soil surface) mixes with surface runoff and may again seep into and return from surface soils before entering a stream channel. Heavier rain falling directly on areas of surface runoff normally will serve simply to dilute the dissolved solids contained in quick-return flow. As rainfall continues, the accumulation of water in the soil causes increasing production of quick-return flow and would be expected to push a high-salt wetting front deeper into the soil. When rainfall decreases at the end of the storm the proportion of runoff entering stream channels as quick-return flow, should increase. As time passes after

rainfall ends, and as surface runoff ceases, subsurface runoff from progressively greater depths in the soil would be expected to enter the stream channels, i.e. as delayed-return flow (Onstad and Jamieson, 1968). Such a sequence of events would be anticipated for essentially all areas within the Mattole basin, but for a specific small tributary basin and particular rainfall rate the timing and quantity of storm runoff following the various flow paths will vary with land slope, vegetation and soil characteristics. Furthermore, when the effects of these variations in flow paths are intermingled with channel travel-time effects, the resulting stream flow at any one time would be expected to be a relatively complex mixture of waters from various points in the basin having different sources within the soil profile.

A related and similar variation in components of stream flow can be observed on a seasonal basis. Although the stream-channel travel-time effects are negligible on a seasonal time scale, one can distinguish periods of primarily surface runoff plus quick-return flow, delayed-return flow and base runoff. During periods of intense rainfall, and for a short time thereafter, especially in November and December, the river flow consists to a major extent of surface runoff and quick-return flow because there has not been an opportunity to build up a large reservoir of water in the soil. As the rainy season continues, an increasing fraction of the stream discharge is due to delayed-return flow, and near the end of the rainy season, stream flow is probably maintained almost entirely by such flow. From late spring until mid-summer the delayed-return flow decreases while the proportion of ground water increases and, after early August, the river flow is probably made up primarily of contributions from ground water. This situation normally continues until late October or early November when a new rainy season begins the cycle again. A schematic representation of this annual cycle is shown in figure 49. It should be noted that the "rain" shown in the figure is the average over the basin for each month over a 10-year period, and the percent of each flow component plotted represents the expected proportion for the rainfall rate shown.

Figure 49 is a conceptual model only and no samples of soil moisture or ground water were obtained to prove the "picture" being presented.

In the discussion to follow, variations in the concentrations of different dissolved constituents will be related to both individual storm events and to seasonal changes. Whers suitable data are available from other streams an effort will be made to compare them with the information from the Mattole River.

Calcium and Magnesium

Ca and Mg are the major cations in the Mattole River at all levels of flow and, during storm runoff, normally reach minimum concentration at or very near peak stream discharge. Although Ca and Mg decrease in concentration during storm runoff; the dissolved load of these elements transported by the river increases greatly, demonstrating that much of the Ca and Mg is derived from leaching of the surface soils. Because Ca and Mg show a greater percentage decrease in concentration than Na and K, the rate of release from the soil of Ca and Mg apparently is not as fast as for Na and K during storm runoff. Because Ca and Mg show higher concentrations than the other cations at both high and low flow it is evident that, in absolute terms, these elements are being leached in greater quantity than the other cations regardless of flow conditions.

Although Ca and Mg generally behave alike, the Ca:Mg ratio (figure 10) rises on increasing discharge during the early part of the rainy season when accumulated salts are being leached from vegetation and near-surface soils, decreases during the main part of the rainy season when leachates are believed to come primarily from shallow mineral soils and then rises as stream flow is derived from deeper soil horizons. The peak in the Ca:Mg ratio occurs in late July as ground water becomes the major flow component.

Thereafter, Ca is essentially constant while Mg continues to increase, so the ratio of Ca:Mg decreases. The Ca probably levels off due to the approach of calcite saturation, whereas the stream is still undersaturated with respect to magnesite. A calculation using the WATEQ program (Truesdell and Jones, 1973) for a sample collected at low flow in early November, 1966 indicated about 3 percent oversaturation with calcite but less than 10 percent saturation with magnesite. As indicated above, these results suggest the possibility that the Ca:Mg ratio of leachates from surface litter and from uppermost mineral soils is greater than that from the lower, but still shallow, soil layers and that the ratio then increases with depth in the soil profile until the Ca concentration is limited by calcite solubility.

The ready availability of Ca and Mg to leaching by rainfall is indicated by leaching experiments done with different concentrations of soil in distilled water (table 14). When air-dried soil was mixed with distilled water in the ratio 0.5 g of <0.18 mm soil to 1 g of water (equivalent to water filling the interstices of soil of 84 percent porosity) the Ca and Mg concentrations after one-hour contact time were in the range observed with stream water during very high flows. The Ca leached per gram of soil ranged from 9 to 37 µg (average = 23). When only 0.01 g of <0.18 mm soil was added per gram of water and allowed to equilibrate for six hours the Ca concentrations were about one fortieth as much as when the higher concentration of soil was used and the Ca released per gram ranged from 12 to 49 µg (average = 30). Data in table 14b show that over 80 percent of the Ca leached in 6 hours from four Mattole soils was released in the first 20 minutes indicating that, after the first 20 minutes the leaching rate declined drastically.

Given the amount of Ca released per gram of soil in 1 to 2 hours contact time, the amount of rain falling in a storm period and the Ca concentration in surface runoff, a rough estimate of the thickness of the soil which must be leached can be calculated. During the storm of early December 1966 more than 130 mm of rain fell on the 4th (U. S. Weather Bureau, 1966) with perhaps 100 mm falling during the afternoon and evening. Stream discharge between 1200 on December 4 and 1200 on December 5 was equivalent to 110 mm of rain falling on the whole basin. Peak river discharge occurred about 2230 on the 4th so, based on travel-time estimates, rainfall maximum is assumed to have been between 1730 and 1800.

COMPOSITION OF LEACHATES FROM MATTOLE BASIN SOILS

Table 14a Composition of leachates from Mattole basin soils (1 hour leach of 1:2 w/w soil:water mixture 1/

Sample number 2/	Approximate Depth range of sample (cm)	pH of leachate	Concentration in mg/L					Concentration in µg/L				Concentration in µg/L					
			Na	K	Mg	Ca	Sr	Al 3/	Fe 3/	Mn 3/	Cd	Cu	Pb	Zn	Cr	PO_4-P	NO_3-N
1a	0-5 measured from top of mineral soil	5.3	4.1	5.7	1.9	7.7	52	105	350	240	.5	8.2	1.4	4.1	0.6	270	70
1b		5.4	4.1	5.5	1.9	7.6	52	110	340	240	.1	6.4	0.8	2.9	.5	260	40
2a		4.9	6.5	11.8	6.6	18.4	240	40	70	650	.09	3.7	0.9	7.3	.4	150	14,000
2b		4.9	6.7	12.1	6.8	18.9	240	40	70	670	.1	3.4	0.6	6.9	.2	145	14,500
3a		5.4	5.1	12.3	4.5	16.1	140	50	105	500	.2	6.8	1.1	2.2	.2	120	2,450
3b		5.4	5.1	12.3	4.5	16.3	150	60	95	500	.2	6.8	1.2	2.2	<.2	125	2,450
4a	15-30 cm	5.1	3.2	6.3	3.4	15.9	125	55	35	230	.2	10.3	.9	3.7	.4	95	470
4b		5.2	3.2	6.3	3.4	16.3	130	60	130	240	.3	10.4	1.1	3.4	.4	95	450
5a		5.1	4.8	1.6	1.2	4.5	35	30	25	40	.1	3.7	<.6	1.0	<.2	30	440
5b		5.2	4.8	1.6	1.2	4.6	35	35	25	40	.06	3.7	-	1.0	<.2	35	420
6a		4.9	4.8	4.5	2.1	6.8	55	40	35	105	.15	4.1	1.4	2.0	.5	15	1,000
6b		4.9	4.8	4.5	2.1	6.8	45	40	35	105	.15	4.1	1.5	1.3	.4	15	1,000
7a		5.5	2.6	7.9	2.4	10.4	110	20	20	85	.06	3.4	<.6	.6	<.2	50	1,250
7b	60-90 cm	5.6	2.6	8.0	2.5	10.3	115	20	20	90	.04	3.1	-	.4	<.2	50	1,300
8a		4.7	4.7	4.0	1.6	2.9	40	40	20	45	.1	3.9	.9	.9	<.2	7	730
8b		4.7	4.7	4.0	1.6	2.8	40	40	20	45	.1	4.0	1.1	.8	<.2	6	800
9a		5.2	2.2	3.9	.7	4.9	60	70	<2	165	.06	.6	<.6	.2	<.2	7	760
9b		5.6	2.3	3.9	.7	4.9	60	85	<2	160	.09	.6	-	.4	<.2	7	760

1/ Material used was sieved to less than 0.18 mm diameter before leaching. Duplicate trials are shown to demonstrate precision. Analysts were G. W. Zellweger and R. J. Avanzino.

2/ Samples 1a, 1b, 5a and 5b - SE¼ Sec 36 T25 R1W; Sample 2a and 2b - NE¼ Sec 14 T25 R2W; Sample 4a and 4b - NW¼ Sec 33 T25 R1W; Samples 6a, 6b, 8a and 8b - SW¼ Sec 32 T35 R1E; Sample 7a and 7b - NE¼ Sec 10 T25 R2w; Sample 9a and 9b - NE¼ Sec 8 T45 R2E

Samples 1e,b - grassy 30° south slope; 2a,b - well grazed, sparse grass, 15° north slope; 3a,b - soil composite, grassy areas; 4a,b - grassy 30° slope; 5a,b - grassy 30° south slope; 6a,b - brushy 30° north slope; 7a,b - tree covered 30° north slope; 8a,b - brushy 30° north slope; 9a,h - grassy 30° east slope.

3/ Solution was passed through a 0.1 µm Millipore filter backed up by a 0.4 µm Nuclepore filter.

COMPOSTIION OF LEACHATES FROM MATTOLE BASIN SOILS

Table 14b Composition of leachates from Mattole basin soils (10g soil/L distilled water)

Sample Number	20 minute leach						6 hour leach					
	pH	concentration in mg/L				concentration in µg/L 1/	pH	concentration in mg/L				concentration in µg/L 1/
		Na	K	Mg	Ca	Zn		Na	K	Mg	Ca	Zn
1a	6.2	0.15	0.60	0.05	0.15	<.1	6.0	0.17	0.79	0.07	0.20	<.1
2a	5.9	.28	1.25	.16	.38	.5	5.9	.21	1.57	.17	.40	.7
3a	6.2	.19	1.11	.12	.40	.1	6.2	.24	1.59	.16	.49	.1
5a	6.2	.21	.28	.05	.10	<.1	5.9	.23	.36	.05	.12	<.1

1/ Cd, Cu and Pb were, respectively, <0.3, <0.04 and <.1 µg/L.

COMPOSITION OF LEACHATES FROM MATTOLE BASIN SOILS

Table 14c Ratios of ions in concentrated and dilute soil suspensions compared to the ratios in the Mattole River (w/w)

Sample Identification	Na/Ca		K/Ca		Ca/Mg		K/Na	
	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.	Conc.	Dil.
1a	0.53	0.83	0.71	4.0	4.0	2.9	1.4	4.6
2a	0.36	0.77	0.63	3.8	2.8	2.4	1.8	4.9
3a	0.31	0.50	0.77	3.2	3.6	3.1	2.4	6.6
5a	1.1	2.0	0.36	3.0	3.8	2.4	0.33	1.6
Mattole River during high flow	0.45		0.1		5.4		.22	
Mattole River during low flow	0.24		0.04		6.2		.16	

High rainfall is believed to have occurred primarily during about an 8-hour period extending from 1400 to 2200 with resulting high stream flows near Petrolia from 1900 December 4 to 0300 December 5. Relatively high discharges preceded and followed this 8-hour period, but the calculations following are based on just this period.

Stream discharge during the 8-hour high-flow period was equivalent to 5.2 cm of rain over the whole Mattole basin. Average Ca concentration in the river during this time was about 8.5 mg/L, so a total of 44 μg of Ca was removed from the basin per cm^2 of land area. If average leachable Ca per gram of soil is 25 μg/g (see leaching data above), about 1.8 g of soil would be required to supply the Ca from each cm^2 in the basin. With a bulk density of surface soil estimated as 1.4, this would mean that a soil column perhaps 1.3 cm deep would be leached to provide the required Ca.

It should be noted, however, that the soils used in the leaching studies summarized in table 14 had dried slowly over a period of months with ample time to release maximum amounts of soluble salts. By the afternoon of December 4, 1966 the Mattole soils had been leached by at least 144 mm of rain in the preceding 6 days, so much of the highly soluble salts would have been leached into the subsoils or carried away by storm runoff. Hence, the 1.3 cm leaching depth calculated above is probably a miminum for the 8-hour period under consideration.

The evaluation of the Ca source for the Mattole River during high flow would appear to demonstrate that considerable subsurface flow must accompany the surface runoff and that the subsurface runoff penetrates a minimum of 1 cm into the soil. The limitations on contact time are such that, considering soil permeabilities, the travel distances of the subsurface runoff within the soil should average no more than a few centimeters. Such a conclusion is compatible with the suggestions made earlier that pickup of dissolved solids by subsurface runoff results from intimate contact with surface soils on a scale of a few centimeters.

The leaching of suspended sediment samples as reported by Kennedy (1971) and of the soil samples described here show that interaction between the stream water and suspended solids at the concentrations found during stream transport is an unlikely process for supplying more than a small fraction of the Ca observed in storm runoff. Hence, a significant thickness of soil must be leached to supply the needed Ca. Similar reasoning can be applied to Na and Mg with generally similar conclusions regarding the need for soil leaching, although the depth of soil leaching required is slightly less for these elements than for Ca.

Sodium

Na in the Mattole River is derived from both sea salts and weathering of rocks and soils in the basin, but sea salt deposition is probably most concentrated in the lower part of the river basin. Examination of figures 15 and 16 for the Mattole River and Conklin Creek during November 1969 shows that it may be possible to detect the contribution of Na to the Mattole River from Conklin Creek (and probably from McGinnis Creek also). In the case of Conklin Creek Na concentration was about 12 mg/L before the stream rise as a result of the partial flushout of sea salts on a previous rise. The Na concentration decreased rapidly on the rise to about 8 mg/L at peak stream discharge and then increased slowly. In the case of the Mattole River the Na concentration began to decline from about 7 mg/L as the river started to rise, but then the Na levelled off as the higher Na concentration from Conklin Creek and McGinnis Creek arrived. As water from up river became a greater proportion of the flow, the Na declined further to its minimum a few hours after peak discharge. Thus, it appears that travel-time effects can be observed affecting Na as well as Cl in the Mattole River.

Review of figure 14 shows that, although on a seasonal basis Na declines in concentration during the winter, the ratio of Na:Sp. Cond. increases then, with maxima during peak runoff. The ratio of soil Na:sea Na shows a decrease during large storms just as seen for the smaller rise in November 1969. However, the maximum in this ratio is in late spring and early summer when about 75 percent of the Na is soil derived. This is not surprising because the winter rains have saturated the soil with low-Na rainfall which has flushed much of the Na away. As this rainfall equilibrates with the soil and rock it picks up Na produced by weathering. It is primarily this soil water that is draining into the streams in May to July. The lack of decrease in the proportion of soil Na in the storm runoff in March 1967 may result in part at least from the displacement of prestorm soil water. Studies by Bottomley (1974) and Sklash and others (1976) strongly suggest that prestorm water displaced by rainfall can be a significant factor in storm runoff.

The increase in the proportion of Na in the dissolved electrolytes during storm runoff is probably due to multiple factors of which two are discussed here. One reason for the Na:Sp. Cond. increase in storm runoff is the relatively high proportion of Na in aerosols carried in from the sea and deposited as dry fallout or dissolved in light rain preceding most storms. Such Na remains at or near the land surface until more rain occurs and in part can be easily flushed away during runoff. This explanation is similar to that of Edwards (1973) who observed a flushout of Na and Cl as well as other salts in November storms A second factor is the effect of "electroselectivity" (Helfferich, 1962) which results in a decided preference of ion exchangers for multivalent ions over monovalent ions under conditions of low ionic strength. Thus, prior to rainfall, there may be on soil grains a thin film of water which contains relatively high concentrations of dissolved salts. Under these conditions Na may be able to compete with Ca and Mg to a significant degree for exchange sites. When rain greatly dilutes the soil solution, exchangeable Na is desorbed and is replaced by Ca, thus reducing Ca release and increasing Na. As the soil gradually dries after the storm and the soil solution becomes more concentrated due to mineral dissolution and to evaporation, Ca will be released and Na taken up on the electrostatic exchange sites. For example, on November 15, 1966 suspended sediment from the Mattole River had approximately 3 percent of the exchange sites occupied by monovalent cations. If one uses the molar selectivity coefficient (Helfferich, op. cit.)[1/] between divalent and monovalent cations calculated for that sample and assumes that the water

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[1/] Molar selectivity coefficient = $\frac{C^{-b}_{A} - C^{a}_{B}}{C^{-a}_{B} - C^{b}_{A}}$ where C^{-} and C are the molar concentrations in the ion exchanger and solution respectively, and a and b are the valences of counter ions A and B, respectively.

was evaporated enough to triple the ionic strength, then, allowing for electroselectivity effects only, the monovalent cations would occupy about 7 percent of the exchange sites. This does not include the effects of changes in activity coefficients, which would work in the same direction as the electroselectivity effects.

The data in table 14 tend to support the argument for electroselectivity as a significant factor in affecting stream quality. The ratio of Na:Ca is consistently lower in the more concentrated soil suspensions than in the dilute suspensions. In a soil-column leaching experiment, also, the first effluent had a considerably lower Na:Ca ratio and higher electrolyte content than the following leachate aliquots. Thus, as interstitial soil solutions are diluted during rainfall, the Na:Ca ratio in quick-return flow might be expected to increase, just as was observed. Because Ca makes up a major part of the cationic contribution to conductivity, the Na:Ca ratio, and hence the Na:Sp. Cond. ratio, should rise with increasing discharge as demonstrated in figure 16.

The total exchange capacity of the soils in the Mattole is certainly sufficient to have a major influence on the chemistry of storm runoff. If one calculates the exchange capacity of the upper 1 cm of soil in the Mattole basin (estimated as 10 meq/100 g cation-exchange capacity), it is almost 10 times that of all the cations transported in solution in the Mattole River during the major storm period of December 1-5, 1966. Thus, a change of a few percent in the exchangeable Na in the soils could result in sizeable changes in dissolved Na in the river. In fact, the change in ionic strength of soil water during rainfall may be much greater than that assumed in the above calculations, with correspondingly greater changes in exchangeable Na.

Potassium

K, being monovalent like Na, might be released from exchangeable sites on soil particles during dilution by rainfall. However, K has other characteristics which result in a somewhat different behavior than Na. K is only about 1/28th as concentrated in sea salts as Na (Sverdrup and others, 1942) and probably only a few percent of the K in river water is due to salts cycled through the atmosphere. As a result of the ionic characteristics of K, it is selectively sorbed by the common soil minerals illite and vermiculite, thereby reducing the equilibrium concentration in solution. Also, considerable quantities of K are released during the decomposition of vegetation in the fall (Slack, 1964). These factors must be considered in understanding the variation in K with discharge and time.

During the stream rise on both Conklin Creek and the Mattole River in November 1969, the K concentration decreased only 10-15 percent, showing the stabilizing effect of the soil on the chemical composition of runoff waters. It also shows that sufficient contact of runoff water with soil and vegetation must have occurred to permit such an "equilibration". A similar stabilization effect is very evident in figure 18 where the K concentration remains between 0.7 and 0.9 mg/L from mid-November 1966 to early June 1967 despite great variations in stream discharge. After rains stopped in mid-May the rate of recovery in K concentration was fairly rapid until early July and by early August the K had stabilized, just as several other elements did.

It seems reasonable to assume that much of the readily soluble K from decaying vegetation was leached away during the rains of November and early December 1966 although continued decomposition of organic matter would be expected after such storms. Thereafter, K was probably derived mainly from the mineral soil except possibly during periods of greatest runoff. The consistent pattern of an initial decrease in K during the early part of a major storm period followed by an increase during peak flow to a value greater than before the storm began occurred in early December 1966, late January and mid-March 1967. Because the time scale of the pattern is different from that to be expected from travel-time effects in the stream channel some other explanation must be sought. Maximum K concentration was observed at or near peak discharge when runoff would have come not only from the less permeable soils with their thin cover of vegetation but also from even the moderately permeable soils which, in the Mattole basin, are commonly higher in organic matter. Therefore, it is possible that the K increase at high flow represents in part leaching of the more organic soils by quick-return interflow.

The stability of K concentration with varying discharge is characteristic of many streams other than the Mattole River. Steele (1968) showed that K varied by only a factor of 3 in concentration in Pescadero Creek, San Mateo County , California, while discharge changed by a factor of 5800. Similarly, the Klamath River near Klamath, California showed a change in K by a factor of 2.4 when discharge increased by a factor of 27. Other streams in northern California showing K behavior of this type include the Eel River at Scotia and Elder Creek near Branscomb (U. S. Geol. Survey, 1973).

This stability of K concentration in streams has implications regarding the release rate of K under various flow conditions. Apparently during storms K is released vary rapidly to storm runoff even after several hundred millimeters of rain have fallen on a basin. On the other hand, the failure of K to increase very much in concentration during delayed-return flow and base runoff indicates that the mineral source for K is only slightly soluble and(or) sorption effects are strong. Thus, although K released from surface materials tends to keep the K concentration up during storm runoff, interaction with mineral matter limits the possible K increase. The result is that the soil behaves as though it were a source of rapidly released, but slightly soluble K.

One aspect of the behavior of K which is consistent in all leaching studies done to simulate rain in contact with Mattole soils is the increased release of K compared to Ca as the ratio of water to soil increases. This can be observed in the data of table 14. When the ratio of water to surface soil was 2:1 by weight, the K:Ca ratio in the leachate was in the range 0.6 to 0.8, but when the water-to-soil ratio was 100:1, the K:Ca ratio was 3 to 4. In the stream, the water-to-soil ratio at high flow is on the order of 100-200:1, but the K:Ca ratio is only about 0.1 or 1/30 to 1/40th that expected from the leaching studies. The explanation may be related in part to the fact that the stream water is a mixture of subsurface runoff, which has been in contact with the soil in a very low water-to-soil ratio (and hence low K:Ca ratio in leachate), and surface runoff, which serves as a diluent. It should be noted that the K concentrations in a six-hour leach (table 14b) average approximately 1.1 mg/L, about equal to that in the river when both water discharge and sediment concentrations are high, but Ca concentrations are only a small fraction of the river concentrations.

Apparently soil suspended in river water at sediment concentrations equal to those occurring at high flow can supply most of the K found in solution, but cannot supply the Ca, Mg or Na observed.

Chloride

Cl in streams is commonly assumed to be derived primarily from atmospheric precipitation, and this is probably true for Cl in the Mattole basin. It is expected to show relatively little adsorption in soils, although the pattern of Cl in the Mattole River during storm runoff suggests that there may be some stabilizing capacity for Cl. Thus, Cl may be carried into the basin and deposited mainly as aerosols during dry periods and during light rains but is probably removed primarily through leaching by heavier rainfall.

An estimate of the possible contribution of rock weathering to Cl carried by the Mattole River can be made using the composition of average shales (Parker, 1967) and the amount of weathered materials removed from the basin in the 1966-67 water year as stream sediment. Such an estimate will certainly be too high because the erosion rate was much greater than normal during the period of study, but it will serve as an upper limit. Weathering shale equal to the 3,565,000 metric tons of suspended sediment carried by the Mattole in the 1967 water year would contribute about 600 metric tons of Cl, which represents nearly 15 percent of the Cl carried by the Mattole River during the 1966-67 water year. This leaves approximately 3370 tons as cyclic salt of the 3970 metric tons transported by the river. Average Cl content of bulk precipitation in the Mattole basin for the rainy season from October 1966 through May 1967 was 1.9 mg/L. If one assumes that runoff of 1.38×10^9 m^3 for the 1967 water year (U.S. Geol. Survey, 1973) was 74 percent of the rainfall (Rantz and Thompson, 1967), then rainfall was 1.86×10^9 m^3 and Cl input from October through May was 3540 metric tons. Thus, it appears that about 170 metric tons more Cl may have been available for river transport than was actually observed. The 170 metric tons is the difference between two much larger numbers, both of which are accurate to no more than ±10 percent. The conclusion, therefore, is that summer dry fallout contributes only a small fraction of the total annual Cl load in the river.

An alternative method of estimating the Cl from dry fallout deposited during the summer months is to calculate and combine the "excess Cl" carried by the stream during the autumn flushout with the Cl which is leached downward to the water table and reappears in part as ground water during the summer low-flow period.

The excess Cl transported during November and December was estimated by determining the difference between the concentration actually observed at a specified discharge in the fall, when flushout was occurring, with the Cl concentration for the same discharge in late spring after flushout was presumed to be complete. This excess Cl, when converted to stream load, was approximately 290 metric tons.

If one assumes a flow of ground water into the stream equal to that observed in August and September continues the year around and, to be conservative, all the Cl in the ground water was derived from summer dry fallout, the Cl contributed by ground water would be 120 metric tons per year. The combined dry fallout, then, is estimated at 410 metric tons, which is about 10 percent of the total Cl carried by the Mattole River during the 1966-67 water year. This 10 percent is also a very approximate figure, but agrees with the previous calculation in suggesting that dry fallout during the summer is a minor factor in the Cl load transported by the Mattole river.

Such a conclusion agrees with that regarding the contribution of dry fallout to stream flow by Gorham (1961) in which he suggested that dry fallout is of little importance in the river discharges of Cl in Australia. Tsunogai (1975) found that only about 20 percent of the sea salts carried by Japanese rivers is due to dry fallout. These conclusions contrast with those of Sugawara (1964, quoted in Tsunogai, 1975) who found that dry fallout accounts for two thirds of the Cl transported by Japanese rivers.

Although it is commonly assumed that Cl is not appreciably adsorbed by soils, the stabilization of Cl in the runoff during prolonged periods of heavy rainfall, when Cl concentration in rain is probably less than 0.1 mg/L would suggest that Cl adsorption may contribute significantly to controlling Cl in runoff in the Mattole basin. For example, between November 12 and December 3, 1966 about 840 mm of rain was recorded in the Mattole basin (U.S. Weather Bureau, 1966) and on December 4 another 130 mm fell in a few hours to give the discharge peak seen in figure 32. Cl concentration only decreased 10 percent from 3.0 mg/L on December 3 to 2.7 mg/L at peak discharge on December 4 despite an increase in discharge from 260 to 1170 m^3/s. Specific conductance decreased 20 percent from 100 to 80 during the same period. Between January 25 and 27, 1967 stream discharge increased from 115 to 790 m^3/s and Cl decreased from 3.3 to 2.5 mg/L. In neither of the instances mentioned were analyses of the rainfall available. However, in the storm of late January 1972, analyses of the rain were available and, while discharge increased from 22 m^3/s on the 19th to 290 m^3/s on the 21st and then to

1250 m^3/s late on the 22nd, the Cl decreased from 3.2 to 2.6 and then to 2.1 mg/L. Cl concentration in heavy rainfall (which probably contributes most to storm runoff) decreased to less 0.02 mg/L in this period. Thus, there appears to be a quickly available reservoir of Cl in the Mattole basin soils to supply Cl when low-Cl rainfall occurs. A possible source for this is the soil anion-exchange capacity which apparently can be equal to or greater than the cation-exchange capacity if kaolinite is a major part of the clay fraction (Grim, 1968). Hanes (1971) has shown that Cl sorption increases with decreasing pH, so the acid soils of the Mattole basin might reasonably be expected to adsorb Cl. If soil has an anion-exchange capacity of only 0.8 meq/100g, or 5 percent of the cation-exchange capacity, the amount of sorbed Cl in the upper 1 cm of soil in the Mattole basin might well be several times that transported by runoff during individual storms.

Even though sufficient exchangeable Cl is available on exchange sites it must be displaced in order to show up in the stream water. One possible mechanism for doing this is the replacement of monovalent Cl by divalent SO_4 upon dilution, just as in the case of Na displacement by Ca and Mg.

In the discussion above, the effect of travel time on Cl concentration during storm runoff was mentioned. Although outflow from Conklin and McGinnis Creeks undoubtedly affect the Cl concentration during the initial phase of a storm rise, these streams drain only a small part of the Mattole basin and almost certainly are not primarily responsible for the great increase in the Cl:Sp. Cond. ratio during storm runoff. The ratio increase is apparently characteristic of the basin as a whole and is believed to be due primarily to airborne sea salt brought in with winter rains and wind storms, as modified by the liquid storage capacity of the soil and its anion-exchange capacity.

In figure 30 the effect of intense, relatively short-duration, storms of November through mid-March can be compared with that of a prolonged series of smaller storms in late March through early May. After each storm pulse in November to mid-March the Cl recovery in concentration was relatively rapid after most of the rain ran off either as surface runoff or as quick-return interflow. However, after the less intense but prolonged rains of late March to early May, the soils were apparently well saturated with water and continued draining throughout the early summer with gradually increasing Cl concentration. In late July and early August the Cl concentration increased at an accelerated rate and then almost leveled off. It is probable that this period of abrupt increase marks the change from predominantly subsurface runoff to mainly ground water, or base runoff.

The explanation of the detectably greater Cl concentration in ground water as compared to subsurface runoff is believed to be due to rock weathering near the water table and to the leaching of sea salts into the soil. At the end of the dry season there is some buildup in sea salts on vegetation and surface soils. The gentle rains of early fall commonly do not cause much runoff (see fig. 45). Such rain would be expected to flush the highly soluble chlorides from summer dry fallout into the soil a short distance and, as heavier rains followed, Cl would be carried along with the downward moving wetting front while the more intense lower-Cl rainfall would contribute to storm runoff.

Some evidence for this can be found in the Cl content of leachates from soils collected in September 1969 after 1.6 cm of rain had fallen and caused only slight runoff (Table 15).

Table 15 Chloride leached from Mattole basin soils, which were collected in road cuts September 23, 1969 (in µg/g) 1/

Soil depth (cm)	Distance of sample site southeast from the ocean (km) 2/			
	1.5	8	15	21
0-5	92	32	24	7
15-30	45	16	8	3
60-90	11	2	2	1

1/ 50 g of the mineral soil was leached once with 100 ml distilled water and the Cl determined after decolorization with H_2O_2.

2/ Alternate descriptions of the sampling sites are as follows: 1.5 km-SE¼ SE¼ Sec 13 T25 R3W, 8 km-SW¼ NE¼ Sec 10 T25 R2W, 15 km-SW¼ NW¼ Sec 33 T25 R1W, 21 km-SE¼ SE¼ Sec 36 T25 R1W.

A consistent pattern of decreasing Cl was found with depth in the soil and distance from the ocean. The decreasing Cl with distance downwind from the ocean presumably is due to the fallout of the larger aerosols near the shore. The decrease in Cl with depth probably represents the effects of a thorough leaching of the profile with low Cl rain during the previous rainy season followed by periods of dry fallout and light rain at the end of the prior rainy season, the fallout of the long summer dry season and washing of Cl into the upper soil by the first fall rain. The light spring and fall rains would not be expected to carry the surficial Cl more than 20-30 cm into the well leached soil and apparently they did not.

Because the load of Cl carried by the Mattole River during the winter approximately equals that brought in by bulk precipitation during the rainy season the question as to when that Cl is deposited deserves further discussion. Rain sampling both at Menlo Park and near Petrolia, California indicates that the Cl concentration during heavier rainfall (more than about 3 mm per hour in the Mattole basin) is less than 0.05 mg/L. Light rain, on the other hand, can contain several milligrams per liter of Cl. The hailstorms are, of course, very significant exceptions.

The rate of Cl deposition can be described by the simple equation:

$$D=RC$$

where D is the amount of Cl deposited per unit time, R is the rainfall per unit time and C is the Cl concentration in the rain. Because C usually becomes very low when R exceeds about 3 mm per hour the rate of Cl deposition is quite small then. Similarly, when rainfall rate is very low the Cl concentration does not usually appear to exceed a few millimigrams per liter (high-chloride rains are exceptions) and once again the rate of Cl deposition is small. However, at intermediate rainfall rates the Cl concentration may be 1 to 3 mg/L and the rate of Cl deposition will reach a maximum. Under such moderate rainfall conditions the infiltration rate over much of the basin may well equal or exceed the rainfall rate and the Cl will move into the acid surface soils and be partially absorbed there and be partially held dissolved in interstitial water. This reservoir of Cl will then be available to contribute to quick-return flow, which becomes important during more intense rainfall. A part of this infiltrating higher Cl water will be carried downward through the soils during the main rainy season and appear later at the surface as delayed-return flow or as ground water.

Dry fallout between winter rains may also contribute significantly to the Cl deposited in the rainy season because high winds associated with winter storms may greatly increase the amount of Cl in the atmosphere. Tsunogai and others (1972) states that Cl in oceanic rain or maritime air increases by a factor of 10 for each 4-7 meters per second increase in wind velocity.

The lack of agreement between average Cl content of rainfall and Cl in stream flow has been noted by several authors (Eriksson,1955; Gambell and Fisher, 1966; and Bricker and others, 1968). The higher average concentration in stream water compared to rain water has commonly been attributed either to connate water or to evaporative concentration. There is need for greater emphasis on the effect of variation in rainfall chemistry with rainfall rate in causing an apparent increase in Cl between rain and stream water. Lowest Cl concentrations are expected during intense rainfall and such rain is most likely to cause storm runoff. Therefore, lowest Cl rain runs off rapidly whereas higher Cl rain is more likely to infiltrate and appear as stream flow later. Normally, most stream sampling is done at times other than during very high flows; hence, unless considerable care is exercised in allowing for the decreased Cl during high flow, the calculated annual average Cl concentration in stream water will be too high. Of course, this problem is accentuated if Cl concentration in rain is compared with low-flow stream samples.

As a result of the rapid runoff of low-Cl water during storms and other factors, the Cl content of ground water is about 2.5 times that of bulk precipitation in the Mattole basin and perhaps 5 or more times the average for that of actual rainfall.

Bicarbonate

Because the major anions in the Mattole River are HCO_3, SO_4 and Cl, the HCO_3, as a fraction of the anions, varies inversely with the sum of Cl and SO_4. Thus, during stream rises early in the rainy season, when both Cl and SO_4 are being leached from surficial soils, the HCO_3:Sp. Cond. ratio and the proportion of HCO_3 in the anions decrease sharply (figs. 22 and 23). Thereafter, the proportion of HCO_3 shows some tendency to decrease on a sharp rise and increase on the decline, but major changes do not occur (fig. 22). Beginning in mid-April 1967, the HCO_3 concentration began to climb and continued to do so until early August, when it levelled off. The HCO_3 is believed to be derived primarily from decomposition of soil organic matter followed by reaction with silicates during the rainy season and from solution of rock carbonates during low flow.

Sulfate

Sulfate represents, along with Cl and NO_3, one of the better examples of a constituent which has accumulated near the land surface during the dry season and is flushed out by the early storm runoff. This is most evident in figure 26 which shows that SO_4 increases briefly from a mean daily concentration of about 35 mg/L on November 5 to 40 mg/L on November 12. The maximum instaneous SO_4 concentration observed on the rise was 63 mg/L, well above the highest SO_4 observed in any tributary (Table 13), indicating that simply flushing out of such tributary channels could not account for the higher SO_4 levels. Further evidence for the leaching of SO_4 from surface soils is the fact that the highest SO_4:Sp. Cond. ratio observed in any tributary in mid-September 1967 was 0.13 whereas the ratio remained above 0.15 for 4 days during the period November 12-15, 1966. A similar increase in SO_4 concentration was observed at the beginning of the 1967-68 rainy season(See Basic Data Section). Thus, there appears to be little doubt of an early fall flushout of SO4. However, the time of maximum SO_4 concentration and maximum ratio of SO_4:Sp. Cond. in the Mattole River precedes peak stream discharge, and it is possible that this timing is due at least in part, to travel-time effects because the tributaries in the middle and lower part of the basin are appreciably higher in SO_4 concentration and SO_4:Sp. Cond. ratio than those in the upper part of the basin. However, even in Conklin Creek (fig. 28) the peak in the ratio occurred 2-3 hours before peak discharge, which suggests that storm runoff during rising discharge has the greatest proportion of SO_4.

Apparently SO_4 is leached from the soil without great difficulty because, after the first major storm of November 1966, the increase in the SO_4:Sp. Cond. ratio on a sharp stream rise continued to occur but only briefly and to a much smaller degree than on the first storm. Also, the SO_4 concentration for a specified discharge declined after successive storm periods, as indicated by the lower SO_4 concentration at minimum discharge in March compared to the SO_4 at a similar discharge in mid-January (Figure 26) and as shown in figure 51.

Just as in the case of Cl, SO_4 increased markedly in late July, 1967 (Figure 28) suggesting that ground water was significantly higher in SO_4 than the delayed-return flow draining from soils which were saturated during the winter.

It is possible that the SO_4 level in mid-October 1966 prior to any fall runoff was lower than indicated in figure 28. No samples were collected before November 5, but there had been a small stream rise in late October 1966 which could very well have raised the SO_4 level. This would help explain the fact that the SO_4 concentration at the end of September 1967 was appreciably lower than at the end of October 1966. A part of this concentration difference may also be due to the greater rainfall, and hence greater soil leaching, during the winter of 1966-67 compared to that in 1965-66.

The processes involved in SO_4 migration during the rainy season can be deduced from information in the soils literature. Jordan and Ensminger (1958) point out that organic sulfur in soils constitutes an important reserve supply for plant growth and, as organic matter decomposes, the sulfur is released mainly as SO_4. This SO_4 is held within carbonaceous material and would be somewhat slower to leach than Cl, which is probably present on more accessible surfaces. At the end of the dry season there is a supply of SO_4 at and near the land surface from decomposed organic matter and also, to some degree, from sea salts and other aerosols. Rainfall would wash some of this SO_4 into the soil where it would be adsorbed in part by the acid soils of the area. Harward and others (1962) have shown that SO_4 adsorption on soils increased significantly with increasing acidity below a pH of about 6 and that kaolinite, an important clay mineral in the Mattole basin, holds SO_4 more strongly than illite or montmorillonite. However, work by Chao and others (1964), indicated that hydrous oxides of Fe and Al may be the most important soil components in causing increased anion adsorption with decreasing pH. Although more strongly adsorbed than Cl, SO_4 is not fixed by the soil (Chao and others, 1962) and will move downward in the soil profile with leaching. As in the case of Cl, the concentration of SO_4 in water infiltrating the soil and reaching the water table is likely to be considerably higher than the average concentration in rain or in storm runoff.

An estimate of the SO_4 derived from sea salt as compared with other sources can be made using the Cl information presented earlier. Assuming negligible fractionation of sea salts and 90 percent of the Cl carried by the Mattole River as cyclic, the SO_4 derived from the sea and carried by the Mattole would be approximately 1060 metric tons. This represents only about 7 percent of the total SO_4 transported by the Mattole River in the 1966-67 water year. Hence, the remainder of the SO_4 is presumed to be derived from decomposition of organic matter, rock weathering, and from atmospheric sources other than sea salt. The SO_4 content of the 1.9×10^9 metric tons of bulk precipitation falling on the Mattole basin was approximately 9,500 metric tons, assuming 5 mg/L SO_4 concentration (Table 1). Of this 9,500 metric tons about 9,000 tons came from atmospheric sources other than sea salt. Not included in this 9,000 tons is the SO_4 deposited during the summer months. Thus, of the total of 14,200 metric tons of SO_4 carried by the Mattole River during the 1966-67 water year over two thirds may have come in through the atmosphere. The remainder could be easily obtained from rock weathering directly, assuming S concentrations in the rock equal to that in an average shale (Parker, 1967). It is quite possible or even probable, that a major fraction of the SO_4 found in bulk precipitation represents that in dust blown from nearby plants and surface soils and does not represent extra-basin material; however, data presently available from the Mattole basin do not permit distinguishing the sources of SO_4 in the bulk precipitation. If there is a high concentration of SO_4 in atmospheric dust and in the exudates covering plants, this would be a logical source for some of the SO_4 flushed out during the rainy season.

Silica

Silica in the stream water appears to be one of the best indicators of the depth in the soil surface profile from which the water has drained. It decreases in concentration and also, in some instances, decreases as a proportion of dissolved solids during the initial part of a stream rise. This is attributed to slower release of silica into overland flow as compared to other more soluble constituents during initial runoff (Kennedy, 1971). It is unlikely that this initial decrease in concentration is a travel-time effect because the water in the tributaries just upstream from the Mattole River sampling site contain higher silica concentrations than the main stream (Table 13). As continued leaching of the soil by rainfall occurs during an individual storm and there is better opportunity for rain to enter the soil and reappear as quick-return flow, the silica concentration and SiO_2:Sp. Cond. ratio increase. Because the soils of the Mattole basin are acid, the equilibrium silica concentration of soil water is expected to be higher than if the soils were more alkaline, for the Fe and Al hydrous oxides show decreased silica adsorption under acid conditions (McKeague and Cline, 1963).

Examination of silica variations on a seasonal basis (fig. 36) shows that, as long as water continues to drain from the acid soils and comprises most of the stream flow, silica concentration remains near 12 mg/L, but as the proportion of soil water becomes small and water draining from the more alkaline rocks near the water table becomes predominant, the SiO_2 declines to 8-9 mg/L. The sharpest change in the relative amounts of soil and ground water occurs late in July and early August, as indicated by the rather rapid decrease in SiO_2 concentration. This decrease in SiO_2 coincides with an increase in Cl and SO_4, as it should, for ground water is relatively high in Cl and SO_4 but low in SiO_2 whereas the reverse situation exists in the soil water comprising delayed-return flow.

pH

The pH of distilled water placed in contact with Mattole basin soils is about 2 units less than the pH of river water during storm runoff (Table 14). This suggests that during storms the rain contacting the surface soils probably has a pH of approximately 5.5 and, as it moves toward the main stream channel, increases in pH. Aeration of such soil leachates in the laboratory after separation from the sediment causes the pH to rise about one unit indicating that just equilibration with the atmosphere causes some of the pH rise as water draining from surface soils moves over the land surface. The cause of the remaining pH rise is not evident, but may be due in part to release of bases from feldspars which are ubiquitous in the sediments transported by the river (Table 10).

There is a well defined tendency for the pH to decrease during rapidly rising discharge resulting from large storms and to increase again within a day or so after peak discharge occurs. It is possible this reflects to some extent source area effects within the basin. The more porous soils in the Mattole basin are normally those which are relatively high in organic matter and, therefore, more acid. During intense rainfall, runoff will be generated from soils that are so porous that they do not usually produce runoff during low intensity storms. Such water may be somewhat more acidic and would be expected to contain higher K concentrations because of leaching of organic matter. Such increased K concentrations do occur at peak flows, as noted previously.

Examination of data obtained by Steele (1968) on Pescadero Creek during high runoff periods reveal that a similar decrease in pH occurs there. During low flow Pescadero Creek has a pH of about 8.0-8.3, but during peak discharge the pH decreases to 7.3-7.4. Johnson and others (1969) report a decrease in pH of stream water during storm runoff in the Hubbard Brook area of New Hampshire. However, the rainfall in that area had a pH of about 4, which is considerably lower than that in the Mattole basin, and this may be the main factor in causing a decrease in stream pH during storm runoff in Hubbard Brook.

Minor Constituents

Aluminum

Aluminum compounds found in soils in areas of high rainfall tend to be very slightly soluble. However, Al can be converted to mobile forms by complexation with organic compounds, which commonly are most concentrated in the upper part of the soil profile (Bear, 1964). One would expect, therefore, that these soluble Al compounds would appear in quick-return flow and this seems to be the case. As shown in figure 38, Al concentration in the Mattole River increased during the stream rise of January 20-22, 1972 and reached a maximum of about 13 μg/L at a pH of 7.7 and a SiO_2 concentration of 11 μg/L. This Al concentration at high flow is about four times higher than the concentration estimated from data on kaolinite solubility in Jones and others (1974), although at lower discharge the Al concentration observed is reasonably near that required by kaolinite solubility. Other evidence for the transport of at least some of the Al as metallo-organic compounds is the concentration of 110 μg/L Al in surface runoff from a grassy slope near Petrolia, collected during a gentle rain in January, 1972. Even after filtration through a 0.1 μm filter the water was slightly colored indicating the presence of dissolved organics. The pH of the sample was 6.4, the SiO_2 was 4.7 mg/L and the specific conductance 19 umhos. Such coloring can result from passage of clay or organic colloids through perforations occasionally observed in membrane filters, but a field extraction from an unacidified aliquot of the sample checked within 5 percent the Al concentration found in an aliquot acidified to about pH 1.5 and allowed to stand for a month before extraction and analysis. Had clay been present the acid would have dissolved some of it and increased the Al in solution considerably.

Further evidence for the presence of 50-110 μg/L Al in soil solutions in the Mattole basin is shown in table 14a. Soil samples were collected at various depths at different points in the basin, air dried and the <0.18 mm size fraction leached with distilled water for 1 hour with a 2:1 ratio of water to soil (w/w). This experiment was intended to simulate the effect of rain falling and running off Mattole soils. These soil solutions have a pH which is in the range 4.7 - 5.7 compared to about 7.5 in the Mattole River. The data in the table suggests that storm runoff has ample opportunity to pick up 10 μg/L or more Al before entering the stream channels. The dissolved Al may decrease as the water moves from the soil environment at a pH of about 5 to the stream channel at a pH of about 7.5.

The increase in dissolved Al during storm runoff is not restricted to the Mattole River. During a separate study of storm runoff from a virgin redwood area in the upper part of the Little Lost Man Creek basin near Orick, California in early November 1974, samples were taken at 1-2 hour intervals over a rise and filtered on site through 0.1 μm Millipore filters prior to acidification to a pH of 1 -1.5 for preservation (Sample collection and analyses by G. W. Zellweger). These samples contained about 3 μg/L Al before the stream rise began, reached a maximum of 20 μg/L near peak discharge and then decreased to 10 μg/L 12 hours later (figure 52). The timing of the Al increase with respect to stream discharge and the range of Al concentration in the Mattole River and Little Lost Man Creek are very similar and suggest that water contacting acid surface soils picks up appreciably more Al than water coming from deeper soils or from the water table.

In summary, the Al concentrations in the Mattole River at low flow are reasonably close to those which might be expected if equilibrium were attained with kaolinite, a major clay mineral in the Mattole basin soils; the tendency for somewhat higher values during storm runoff is attributed at least in part to complexing by soluble soil organics. The rate of equilibration of Al with the soil is fast enough that there is no evidence of a depression in concentration due to dilution by rainfall; in fact, the Al concentration tends to increase during peak runoff when quick-return flow is probably a significant component of stream discharge.

Barium

The barium concentration in the Mattole River at low flow is about 0.05 mg/L. Mineral solubility is the most likely control on Ba concentration. The solubility of barite ($BaSO_4$) is 2.3 x 10^{-4} gms/100 m at 20°C (Rosler and Lange, 1972), giving a solubility product of about 9.7 x 10^{-11}. With SO_4 concentration at about 30 mg/L at low flow, the calculated Ba concentration in the Mattole at saturation with barite is 0.08 mg/L. This concentration is close enough to the observed value to suggest that barite might be the control. This agrees with Hem's (1970) observation that barite is probably the control on Ba solubility in natural waters. During higher flow both Ba and SO_4 tend to decrease in concentration and, because equibibrium is not attained, the kinetics of dissolution of soil minerals probably controls the Ba concentration in Mattole water.

Cadmium

Cadmium is present in Mattole River water in concentrations well under 0.1 μg/L. In a comparison study of Mattole River water with four other northern California streams done in the spring of 1975 (Table 16), dissolved Cd was found to range in these streams from 0.01 to 0.03 μg/L. Such values are consistent with the results of a reconnaissance of minor elements by Durum and others (1971) in which 54 percent of the samples contained less than 1 μg/L Cd.

Table 16 Composition of waters from five northern California streams[1]

Stream	Time of collection	Specific conductance µmho/cm at 25°C	pH	Concentration in mg/L									Concentration in µg/L								
				Na	K	Ca	Mg	HCO_3	SO_4	Cl	F	SiO_2	Ag	Cd	Cr	Cu	Mn	Pb	Zn	NO_3-N	PO_4-P
Little Lost Man Creek near Orick, CA.	4-23-75 1100	-	6.4	4.6	0.4	2.8	1.0	17	1.7	5.8	-	7.0	<.05	0.02	0.7	0.8	1.3	0.1	0.6	6	13
Mattole River near Petrolia, CA.	4-24-75 1715	108	8.0	4.9	.7	13	2.0	45	12	2.4	.1	8.6	<.05	0.03	.7	1.0	3.1	.1	.6	29	25
Eel River near McCann, CA.	4-25-75 1230	141	7.6	3.5	.6	17	4.9	74	9.1	1.5	.0	8.3	<.05	.02	1.0	1.0	5.1	.1	.4	8	14
Klamath River near Klamath, CA.	4-23-75 1715	144	7.6	5.3	.8	14	6.7	81	6.9	2.2	.1	15	0.05	.03	1.5	1.3	3.5	<.1	.5	14	15
Pieta Creek near Hopland, CA.	4-25-75 1215	222	8.1	6.8	.7	25	10	132	9.9	27	.1	13	<.05	.01	.8	1.0	.9	.1	.2	7	14

[1] Analysts were G. W. Zellweger and R. J. Avanzino.

Hem (1972) investigated the solution chemistry of Cd and calculated equilibrium concentrations of Cd with carbonate solids in 80 stream samples for which sufficient chemical data were available. About 70 percent of these samples were below saturation with respect to carbonate solids. Inasmuch as the hydroxide species are even more soluble than the carbonates under conditions present in normal streams, it seems evident that some other control(s) must limit Cd solution concentration. Gardiner (1974) studied the uptake of Cd by river mud and found concentration factors for the muds of 5,000 to 50,000, depending upon mud composition and other variables. Equilibration rate was relatively rapid. In Mattole water (Table 17) the concentration of Cd sorbed per gram of solid averaged about 6,000 times as great as that in solution when the suspended sediment concentration was 110 mg/L and the pH was 8.0. This corresponds reasonably well with Gardiner's data. Gardiner (1974) considered humic material to be the major component of river mud responsible for the Cd sorption.

In the Mattole basin much of the runoff has had intimate contact with humic materials as well as with inorganic materials in surface soils having a high ratio of solids to liquid, thus presenting an excellent opportunity for equilibration. The data in Table 14 indicate the acid soils of the Mattole basin contain Cd in interstitial solutions about 10 times the concentration found in Mattole River water suggesting that, as soil water moves into the stream environment at a higher pH, the Cd concentration decreases. The data in Table 17 show that as pH increases the distribution coefficient increases also, causing a greater fraction of any Cd present to be held on the stream sediment. The overall result of the movement of soil water into the Mattole River would appear to be an increase in pH of 1.5 to 2.5 units and a decrease in Cd concentration by a factor of about 10. The Cd decrease apparently results by increased adsorption on stream sediment as pH rises. A part of this pH rise is thought to occur during aeration of rivulets on the slopes, so an appreciable fraction of the Cd may be lost from solution before runoff actually enters the main stream channel.

Table 17 Distribution coefficients for Cd, Cu, Pb and Zn on Mattole River sediments in freshwater and seawater 1/

Date sediment collected	Water contacting sediment	Metal 2/ added to suspension	pH	Element adsorbed			
				Cd	Cu	Pb	Zn
11-21-66	Fresh	Hi	8.0 3/	3,400	13,000	45,000	19,000
	Fresh & HCl	Hi	7.0	1,200	11,000	61,000	4,900
1-20-67	Fresh	Hi	8.0	8,100	35,000	170,000	54,000
	Fresh & HCl	Hi	7.0	2,300	23,000	160,000	8,900
3-16-67	Fresh	Hi	8.0	3,700	14,000	54,000	22,000
	Fresh	Lo	8.0	5,800	16,000	98,000	30,000
	Fresh & HCl	Hi	7.0	1,700	12,000	66,000	5,000
	Fresh & HCl	Lo	7.0	2,300	17,000	104,000	6,850
	Fresh & HCl	Hi	6.0	-	7,000	42,000	-
	Fresh & HCl	Lo	6.0	550	6,800	45,000	2,200
	Sea Water	Lo	7.9 4/	<300	5,000	23,000	3,000

1/ Suspension of 110 mg/L sediment placed in a fresh water sample obtained July 31, 1975. In seawater the concentration of added suspended sediment was 400 mg/L. Analyses by G. W. Zellweger. Equilibration time was 6 hours.

2/ Initial concentration of metals in solution prior to addition of sediment varied slightly from sample to sample but was approximately 2, 10,20 and 10 µg/L for Cd, Cu, Pb and Zn, respectively, in the "Lo" samples and 4, 20, 40 and 20 µg/L Cd, Cu, Pb and Zn, respectively for the "Hi" samples.

3/ Measured composition of stream water at pH = 8.0 was as follows: Na - 8.2, Ca - 35, Mg - 5.5, K - 1.4, Sr - 0.30, HCO_3 - 116, Cl - 3.9 mg/L. SO_4 was estimated at 27 ± 2 mg/L from an ionic balance and from analyses of other low-flow samples.

4/ Chloride content of the seawater was 19,000 µg/L indicating a salinity of about 33.4 $^0/00$.

Given the Cd concentration in Mattole water of 0.03 µg/L (table 16), its concentration in Mattole sediment (0.9 µg/g table 8) and an estimate of the distribution coefficient of exchangeable Cd at pH 7.5 of perhaps 4,000 (table 17), a calculation can be made of the fraction of Cd on Mattole sediment which is exchangeable under such conditions.

If $K_d = \frac{C_x}{C_s}$ where K_d is the distribution coefficient, C_x is the concentration of exchangeable Cd on sediment in µg/g and C_s is the concentration of Cd in solution at equilibrium in mg/L, then substituting,

$$4000 = \frac{C_x}{3 \times 10^{-5}}$$, therefore C_x = .12 µg/g exchangeable Cd and

$$\frac{.12 \ \mu g/g \text{ exchangeable Cd on sediment}}{0.9 \ \mu g/g \text{ total Cd in sediment}} = .13.$$ This calculation suggests that about 13 percent of the Cd on Mattole sediment may be exchangeable. If true, then detectable amounts of Cd may be released when the Mattole sediment encounters seawater because the K_d for seawater is less than 300.

Desorbable Cd was determined for six samples of suspended sediment from the Mattole River by placing 1.6 gm of sediment in 800 mL of seawater for a period six hours at pH 7.9. Original Cd concentration in the seawater was 0.11 µg/L and concentration after addition of sediment ranged from 0.14 to 0.21 and averaged 0.17 µg/L. Thus, assuming a total of 0.9 µg/L Cd in the sediment, about 3 percent of the total Cd in the sediment was desorbed by the seawater.

The decrease in the Cd distribution coefficient between pH 8 and pH 7 is large compared to that of Cu and Pb, which are discussed later. Calculations presented by Zirino and Yamamoto (1972) and Long and Angino (1977) indicate that in freshwater the major Cd species would be Cd^{++} at pH 6 through 8. Thus, the K_d for Cd is probably controlled by competition between H^+ and Cd^{++}. In seawater, however, Cd forms stable complexes with Cl and only a few percent of the Cd is present as Cd^{++}. Therefore, the K_d in seawater is much lower than in freshwater at a similar pH.

Chromium

Chromium was not detected by spectrographic analysis in any of the freeze-dried water residues from the Mattole River (Table 4) and the Cr concentration must, therefore, be less than about 4 μg/L during moderate to low flow. Durum and Haffty (1961) found less than 4 μg/L Cr in at least one sample from 10 of the 15 North American streams studied, although considerably higher values were observed in some polluted streams. Kharkar and others (1968) sampled the Mad, Klamath, Russian and Eel Rivers of northern California during November, 1966 and found 0.7-3.1 μg/ Cr in solution. Table 16 shows the Cr content of 5 northern California streams, two of which were also sampled by Kharkar and others (1968). Although their samples were taken in the autumn and ours in the spring, their value for the Klamath River was 0.72 μg/L versus our value of 1.5 μg/L and their value for the Eel River was 0.71 μg/L versus our 1.0 μg/L, suggesting no large seasonal changes in Cr concentration.

Cobalt

Co was present in concentrations of less than 3 μg/L in Mattole River water. This corresponds to the analyses of Durum and Haffty (1961) and Durum and others (1971), which indicate the median Co level in streams is less than 1 μg/L. Hem (1970) has pointed out that in many streams the solubility of $CoCO_3$ would set an upper limit on Co solubility of about 10^{-7} molal (6 μg/L).

Copper

Cu concentrations in the Mattole River during the January, 1972 stream rise averaged about 0.4 µg/L. Five northern California streams (Table 16) averaged about 1 µg/L during April, 1975. If one assumes Cu contamination of a few tenths of a microgram per liter, which can be derived even from a leached membrane filter, it is possible the median true natural Cu concentration in some clean streams is appreciably less than 0.5 µg/L. Kubota and others (1974) reported Cu concentrations of about 0.5 µg/L in primarily rural streams tributary to Cayuga Lake, New York and the same concentration in the lake itself. Such values are significantly lower than those reported by Durum and Haffty (1961) for North American rivers; however, Cu is a widespread industrial pollutant and such contamination may account for their higher values.

Hem (1970) shows cupric oxide or hydroxycarbonate minerals may limit Cu solubility at pH 8 to about 6 µg/L. At the pH values of 7.3 to 7.8 observed during the January, 1972 rise this limit would be appreciably higher. Some factor other than the hydroxycarbonate minerals would appear to limit the Cu concentration in clean streams. Wedepohl (1974) feels Cu concentrations in natural waters can be controlled as much by adsorption processes as by solubility effects. In experiments in our laboratory (Table 17) the distribution coefficient of Cu between Mattole sediment and water ranged from about 12,000 to 30,000 at pH 7.5, depending upon the particular sediment sample used. As in the case of Cd, Cu concentration is high in soil leachates compared to that in the Mattole River and greater Cu adsorption on stream sediment would be expected with increasing pH.

During storm runoff in the Mattole River a pH of 7.5 was fairly common, and this was not greatly different from the pH present in the water sample whose composition was reported in table 16. If the distribution coefficient of Cu at pH 7.5 is taken as about 15,000 and Cu in solution as 1 µg/L, a calculation of exchangeable Cu can be made, as was done in the case of Cd, and is found to be about 15 µg/g. This represents approximately one third of the acid-extractable Cu in the Mattole sediment (Table 8.). Desorption of Cu from sediment by seawater at pH 7.9 was done as for Cd. The Cu concentration of the seawater prior to equilibration with the sediment for six hours was 0.26 µg/L and after equilibration with six different sediment samples ranged from 0.51 to 0.85 and averaged 0.64 µg/L. Thus, about 0.5 percent of the acid-extractable Cu was desorbed by seawater. The desorbed Cu is much less than one might expect from the distribution coefficients reported in table 17. A possible explanation for the discrepancy is the tendency for the transition metals to become increasingly "fixed" on sediments as time after initial adsorption increases (Jenne, 1968). The distribution coefficient used above to calculate that about one third of the acid-extractable Cu was exchangeable was based on a six-hour equilibration, whereas most of the Cu on the sediment placed in the seawater had been there for years and had had plenty of time to be fixed.

Cu in freshwater from the Mattole shows relatively little decrease in distribution coefficient between pH 8 and pH 7 compared to Cd (Table 17). Calculations by Zirino and Yamamoto (1972) and Long and Angino (1977), when applied to freshwater samples, indicate that only about 1 percent of the Cu in solution is present as Cu^{++} at pH 8, whereas perhaps 20-30 percent of the Cu would be present as Cu^{++} at pH 7. If Cu^{++} were the only species adsorbed the K_d would be expected to increase markedly going from pH 8 to pH 7. The data in table 17 show some increase for two of the three samples tested but not to the extent one might expect if only Cu^{++} were being sorbed, so the reason for the small change in K_d between pH 8 and pH 7 is not evident.

The pH and alkalinity of the Mattole stream water are similar to that of seawater and major differences are in concentrations of Cl, SO_4 and predominant cations. Because Cu-chloride complexes comprise less than one percent of the Cu species in seawater and hydroxide, carbonate and bicarbonate complexes are major species (Zirino and Yamamoto, 1972; Long and Angino, 1977), the relative proportion of the complexes in seawater and Mattole River water should be similar. However, the activity coefficients of Cu in seawater would be appreciably less (about one third as much) than in Mattole water and this would cause a decrease in the distribution coefficient, as observed. Competition with Ca and Mg in seawater would also tend to reduce the distribution coefficient, although no data were obtained regarding the selectivity of Mattole sediment for Cu compared to Ca and Mg. The difference, then, between the distribution coefficient of Cu in seawater and Mattole water at about pH 8 can be readily explained from the information available.

Iron

Iron concentrations in Mattole River water are considerably greater than those to be expected from dissolution of hydrous ferric oxides (Jones and others, 1974). However, several authors (e.g., Delong and Schnitzer, 1955; Hem, 1960) have called attention to the ability of natural organic compounds to form soluble highly stable Fe complexes, and it is believed such organic complexes are involved in holding the Fe concentrations above the values calculated. Further support for this hypothesis is provided by the fact that one rivulet sampled during the January, 1972 study on the Mattole, which was draining from a grassy slope underlain by a black mineral soil, had a pH of 6.4 and an Fe content of 25 μg/L. It is unlikely this Fe concentration was due primarily to dissolution of suspended solids passing the filter during processing because (a) the Fe was extracted from the water at a pH of 8.6 shortly after sample collection (Kennedy and others, 1974), (b) an aliquot of the sample held acidified for a month contained extractable Fe of 34 μg/L, indicating no more than one third of the acid soluble Fe was derived from Fe-containing solids and (c) the dissolved Al content of this sample was 110 μg/L based in a field extraction and 115 μg/L based upon extraction of an acidified aliquot one month later. This sample showed a slight orange-brown coloration even after filtration through a 0.1 μm membrane filter, suggesting the presence of dissolved organic matter. The pH of 6.4 in this sample was the lowest observed in any water collected in the Mattole basin (exclusive of rain) and probably represents the interaction of rain (falling during the time of sample collection) with acidic surface soil.

The increase in dissolved Fe during rising discharge of January 21 and 22, 1972 would be expected if overland flow and quick-return flow picked up soluble organic matter and Fe-organic compounds from surficial soils. The water collected on the 23rd and 24th had a longer contact time with the soil and probably had a much higher percentage of deeper interflow. Such interflow would have had an opportunity to lose some of its organic matter and Fe-organic complexes to soil sorption before entering the stream system.

A somewhat similar study was done on the Fe content of runoff from an early fall storm on Little Lost Man Creek near Orick, California in November 1974. In that case the Fe concentration in stream water passing a 0.1 mm Millipore filter backed by a 0.4 µm Nuclepore filter was 2-3 µg/L prior to storm runoff, increased to about 20 µg/L shortly before peak storm discharge and then decreased again to about 7 µg/L within 24 hours after peak runoff (figure 53, sample and analysis by G. W. Zellweger). The data from both the Mattole River and Little Lost Man Creek, then , indicate an increase rather than a decrease in dissolved Fe during storm runoff from vegetated areas in northwestern California.

Work by Lengweiler and others (1961), Hem and Roberson (1967) and Kennedy and others (1974) has established the need for removal of <0.45 µm particles if valid concentrations for dissolved Fe are to be obtained. Until more data on the Fe content of waters passing 0.1 µm or smaller filters are available from other streams, it will not be possible to make a reasonable estimate of the average concentration of dissolved Fe in surface watere.

Lead

Lead concentration in Mattole River waters was less than 0.3 µg/L in samples collected in January 1972 and 0.1 µg/L in an April 1975 sample. Such concentrations compare with an average for streams in Maine of 0.26 µg/L (Turekian and Kleinkopf, 1956) and with <1 µg/L found by Durum and others (1971) in less contaminated streams in the United States. Kubota and others (1974) detected less than 1 µg/L in several of the cleaner streams of the Cayuga Lake basin in New York.

Hence, a concentration of <1, and probably <0.5 µg/L Pb appears to be characteristic of many unpolluted streams.

Hem and Durum (1973) calculated the solubility of Pb in surface waters assuming that the carbonate or hydroxide might control the concentration. Their calculations indicate that at the HCO_3 concentration present in Mattole waters (35-135 mg/L) in the 7.5-8.0 pH range Pb could dissolve to the extent of at least 5-10 µg/L. This predicted Pb concentration is considerably higher than actually observed and suggests that precipitation of $PbCO_3$ and $Pb(OH)_2$ does not control Pb concentrations in the Mattole. Nriagu (1974) proposed that Pb chlorophosphates, might serve to control the migration and fixation of Pb in the environment. Using data from the Mattole River samples collected January 1972 the solubility of Pb was calculated assuming that chloropyromorphite, $Pb_5(PO_4)_3Cl$, served as a control. Maximum dissolved Pb was calculated to range from 0.06 to 0.13 µg/L during the period of storm runoff. This suggests that chloropyromorphite could be an effective control on Pb concentration in Mattole waters.

An alternative, and perhaps more common control is an adsorption process. The distribution coefficients presented in table 17 show a very strong affinity of Pb for Mattole sediments and could readily account for the concentration of 0.1 μg/L found in the April 1975 sample. If the distribution coefficient for Pb at pH 7.5 is estimated as 80,000, a calculation of the exchangeable Pb on Mattole sediments, made as for Cd and Cu, is 8 μg/g, or about 40 percent of the acid-leachable Pb on Mattole sediments. However, when 800 mL of sea water of pH 7.9 containing approximately 0.05 μg/L of Pb was equilibrated for six hours with 1.6 g of various suspended-sediment samples from the Mattole River no detectable increase in Pb concentration was found. As for Cu, if adsorption on sediments controls Pb concentrations in the Mattole, it seems probable that much of the Pb in the sediment is fixed due to long contact time and short term equilibrations are not a true measure of the distribution coefficients to be expected after equilibration times on the order of months or years.

The six-hour equilibrations resulted in a higher K_d for Pb at pH 7 than at pH 8 in two of the three samples studied (table 17) and in the third sample there was very little change in K_d. The explanation for the failure of the K_d to decrease at pH 7 compared to pH 8 is believed to be due to the different proportions of Pb species at the two different pH values. The work of Zirino and Yamamoto (1972) would indicate that at pH 8, low chloride concentrations and alkalinities close to that of seawater (true for the Mattole water used for equilibration), perhaps 95 percent of the Pb in solution would be an uncharged $PbCO_3^0$ or $PbHCO_3^+$ species and only 2-3 percent would be Pb^{++}. At pH 7, $PbCO_3^0$ or $PbHCO_3^+$ species would total 80-85 percent and Pb^{++} about 15 percent. Calculations by Long and Angino (1977) indicate perhaps 20-30 percent Pb^{++} at pH 8 and about 70 percent Pb^{++} at pH 7, suggesting considerably higher proportions of Pb^{++} than Zirino and Yamamoto reported. If the Pb^{++} were the species adsorbed most strongly, the factor of 3 to 5 increase of that species at pH 7 over pH 8 might explain the tendency for the K_d to increase or hold constant as pH decreases even though the increased competition of Pb^{++} with H^+ for adsorption sites would be expected to decrease the K_d at the lower pH. There is some uncertainty, however, as to the degree of adsorption of Pb complexes compared to adsorption of Pb^{++}, so the reason for the observed change in distribution coefficient is not evident. This behavior of Pb at pH 8 and 7 contrasts with that for Cd and Zn, which show decreasing K_d values with decreasing pH. As pH decreases from 7 to 6, however, Pb follows Cd, Cu and Zn in showing decreased K_d values.

The tendency for the K_d to increase as the amount of added trace metal decreases is consistent for Cd, Cu, Pb and Zn at pH 7 and pH 8. Such an increase in K_d with decreasing concentration has been reported by others (e.g., Wahlberg and Fishman, 1962). This suggests that, at the concentration levels actually present in the Mattole River the K_d values may be considerably higher than those shown in table 17 because the stream concentrations are at least a factor of 10 lower than those used in the equilibration experiments. It also implies that as the dissolved trace metal increases in concentration the K_d will decrease. Thus, as pollution of a stream increases, a progressively smaller fraction of the trace metals may be removed by adsorption.

The K_d of Pb in seawater is lower than in the Mattole water at pH 6, just as in the case of Cd and Cu, and is about one fourth that in fresh water at pH 8. This decrease in K_d in seawater compared to freshwater is presumably due to the large decrease in activity coefficient as the ionic strength increases as well as to the formation of chloride and sulfate complexes (Zirino and Yamamoto, 1972).

Yet another factor affecting the K_d values is the character of the individual sediment sample. The K_d values for Cd, Cu, Pb and Zn are consistently higher for the sample collected on January 20, 1967 than for either of the other samples, suggesting that there can be considerable variation in K_d with time of sample collection, due, perhaps, to changes in the character of the sediment.

Manganese

Manganese, like iron, is associated with fine-grained soil particles but is only about 1/50 as concentrated as Fe in shales (Turekian and Wedepohl, 1961; Vinogradov, 1962). Furthermore, the concentration of dissolved Fe was generally 2-20 times less than the Mn in Mattole waters, so the percentage error in determining dissolved Mn is much less than for Fe if only a small quantity of clay passes through a filter and is dissolved by acid during preservation. The average concentration of dissolved Mn in the Mattole River water during the storm runoff of January 20-24, 1972 was 3-4 μg/L with perhaps some slight increase during high discharge. Spectrographic analyses of 10 water residues, which include any Mn in solids passing a 0.45 μm membrane (Table 4), averaged 6 μg/L and showed no consistent relation to water discharge. Consideration of both types of data indicate that a best value for the average dissolved Mn in the Mattole during moderate to high flow is about 3 μg/L. Such a value compares with 4 μg/L in Maine (Turekian and Kleinkopf, 1956) and an average of 3 μg/L for the northern California streams in table 16.

Table 14a shows the Mn content of leachates from surficial soils ranged from 240-660 μg/L. This implies the Mn content of quick-return flow at its source may be 10-100 times of that found in the streams and suggests a marked decrease in Mn content as the water moves from intimate contact with the soil into rivulets and on into the main streams. Soil leachates from the 60-90 cm depth contained 45-160 μg/L Mn, indicating even delayed-return flow at its source may contain considerably more Mn than stream water.

During storm runoff from Little Lost Man Creek in November 1974, dissolved Mn increased by a factor of about 2.7 from 0.8 to 2.2 μg/L and then decreased to 1.0 μg/L within one day after peak discharge. During this same period Al and Fe increased by a factor of 6-7. Apparently all three elements are enriched in quick-return flow from the Little Lost Man drainage. The thick porous organic material at the land surface probably prevents surface runoff from being an appreciable fraction of the storm runoff.

Hem (1970) has discussed the solubility of Mn in natural waters and concluded that in the pH range 7-8 the dissolved Mn in a system containing 100 mg/L HCO_3^- would probably be 100-1000 μg/L. Such a concentration is more than 25 times that observed in Mattole River water; this suggests that solubility of oxides, carbonates or hydroxides does not control the concentration of dissolved Mn in the Mattole.

The essentially constant Mn concentration during widely varying discharge in the Mattole River and the great difference between the Mn content of soil leachates and stream water argue that steady state conditions are achieved rather rapidly in the river system, ie. in a matter of a few hours. This, plus a Mn concentration well below that expected from solubility considerations suggests that adsorption phenomena may control the Mn in stream water under "clean-stream" conditions.

Molybdenum

Molybdenum was determined only in water residues (Table 4) from Mattole River water, so data are limited. The concentration of Mo averaged about 1.5 μg/L and tended to decrease with increasing stream discharge. This is in agreement with observations of Durum and Haffty (1961) in which, of 15 streams studied, 8 showed a Mo decrease with increasing discharge, one did not show a significant change and 6 had concentrations so low that either no conclusion could be drawn or the samples were taken at a controlled-flow site where the discharge had no obvious relation to runoff rate. In the Mattole, Mo changed by a factor of 3-4 while discharge changed by a factor of 800, so there is an appreciable ability on the part of the soils to stabilize the Mo concentration during storm runoff.

The Mo concentration found in Mattole water is in the range 0.6-1.8 μg/L reported by Turekian (1969; pers. com. K. Sugawara) for Japan and by Kharkar and others (1968) for U. S. streams. Voegeli and King (1969), in a survey of Mo concentrations of Colorado streams, state that values greater than 5 μg/L should be considered anomalous and may indicate Mo mineralization. Median Mo concentration for Colorado streams was in the range 1-2 μg/L although values up to 3800 μg/L were observed near mineralized areas. Such data suggest that the Mo concentration commonly observed is not limited by the formation of insoluble solids with the usual dissolved stream constituents.

Barrow (1970) studied adsorption of MoO_4 on various Australian soils and found that MoO_4 sorption increased with decreasing pH, just as for SO_4 and PO_4. Thus, the acid Mattole soils would be expected to sorb available MoO_4. Hem (1970) states that MoO_4 is probably the predominant Mo species in natural water. Because Mo is accumulated by vegetation, it might be flushed out from decaying vegetation during early fall storms, and the sample collected on 11-12-66 (table 4) on the rising stage of the Mattole River during the first major storm runoff of the season contains the greatest Mo concentration observed in any Mattole sample. The increase is slight, however, and more detailed information is needed before any definite conclusions can be drawn regarding the fall flushout of Mo.

Nitrogen

Nitrogen is a necessary nutrient for all plants and, when plants die and decompose in the soil, much of the nitrogen is recycled into new plant growth. Stanford and Epstein (1974) state that the rate-limiting step in soil N mineralization is the conversion of organic N to NH_4-N. The NH_4-N is oxidized rapidly enough to NO_3-N under normal aerated soil conditions that NH_4-N does not accumulate. These authors studied the rate of N mineralization as related to soil water content and found that the rate of mineralization was minimum when the soil was air dried and increased with increasing moisture content up to a maximum, which varied from soil to soil. In the Mattole basin, at the end of the rainy season, the soils are very high in moisture. As water drains from the soil, plants remove water by transpiration, and air drying of surface soil occurs. The work of Stanford and Epstein (1974) suggests that the rate of N mineralization passes through a maximum during late spring or early summer in the Mattole basin and then decreases during the latter part of the dry season. The NO_3-N so formed and not taken up by plants would be available at and near the land surface for leaching by rain at the oneet of the next wet season.

Many authors have reported on the migration of NO_3-N in soils (eg. MacGregor and others, 1974), and it is apparent that mobilization of the mineralized N can occur with relative ease. After NO_3-N has been leached from surficial litter into the mineral soil, it is available to the microbiota and to plants for uptake. Nevertheless, some of the NO_3-N might be expected to get through the root zone in the upper soil, and it could then percolate on down to the water table without appreciable further removal from solution. This would increase the NO_3-N content of ground water. Normally, enriched ground water as a source of NO_3-N in stream water would be undetectable because, at the time of the year when ground water comprises a major part of flow, streams carry little suspended sediment, are rather clear and there is opportunity for biota to remove much of the NO_3 before it has traveled far in the stream. However, in a study conducted by M. J. Sebetich (oral commun., 1974) on Little Lost Man Creek, a stream draining an area of virgin redwoods in northern California, it was possible to sample stream flow which had been exposed to relatively low light levels during its passage from the ground water sources to the sampling site. The NO_3-N concentrations were about 10 μg/L from mid-April to the end of May, increased to 15 μg/L in mid-June, 28 μg/L in late July and 50 μg/L in mid-August (figure 54; analyst was R. J. Avanzino). By early October, NO_3-N had increased only slightly to 53 μg/L. The most rapid rise occurred in a 2-week period in early August when, if chemical patterns in the Mattole River are indicative, the source of stream flow is probably changing from primarily soil-water drainage to water coming from the water table. Thus, in Little Lost Man Creek ground water appears to have a NO_3-N concentration about 5 times that in a delayed-return flow.

Approximately 3/4 mile downstream from the site described above on Little Lost Man Creek another set of samples was taken for comparison. The intervening stream reach was rather well lighted and the NO_3-N was observed to decrease by 73-93 percent below concentrations at the upper station during the period mid-July to early October. Such a decrease during stream transport would be expected to prevent detection of seasonal NO_3-N variations in ground water if it occurred in the Mattole River basin, as seems very probable.

The pronounced increase in NO_3 during storm runoff in the Mattole basin early in the rainy season was observed also in storm runoff in Little Lost Man Creek in November 1974. Prior to the stream rise NO_3-N in Little Lost Man Creek was 40 µg/L but then it rose rapidly with increasing discharge and peaked, as did Al and Fe several hours before peak discharge. During the following 24 hours after reaching a maximum of 150 µg/L the NO_3-N decreased to 65 µg/L.

The behavior of NO_3 in the Mattole basin and in the Little Lost Man drainage is consistent with the idea that surface runoff carries some NO_3 due to contact with surface soils but the greatest concentration of NO_3 is in quick-return flow. In the Mattole basin, NO_3 tends to decrease with initially rising discharge before increasing with further increase in discharge and this is as it should be if the leaching pattern described earlier is applicable. That is, the light rain preceding the main storm leaches NO_3 from surficial materials into the upper soil and, when rainfall exceeds infiltration rate, the surface runoff passes over material that has just been leached of some of its NO_3. Also, the surface runoff is probably produced in greatest volume from relatively impermeable areas which normally would not be associated with highly organic soils. With increasing rainfall intensity and moisture content of the soil, some of the more permeable, more organic, soils begin to contribute quick-return flow to the storm runoff, and NO_3 in the stream increases. In the Mattole basin, peak discharge is believed to be comprised of a combination of surface runoff and quick-return flow with the peak in surface runoff preceding peak discharge and peak in quick-return flow following peak discharge. The lag of peak NO_3 concentration behind peak discharge would be consistent with a peak in quick-return flow then, if maximum NO_3 does indeed occur in quick-return flow.

In Little Lost Man the peak in NO_3 coincided with the peak in discharge, and this is to be expected because it seems probable there is essentially no surface runoff from the deep, highly porous organic soils of the virgin redwood forest. Therefore, the increase in discharge is assumed to be composed entirely of quick-return flow.

The movement of NO_3 during storm runoff would be expected to resemble that of Cl in many respects because both are concentrated at or near the land surface (but by different mechanisms) during the summer dry season, both are sorbed only slightly by soils and do not form low-solubility compounds with most cations. The main difference is that NO_3 will be preferentially taken up by plant roots from soil water compared to Cl. In the case of Conklin Creek during the detailed study of November 1969, the Cl concentration decreased during the stream rise, but the ratio of Cl to specific conductance increased then and reached a maximum 5-6 hours after peak discharge. The ratio of NO_3 to specific conductance also was maximum about 6 hours after peak stream discharge. In the Mattole River during the same period the relation between NO_3 and Cl was obscured because of travel time effects within the river system. Cl is deposited with sea salts in decreasing amounts as one goes upstream, so there is a tendency for runoff from the lower basin to contain more Cl than average and the peak in Cl concentration arrives earlier than it otherwise would. As noted in the discussion of Cl earlier, Conklin Creek and McGinnis Creek contain enough Cl so that storm runoff from these two streams can be clearly seen arriving early at the sampling site on the Mattole River (fig. 32). Without the anomalous Cl in lower basin runoff it is probable the ratio of Cl to specific conductance would, like the NO_3:Sp. Cond. ratio, lag peak discharge.

Phosphorus

P is of considerable interest in stream water not only because it is an important nutrient required for biota but because it may be a control on the solubility of some of the trace metals. PO_4-P concentrations of <50 μg/L appear to be characteristic of a number of natural waters which are not seriously contaminated. Kunishi and others (1972) found that runoff from agricultural land carried P concentrations of 12-65 μg/L, but when these solutions encountered phosphate-deficient sediment the dissolved P decreased to 3-5 μg/L. Johnson and others (1975) observed "dissolved molybdate-reactive phosphorus" concentrations of 5 to 60 μg/ in a rural stream in central New York, with maximum concentrations occurring during storm runoff. Silker (1964) reported a range of 1 to 50 μg/L phosphorus in the Columbia River. Spectrographic analyses of stream water residues (sensitivity varies inversely with dissolved solids content) by Durum and Haffty (1961) indicate that many North American streams contain less than 100 μg/L P. Little Lost Man Creek in northern Humboldt County, California, contained 10-15 μg/L P from mid-March to early October, 1974 (M. J. Sebetich, written commun., 1974). The samples were obtained at a point on the stream which marks the outlet of the poorly lighted upper part of the stream channel. P uptake by biota in the stream is believed to be limited by the relatively low light level in the upper stream channel, so the control is probably mainly inorganic. The fact that PO_4-P remained essentially constant in Little Lost Man Creek while discharge decreased during the summer by a factor of at least 20, and the source of the water changed from mainly soil water to ground water, indicates an effective and ubiquitous control.

In the Mattole River and in Conklin Creek the PO_4-P level is in the range 25-40 μg/L during storm runoff when stream biota are probably not an important control. The relative stability of PO_4-P concentration with varying stream discharge in the Mattole basin also argues for a strong stabilizing mechanism. At low flow in the Mattole there is considerable algae growth, and it is probable that the biota exert considerable control over both PO_4 and NO_3 concentrations.

Kittrick and Jackson (1955) demonstrated the rapid removal of PO_4-P from solution by hydrous oxides of Fe and Al similar to those found in soils. Reaction rate decreased logarithmically with time and increased with decreasing pH in the range 4.5 to 2.5. Apparently increasing acidity releases more Fe and Al from soil minerals and this results in a better opportunity for the formation of Fe and Al phosphates. Swenson and others (1949) reported that soluble soil organics could displace some of the P from Fe or Al phosphates so formed through the formation of more stable Fe or Al-organic compounds.

The P concentration pattern observed in the Mattole basin appears to be explicable as follows. Decomposing vegetation at and near the land surface contains a supply of leachable P and soluble organics (Cowen and Lee, 1973) which can be removed by rainfall. When surface runoff occurs, some of the P is picked up directly from surficial organic litter and some of the soluble organics may penetrate the uppermost mineral soil and displace some P from Fe and Al phosphates. Thus, both surface runoff and early quick-return interflow may carry increased dissolved P. However, PO_4-bearing water penetrating below the highly organic mineral soil may well lose some of the PO_4 due to sorption on the acid soils thereby setting up a new equilibrium at lower PO_4-P concentration, which is soon reflected in the composition of the quick-return flow and later in delayed-return flow.

In storm runoff from Little Lost Man Creek in November 1974, PO_4-P was 11 μg/L before runoff began and increased to a maximum concentration of about 30 μg/L at the same time that Al, Fe and NO_3-N peaked. By 24-hours after peak discharge PO_4-P was down to 14 μg/L and gradually decreasing. If, as seems probable, there was little or no surface runoff from the Little Lost Man basin, the increased PO_4 was carried by quick-return flow.

In the leaching study shown in table 14a, the readily available solutes raised the PO_4-P concentration in the leachate to 120-270 μg/L, which is 5-10 times as great as that found in Mattole stream water. Thus there may be appreciable reequilibration of PO_4 with suspended sediment in the stream if the leachate concentrations are similar to those found in quick-return flow at its source in the soil. The fact that Kunishi and others (1972) observed such reequilibration in a stream would support such a hypothesis for the Mattole basin.

The mechanism(s) for maintaining the PO_4 concentration in the range 10-30 μg/L under a wide variety of stream conditions have not been determined in this study. Whatever the mechanism(s) for this stabilization it appears that the period required for operation is relatively short, ie. a matter of a few hours.

Strontium

Strontium concentration in stream waters can vary from 0.007 to at least 13.7 mg/L in the United States (Skougstad and Horr, 1963). The higher values reported were most common in the more saline waters of the southwest and in celestite-rich limestone areas south of the Great Lakes. These authors found, however, that streams on the Atlantic slope, in the southeastern United States, and in the upper Great Lakes and Pacific Northwest rarely contained more than 0.5 mg/L Sr. The maximum Sr concentration observed in the Mattole River was 0.34 mg/L in early November 1966 and the minimum was 0.08 mg/L during very high flow. The ratio of Ca to Sr decreased from about 120 during low flow to about 90 during high flows suggesting a greater rate of release of Ca relative to Sr in weathering of rock as opposed to weathering of surficial soils.

The control on the Sr concentration in Mattole waters may well be availability from weathering of host minerals as indicated by Skougstad and Horr (1963) rather than the existence of slightly soluble Sr compounds. Calculation of the equilibrium concentration of Sr in the low-flow water sample collected November 10, 1966, and use of the equation

$$\frac{[HCO_3^-][Sr^{++}]}{[H^+]} = 15.1$$

Hem, 1970, indicates that the observed Sr value is only about 4 percent of that at saturation with $SrCO_3$ (strontianite). The same sample was essentially saturated with calcite ($CaCO_3$).

Zinc

Zinc is a widespread contaminant of the environment and is present at low levels in most sampling and filtration equipment; hence, it is very difficult to determine Zn accurately at the < 1 μg/L levels found in clean streams. When great care is used to obtain uncontaminated samples the concentrations observed cluster around 0.5 μg/L (table 16) for the Mattole River and four other Northern California streams which are relatively clean. Such a low value seems reasonable in the light of the distribution coefficient (about 30,000 at pH 8.0) observed when Zn is added to a suspension of stream sediment in Mattole water. Comparison with previous studies indicate that the 0.5 μg/L value is much less than that normally found in other U. S. streams. Many of the streams studied by Durum and others (1971) contained 10 μg/L of Zn or more, but about 12 percent were less than 10 μg/L. Kubota and others (1974) found 0.8-1.9 μg/L Zn dissolved in 4 out of 8 rural streams in central New York. The other four rural streams ranged from 2.2-8.0 μg/L and four urbanized streams ranged from 1.4-3.5 μg/L Zn. However, even with these relatively low Zn levels compared to those reported by Durum and others (1971), the associated suspended particulate material averaged 1044 μg/g Zn, which is at least 10 times that reported by Turekian and Wedepohl (1961) for shales and 20 times that found in fine-grained suspended sediment in the Mattole River.

Kennedy (1956) found <2 μg/L Zn in several streams (pH = 8.2 - 8.7) within the southwestern Wisconsin lead-zinc district and <2 μg/L in streams on the border of the Coeur d'Alene mining district (Kennedy, 1960) in northern Idaho where stream pH was generally in the range 7.0 - 7.3 (V. C. Kennedy, Unpublished data, 1951). This widespread tendency for Zn solution to be <2 μg/L in unpolluted, or even slightly polluted streams, argues for a very effective natural control on Zn concentration below the 2 μg/L level.

Hem (1972) considered the solubility controls on Zn in natural waters and concluded that $ZnCO_3$ and $Zn(OH_2)$ are unlikely controls on Zn solubility in natural streams. His data for Zn silicate also indicate solubility of this compound is unlikely to suppress Zn concentrations to less than 2 μg/L. Loganthan and Burau (1973), in a study of the sorption of heavy metal ions by hydrous manganese oxide, concluded Zn could displace Mn from the lattice and hence be selectively sorbed. Such a conclusion would agree with Jenne's (1968) proposal that Mn and Fe are the major agents controlling the concentration of heavy metals in water. Jenne envisioned an adsorption followed by fixation. Duursma (1970) reported a distribution coefficient for Zn between Var river water (near Nice, France) and river sediment of 15,000 at pH 8.18, indicating a strong preference for the Zn over the major elements in solution. Some highly selective sorptive mechanism appears to be the most probable control of Zn concentrations in unpolluted waters.

A calculation of the percent of exchangeable Zn on Mattole sediments at pH 7.5 can be made, using an estimated distribution coefficient of 15,000. Such a calculation, assuming 0.6 μg/L Zn in solution from table 16, indicates that about 9 μg/g of exchangeable Zn is present on Mattole sediment. This means that about one fifth of the 50 μg/g acid-leachable Zn (Table 8) in Mattole sediments is exchangeable, if short-term equilibration studies can be applied. When 1.6 g of Mattole suspended sediment was equilibrated with 800 mL of seawater containing 0.3 μg/L of Zn for a six-hour period, no detectable (ie. less than 0.1 μg/L) Zn was desorbed. If the K_d of 3,000 in table 17 is applied to such a system and one fifth of the acid-leachable Zn were exchangeable, the dissolved Zn should have increased by more than 1 μg/L. It appears, therefore, that very little of the acid-leachable Zn is available for exchange from sediments which have been dried and held for several years before desorption experiments with seawater were done. If, as seems possible, Zn concentration in interstitial soil solutions is as high as indicated in table 14a, there should be a considerable quantity of newly sorbed Zn on the Mattole River sediments being transported by storm runoff. If so, some of this Zn might be displaced when entering the marine environment. However, desorption in the field immediately after sample collection would be required to demonstrate this, and such work has not been done.

Zn adsorption on Mattole River sediment is markedly affected by pH changes. Unlike Pb and Cu, which show either an increase or slight decrease in K_d as pH was changed from 8 to 7, the K_d for Zn decreases by a factor of 4 to 5 (table 17). The K_d for Zn decreases by another factor of 2-3 as pH changes from 7 to 6. Based on the work of Zirino and Yamamoto (1972) about 25 percent of the Zn at pH 8 is present in solution as Zn^{++}, over 60 percent as $Zn\ (OH)_2^0$ and 5-10 percent as $Zn\ CO_3^0$. However, at pH 7, Zn^{++} is about 90 percent, $Zn\ (OH)_2^-$ and $ZnCO_3^-$ are both less than 5 percent and $ZnHCO_3$ is about 5 percent of the dissolved Zn. Thus, Zn^{++} concentration more than triples in going from pH 8 to 7, but the K_d decreases four to five fold. This suggests that H^+ competes unusually well for exchange sites and(or) that adsorption of $Zn\ (OH)_2$ is important. The fact that the K_d decreases only 2-3 fold in going from pH 7 to pH 6 suggests that competition by H^+ alone is not the only factor controlling Zn adsorption.

The K_d of Zn in sea water was only about one tenth that in freshwater near pH 8. The reason for the great decrease in the K_d is not evident, although at least two factors would tend to produce this decrease. One is the decrease in activity coefficient of Zn in going from fresh to seawater. The other is the formation of chloride and sulfate complexes in seawater. Zirino and Yamamoto (1972) calculated that only about 20 percent of the Zn would be held in chloride or sulfate complexes in seawater at pH 8. Hence, it seems likely that these two factors alone could not account for the great change in K_d which was observed. Other explanations are not readily available, although there is a possibility that competition of Zn with major cations in sea water may contribute to the K_d observed,

Sediment Composition

The composition of the Mattole River sediments can be compared with that of sediments from other streams in the United States. Analyses are shown in table 18 for some of the size fractions of stream sediments whose mineralogy and cation-exchange capacity were reported by Kennedy (1965). The major elements as well as the minor elements B, Ba, Co, Cr, Ga, Mn, Nb, Ni, Sc, Sr, Ti and V in Mattole River sediments are generally within a factor of 2 of the median value for various U. S. rivers. The concentrations of La, Y and Zr tend to be low in Mattole sediments compared to other streams. Be, Ce and Sn were detectable in the sediments of several of the U. S. streams studied, but were below detection in Mattole sediments. Na was normal in Mattole clay but above average in the silt and sand fraction, perhaps due to the presence of plagioclase feldspars. No analyses for Ag, Bi, Cu, Pb, or Zn are given for the sediments from various U. S. rivers because they were size separated using soldered brass sieves and contamination with these metals was evident. There is a possibility of Sn contamination also and this may account for the difference between the Sn content of bed clay and suspended clay. Considerably more sieve abrasion would be expected in removing fines from a large volume of bed sand than in removing a little sand from suspended silt and clay.

Table 18 Spectrographic analyses of sediments from streams in the conterminous United States 1/

Element	Concentration in air-dried sediment in weight percent									
	Bed clay <4μm 2/		Suspended clay <4μm 2/		Bed silt 4-62μm 2/		Suspended silt 4-62μm 2/		Bed sand 62-1000μm 2/	
	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median
Al	7->10	>10	>10	>10	7->10	>10	7->10	>10	0.3->10	7
Ca	0.07-0.5	0.15	0.07-0.15	0.1	0.15-7	1.5	0.3-1	0.7	0.2-7	2
Fe	2-7	5	3-7	7	2-7	3	2-5	5	0.3-10	1.5
K	1-5	3	1-5	3	1.5-5	2	2-5	3	0.7-3	1.5
Mg	0.3-3	1.5	0.5-3	1.5	0.2-5	1.5	0.7-2	1	0.03-5	0.5
Na	0.2-1.5	0.7	0.2-1	0.7	0.5-3	1	1-2	1.5	0.1-2	1
	Concentration in air-dried sediment in mg per kg									
B	<20-100	50	<20-100	40	<20-70	50	<20-70	40	<15-30	<15
Ba	200-700	500	300-700	500	500-1500	700	700-1500	700	70-1500	700
Be	<1-2	1.5	1.5-2	2	<1-2	1.5	<1-2	2	<1-2	<1
Ce	<150-150	<150	<150-150	150	<150-200	150	<150-150	150	<150	<150
Co	<5-30	20	<5-20	10	<5-20	15	<5-15	10	<5-30	7
Cr	70-300	100	70-150	100	70-700	150	70-150	70	<1-1000	20
Ga	20-50	30	50	50	10-30	20	15-50	30	2-30	10
La	<20-70	50	<20-100	70	<20-200	70	70-100	70	<20-70	<20
Mn	300-3000	700	300-700	700	300-1500	700	300-700	700	100-5000	700
Mo	<5-7	<5	<5-10	<5	<5-10	<5	<5	<5	<5	<5
Nb	<10-10	10	<10-15	<10	<10-20	10	<10-15	10	<10	<10
Nd	<100	<100	<100	<100	<100-200	<100	<100-100	<100	<100	<100
Ni	30-300	70	20-100	70	20-300	50	20-70	50	<3-150	15
Sc	10-50	20	15-30	20	10-50	15	10-20	15	5-30	5
Sn	20-100	50	10-30	20	<10-100	20	<10-30	15	<10	<10
Sr	15-150	50	30-70	70	70-200	200	70-700	200	<2-1000	150
Ti	1500- 5000	3000	1000- 5000	3000	3000- 15,000	5000	3000- 15,000	5000	500- 15,000	1500
V	70-200	150	70-150	100	50-300	100	50-100	100	<10-500	50
Y	20-70	50	20-70	50	20-150	50	50-70	50	<10-70	15
Yb	1.5-70	5	2-10	5	3-50	5	5-10	5	1-50	1.5
Zr	70-200	100	70-100	100	30-3000	500	100-2000	200	20-500	70

1/ Analyst was Nancy M. Conklin. Semiquantitative spectrographic analyses yielded concentrations reported as midpoints of six geometric classes per order of magnitude. Thus, concentrations are shown as 1, 1.5, 2, 3, 5, 7 times 10^n. Samples of bed clay and bed silt were from Brandywine Creek at Wilmington, Del.; Juniata River at Newport, Pa.; Yadkin River at Yadkin College, N. C.; Licking River at McKinneysburg, Ky.; Green River at Munfordville, Ky.; Mississippi River at St. Louis, Mo.; Kansas River at Wamego, Kans.; Elk Creek near Hobart, Okla.; Colorado River at Columbus, Tex.; Colorado River near Cisco, Utah; Big Horn River at Kane, Wyo.; Cosumnes River at McConnel, Ca.; Cache Creek at Yolo, Ca.; Mad River near Arcata, Ca.; Crooked River near Post, Oreg. Bed sand samples were for the same sites as for bed clay and bed silt except that no samples were obtained for the Colorado River at Columbus,Tex. and the Bighorn River at Kane, Wyo. Suspended clay and silt samples were from Bradywine Creek at Wilmington, Del.; Yadkin River at Yadkin College, N. C., Kansas River at Wamego, Kans.; Elk Creek near Hobart, Okla.; Pecos River at Santa Rosa, N. Mex. and San Juan River at Bloomfield, N. Mex. In addition, one suspended silt sample was analyzed from the Mississippi River at St. Louis, Mo. There were 15 samples each of bed silt and clay analyzed, 13 samples of bed sand, 6 samples of suspended clay and 7 samples of suspended silt.

2/ Size separation of clay and silt was done by sedimentation in distilled water following air-jet dispersion (Chow and Davidson, 1953). Silt-sand separation was done by wet sieving. Cation-exchange capacity and sediment mineralogy of these sediments were reported by Kennedy (1965).

SUMMARY AND CONCLUSIONS

Study of the Mattole River, a stream in northern California which is essentially unpolluted chemically, has provided insight regarding the processes that control the chemical quality of such streams during both low flow periods and during storm runoff. The concentrations of dissolved constituents in a stream are related to the source of the water, i.e. surface runoff, subsurface runoff or ground water, and are also determined by the rainfall intensity, hydrology, geology, topography, climate, season, soil texture and chemistry of each constituent.

During a storm period, when water containing very low dissolved salts falls as rain, the runoff into stream channels can cause either an increase or decrease in concentration of a dissolved constituent or cause very little change, depending upon the nature of the constituent, Nitrate is a prime example of a constituent that increases in concentration during a storm rise, because in clean streams it is commonly derived from decaying organic matter at or near the land surface and is not significantly adsorbed by soil. Sulfate, phosphate, molybdate and potassium are also concentrated at the land surface by growing plants and later released by decomposition of these plants, but reaction with the soil tends to suppress rapid large percentage variations in the concentration of these constituents in runoff water. Na and Cl are concentrated at the land surface due to dry fallout and washout of aerosols in light rain. They decrease in concentration during storm runoff, but the decrease is not as great proportionally as for the other major constituents. Al and Fe show some increase during storm runoff, probably because of complexation by soluble organics leached from surface materials.

Cations showing the greatest percentage decrease in concentration during storm runoff are Ca, Mg and Sr, presumably due in part to a relatively slow release from solids. The alkaline earths are released less rapidly than the alkalis also because of increased adsorption of the divalent cations on soil when dissolved salts in soil water are diluted.

Silica is a major constituent whose concentration changes are not in phase with stream discharge. Release rate during storm runoff is not great enough to prevent some silica decrease during the early phase of a stream rise, but as the proportion of quick-return flow in Mattole increases, so does the silica concentration.

The concentrations of Ca and HCO_3, the major dissolved constituents in the Mattole River, decrease by a factor of only 5-6 while stream discharge increases by a factor of 1000. Thus, the release of these constituents as dissolved load must increase by a factor of 150-200 during peak storm runoff. It is probable that this load increase results from three major causes: (a) an increase in the rate of release from soil solids due to the greater concentration gradient between the surface of the solids and the surrounding leaching solution, (b) a removal by leaching of soluble soil salts and displacement of relatively concentrated interstitial soil solutions and (c) a much greater area of soil is being leached due to expansion of the fraction of the basin contributing surface and subsurface runoff to the stream channel during intense rainfall. In the case of dissolved nitrate, which increases with increasing discharge, the load will show an even greater percentage increase than the discharge.

The concepts of surface runoff, subsurface runoff (quick-return and delayed-return) and ground water flow, or base runoff sre useful in visualizing the paths which rainfall takes on its way to the stream, but there is probably very little surface runoff entering the stream system which does not have mixed with it water which has been in intimate enough contact with the uppermost soil to have picked up significant quantities of dissolved solids. Similarly there is a continuum in composition between water which has seeped downslope through a few centimeters of permeable soil acting as a temporary barrier on the land surface and water which has penetrated a meter or more into the soil and moved laterally several meters or tens of meters before entering an incised stream channel. Nevertheless, there do appear to be changes in the stream chemistry associated with specific parts of the storm hydrograph which suggest that, in the Mattole basin at least, the waters derived from different parts of the soil profile have certain distinguishing characteristics which manifest themselves in the runoff. Although there appear to be no detectable changes in the discharge hydrograph indicative of the transition from mainly surface runoff to mixed surface and subsurface runoff there is some suggestion, in the case of isolated storm events, of a change in slope in the declining limb of the discharge hydrograph which approximately coincides with the silica concentrations reaching a plateau. This "break" in the declining discharge hydrograph may represent the cessation of surface runoff.

Variations in rain chemistry and in the proportion of rain infiltrating the soil compared to that contributing to surface runoff can have significant effects on stream chemistry. An inverse relation between rainfall intensity and concentration of dissolved solids in rainfall seems to be rather consistent for individual storms, so the dissolved solids concentration in rain is least when surface runoff is a significant component of stream flow. Conversely, when rainfall intensity is low, dissolved salt concentrations are higher and a greater proportion of the rainfall infiltrates. Because low-Cl rainfall is preferentially carried away in storm runoff, the rain left behind will contain Cl in above-average concentrations. This process, plus the effects of dry fallout and evapotranspiration cause the ground water to contain considerably more Cl than that of the average rain falling on the Mattole basin.

High-chloride rain associated with hail near the end of storm periods appears to have occurred at least twice during this study and resulted in a detectable increase in stream Cl in one instance. If such phenomenon could be predicted from the storm type, it would offer interesting possibilities for tracing the path of rain through a stream system.

Although almost all of the Cl on the Mattole River is derived from Cl in rain, only about 30 percent of the Na is obtained from that source. Most of the Na comes from rock weathering, and the proportion of soil-derived Na in the river varies seasonally and with individual storms. In general, the proportion of soil Na decreases during a storm rise and increases on the fall. This is attributed to the removal of some accumulated sea salts by initial storm runoff, dilution of interstitial soil water and release of weathered Na from the soil into the quick-return and delayed-return flow, Toward the end of the rainy season, when there had been an opportunity for an extensive buildup of soil moisture, the stream chemistry reflected the pickup of greater quantities of soil Na, and significant decreases in the proportion of soil Na were not observed on stream rises.

The effect of suspended sediment upon the chemical composition of stream water varies widely with the chemical characteristics of the particular constituent. In the case of the anions NO_3, HCO_3, SO_4 and Cl, reaction with stream sediment is probably slight and the concentrations of these ions in stream water are controlled by processes occurring within the soil profile. This is true also to a major extent for Na, which does not compete well for exchange sites on stream sediment under the conditions of low ionic strength existing in the Mattole River. Ca, Mg and K are sorbed to a considerable degree by stream sediments, so the sediments act to buffer the concentrations of these ions in stream water. Silica interaction with sediment is pH dependent; thus, as slightly acidic subsurface runoff enters the stream system and pH increases, there may be a tendency to either gain or lose silica to stream sediment depending upon whether the silica is above or below the equilibrium concentration.

Al, Fe and Mn were much higher in concentration in acidic soil extracts than in the stream water, and it is probable that interaction of these elements with stream sediments results in decreasing concentration associated with increased pH in the stream. However, complexation of the Al and Fe, particularly, would be expected to hinder the removal of these elements from solution. Cd, Cu, Pb and Zn are all strongly adsorbed by stream sediments with short-term distribution coefficients under normal stream conditions of 2,300 to 170,000. The concentrations of these elements in stream water are largely or completely controlled by reactions in the stream system, resulting in a great reduction in concentration compared to the acidic soil solutions. Depending upon the chemistry of the individual constituent, therefore, there may be almost no control or essentially complete control of concentration of a dissolved constituent by stream sediment. As a generalization, with some notable exceptions, most of the major dissolved constituents in the Mattole River tend to decrease with increasing stream discharge and most trace constituents tend to decline very little, or actually increase, with increasing discharge.

When stream sediment enters brackish water the major exchangeable cations are Ca and Mg with some K and relatively little Na. As salinity increases the proportion of exchangeable Ca decreases while the proportion of the other three elements increases. At about 3 parts per thousand salinity the proportion of exchangeable Mg reaches a maximum and then decreases thereafter along with Ca while exchangeable Na and K continue to increase. In seawater Na is the major adsorbed cation with lesser amounts of Ca, Mg and K.

The large volume of sediment transported by the Mattole River means that a sizable supply of dissolved Ca is provided to the ocean each year whereas the sediment removes equivalent Na, K and perhaps some Mg from seawater.

Cd, Cu, Pb and Zn are tightly held on Mattole River sediments at the pH normally observed in the stream; however, pronounced changes in the distribution of these metals between solids and solution can occur with changing pH. In general, decreased adsorption occurs with decreasing pH, but where great changes in complexing coincide with decreasing pH (as for Pb in the pH range 7-8) the adsorption can increase with decreasing pH. When Mattole sediments contact seawater a much smaller fraction of these trace metals are desorbed than might be expected from six-hour equilibration experiments. In fact, no detectable release of Pb and Zn was found when dried Mattole sediment was placed in seawater The equilibration experiments suggest that the K_d of Cd, Cu, Pb and Zn on Mattole sediment varies not only with pH but also with concentration of dissolved trace metals, salinity, flow conditions as reflected in sediment character, degree of complexation, contact time with the sediments and the chemistry of the individual elements.

Much can be learned from storm hydrographs about rainfall-runoff characteristics of a basin which can have implications for stream chemistry. In the Mattole River there is a rapid response to rainfall because of the relatively low soil permeability in the central and lower basin. This results in considerable dilution of dissolved salts in the stream during storms despite the rapid release of solutes by the soils. During heavy rainfall 70 percent or more of the rain can appear as storm runoff within one day after rainfall ends, indicating that the basin as a whole sheds water rather effectively. Although the average depth of the soil cover in the basin is probably 1 to 3 meters, the bedrock is highly compacted due to extensive folding and faulting. This means that no large reservoir of ground water is available to support dry-weather flow and the range of discharge of the Mattole River reflects this fact. During major storms stream discharge can exceed 1000 m^3/s, but at the end of summer a flow of 1 m^3/s is common. Water draining from the acid soils above the bedrock during late spring and early summer contain higher silica concentrations and lower Ca concentrations than the late summer flows which may have reached near equilibrium with the bedrock and become saturated with calcium carbonate.

Although leaching studies done as part of this work suggest reasonable explanations for most of the observed variations in stream chemistry, there are some results that emphasize the need for a much better understanding of the solid-solution reactions occurring during the few hours time between rain falling on the land and its appearance as storm runoff. For example, all of the leaching studies done on the Mattole soils have uniformly shown much higher K:Ca ratios than are observed in the stream. As the water:soil ratio decreased, however the K:Ca ratio also decreased sharply (table 14) suggesting that a very low water:soil ratio might produce the ratios observed in the stream. Also, none of the laboratory experiments involving mixing of distilled water and soil samples for several hours have indicated that the pH should be as high in the stream as was measured. Research on this area should be highly rewarding, not only in explaining the apparent discrepancy between laboratory experiments and stream sampling but in understanding the pathways of rain from soil to stream.

The most effective way of determining the patterns of chemical variation during storm runoff for various constituents in an untested stream would appear to be to sample frequently during periods of rapidly changing discharge, especially during and shortly after a stream rise, and less frequently at other times. A minimum sampling program would require thorough coverage during at least two storms, one following a prolonged dry period and the other closely following two or more previous storms. In addition, weekly sampling during a long dry period following a wet season should be effective in defining the die-away curve.

The information derived from such a sampling program for a particular stream would provide a much better understanding of the variations in chemical quality with time and discharge than an equivalent number of samples taken at set time intervals. Thus, in terms of knowledge per unit cost, the intensive sampling approach appears to be superior to long-term periodic sampling However, after the basic pattern of chemical quality variation is established, intermittent sampling based upon knowledge of that pattern can be done effectively to monitor long-term changes in stream chemistry.

Attempts to predict the chemical composition of streams, either seasonally or for individual storms, must take into account the fact that there will be a gradual buildup of readily soluble salts in the soil between rains and that these salts, either as solids during the dry season or in interstitial soil water during the rainy period, will be displaced easily by rainfall. The more thorough the leaching, the greater the rate of solution of remaining soil constituents will be. Considering that each type of terrain in a basin will respond in a different manner to this leaching and drying cycle, predicting the chemical composition of streamflow from rainfall records and from the soil properties usually measured becomes a formidable task in even a small basin.

Further progress in understanding the flow paths by rainfall during storm runoff can probably be achieved best by detailed studies in a variety of small areas of uniform terrain. Combined information on the chemistry, isotopic composition and quantity of rainfall, soil moisture and surface runoff should permit determining the degree to which the storm runoff is composed of surface runoff and subsurface runoff. Very frequent sampling of rainfall and runoff and occasional sampling of soil moisture would provide information regarding the kinetics of the processes contributing to the composition of stream water. It is this type of research that seems necessary if quantitative predictions of stream quality during storm runoff are to be made.

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ILLUSTRATIONS

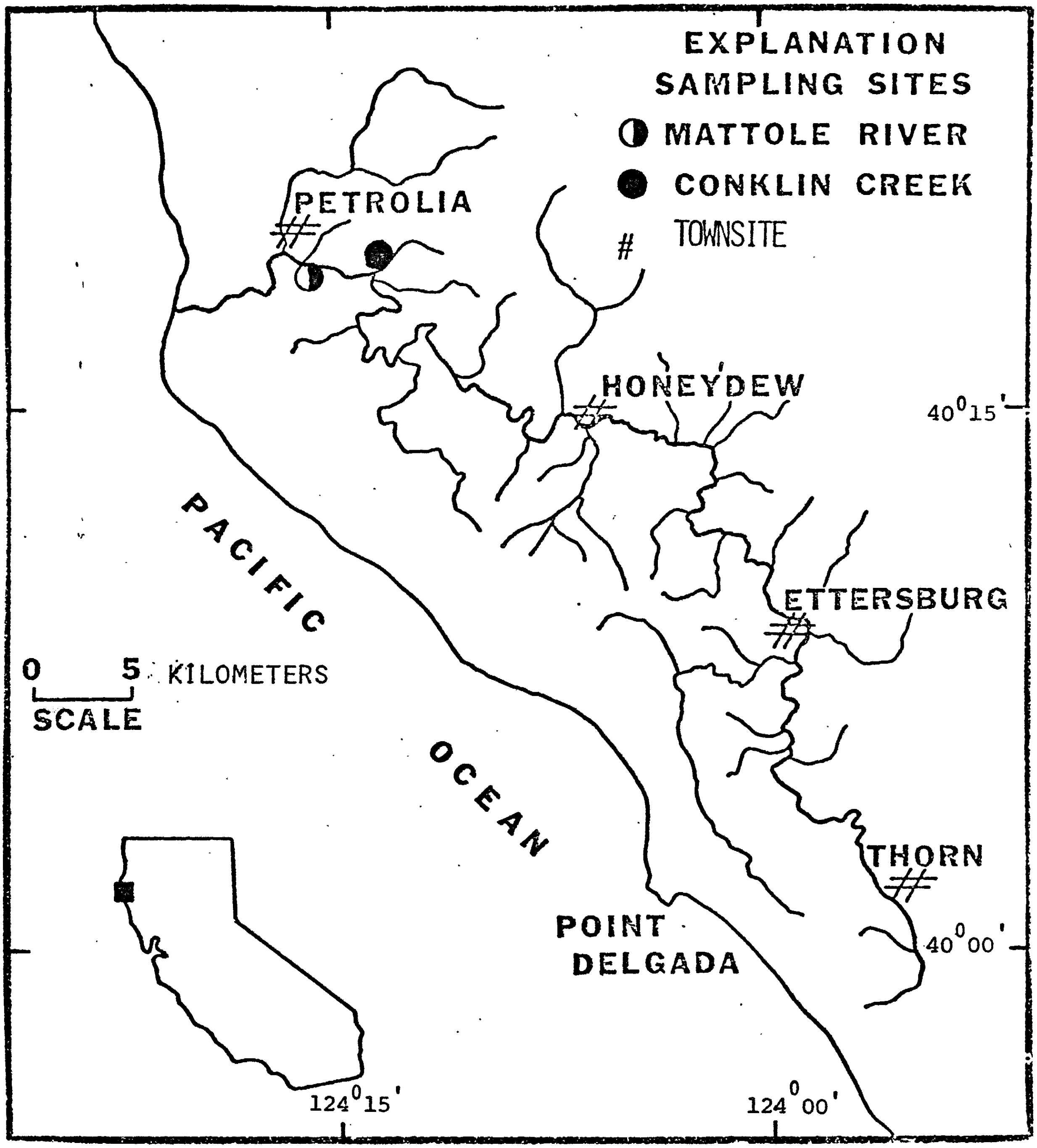

Figure 1. Map of the Mattole River basin in northern California.

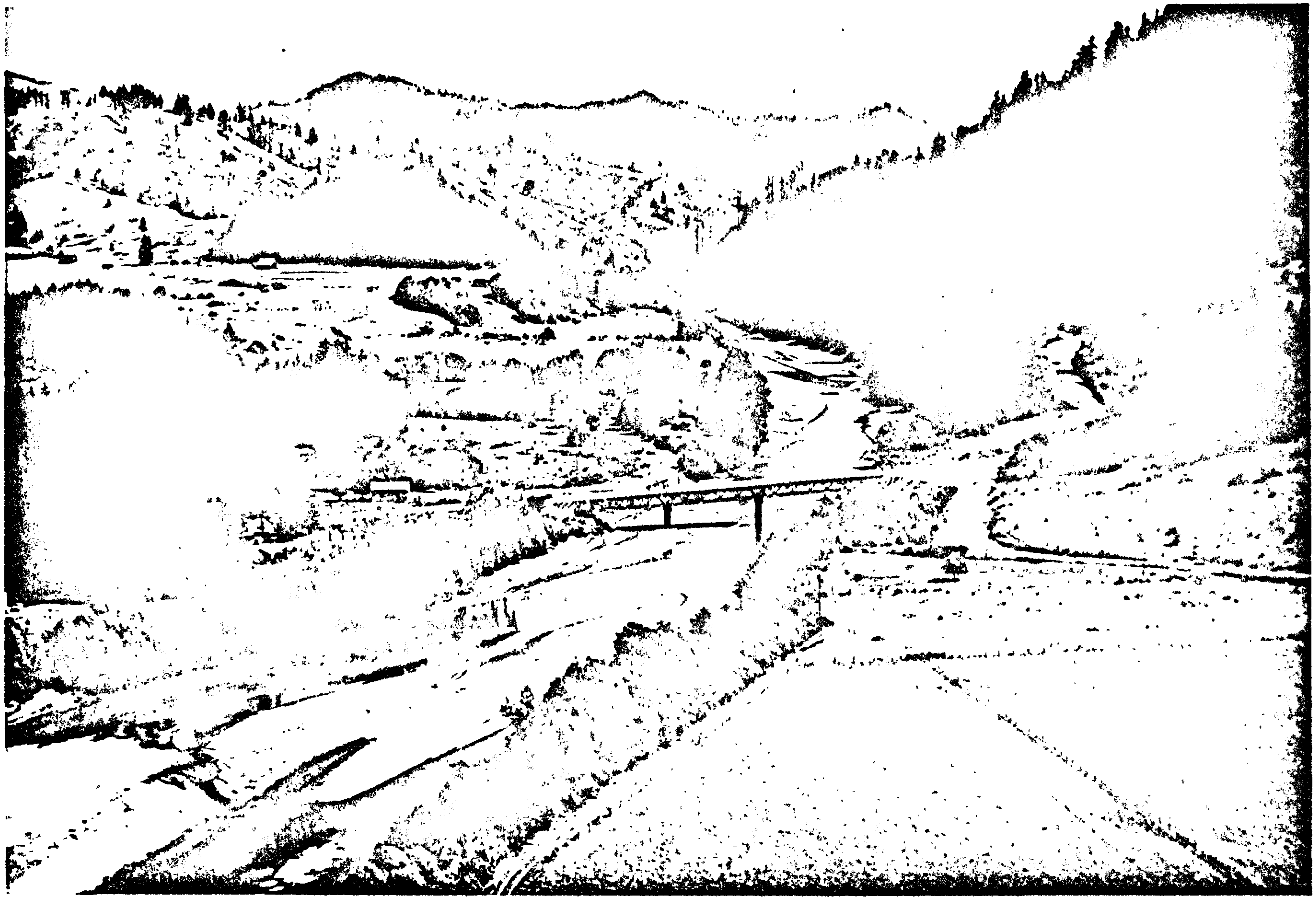

Figure 2. Aerial photograph of the lower Mattole River basin adjacent to the bridge sampling point.

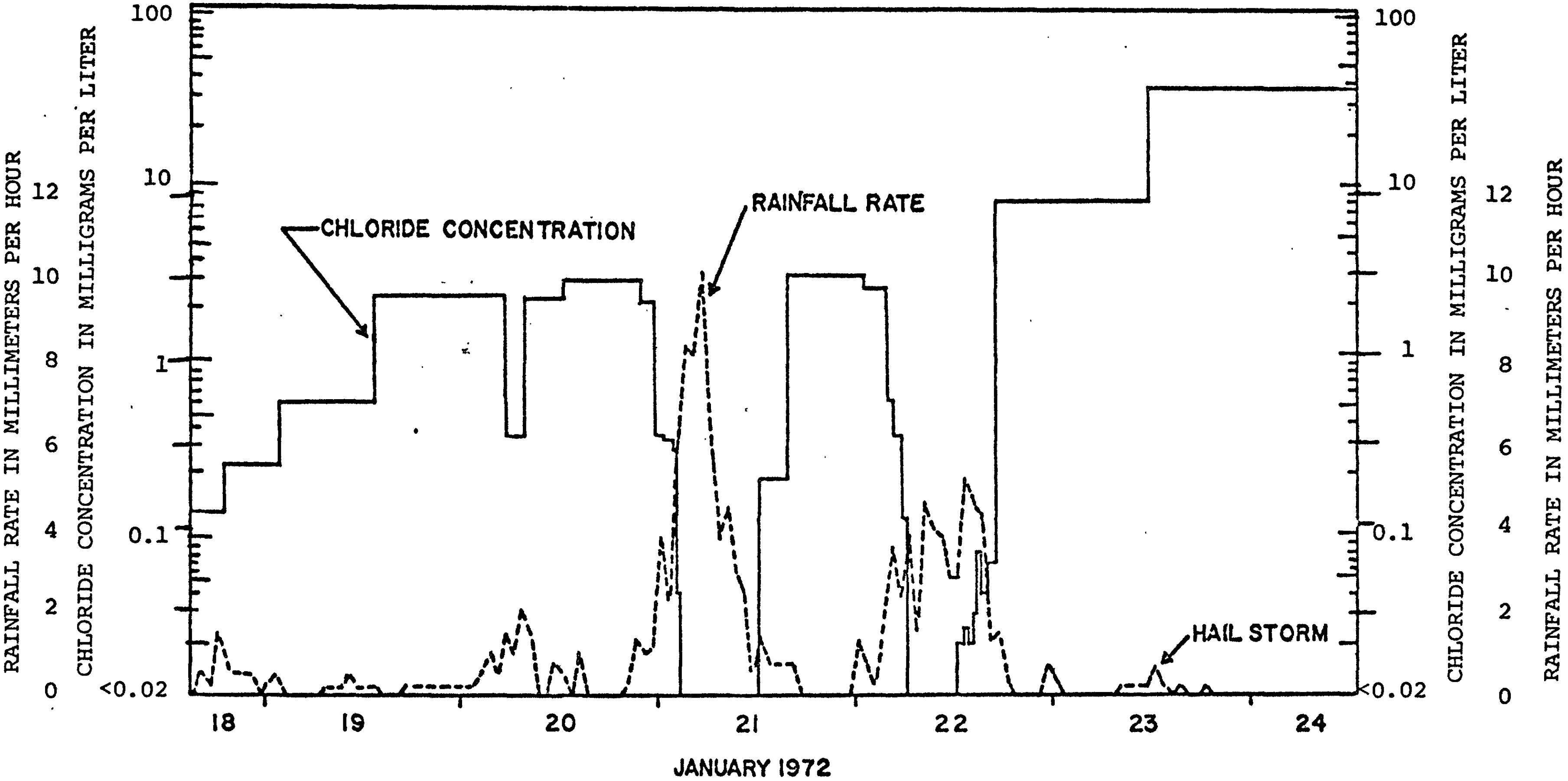

Figure 3. Graphs of rainfall rate and chloride content at Petrolia, California, January 18-24, 1972.

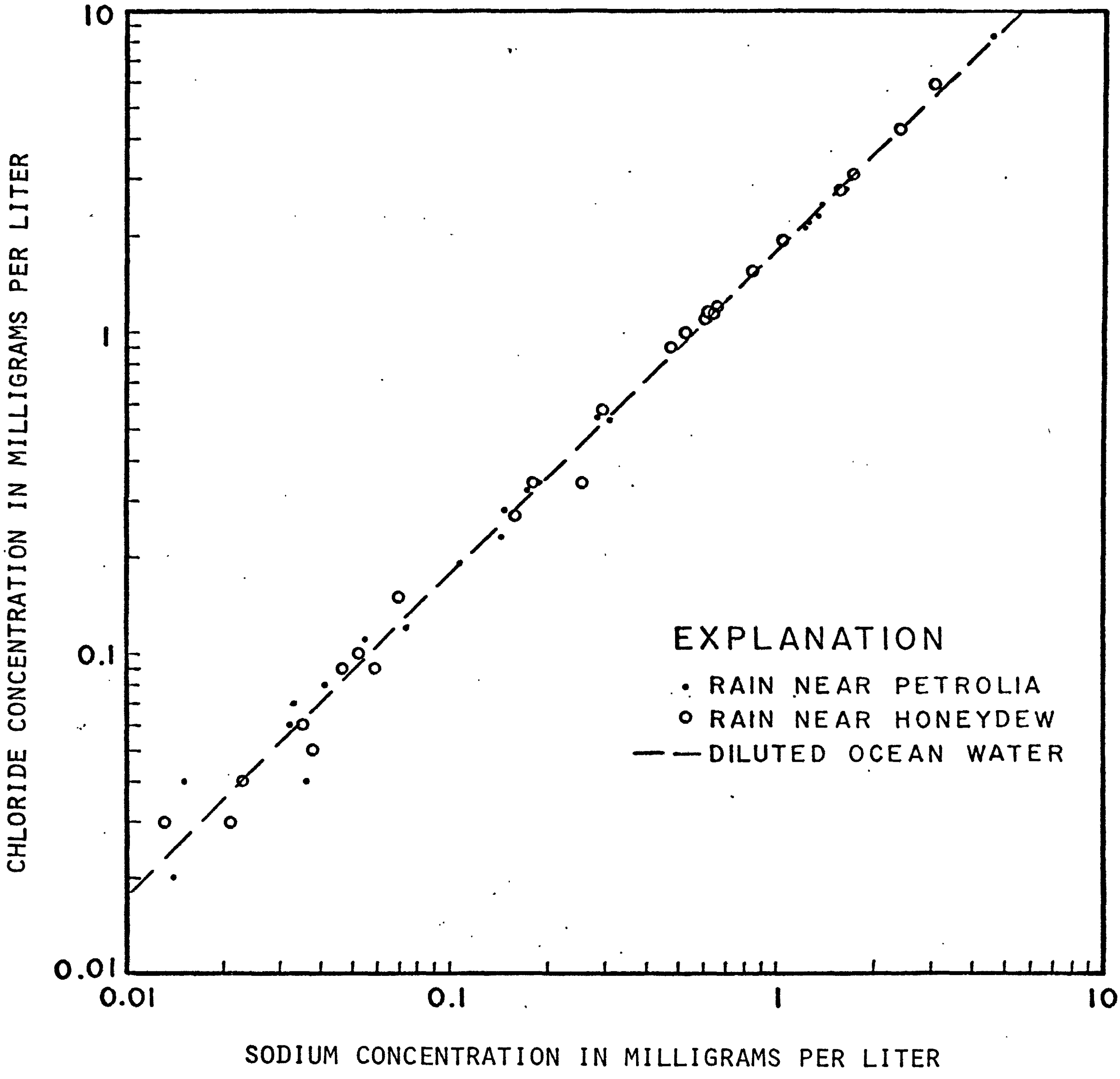

Figure 4. Chloride plotted against sodium for rainfall collected January 18-24, 1972 near Petrolia and Honeydew, California.

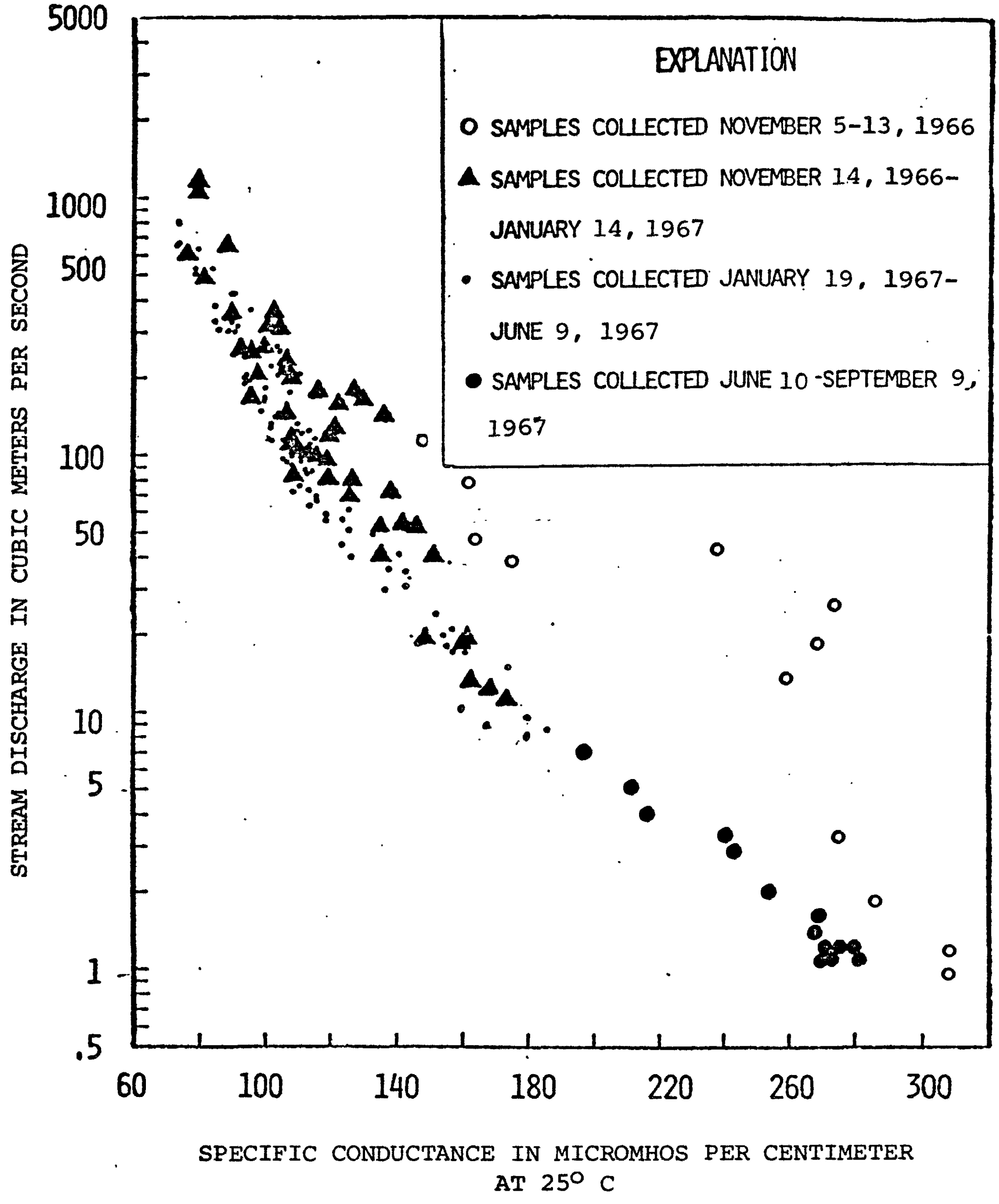

Figure 5. Graph showing relation of stream discharge to specific conductance in the Mattole River during the 1966-67 water year.

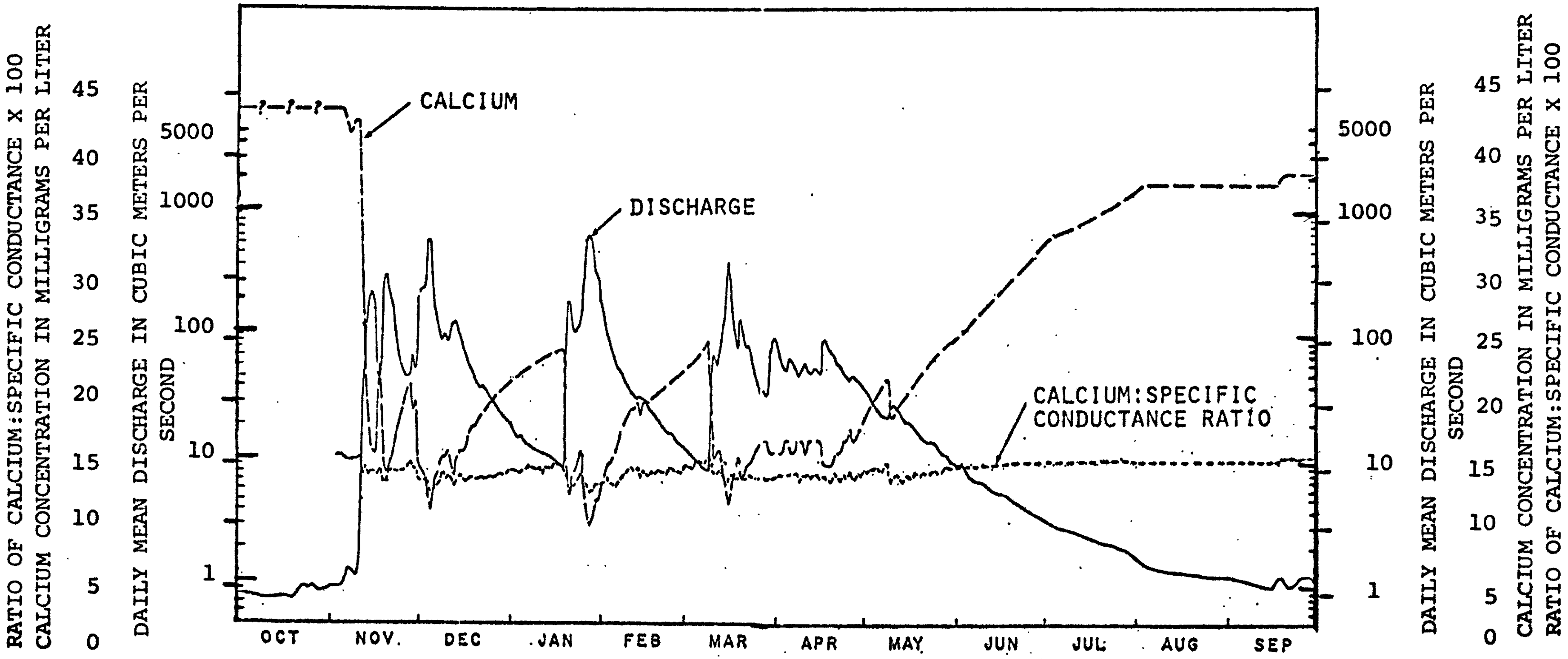

Figure 6. Graphs of daily mean discharge of the Mattole River, calcium concentration and calcium: specific conductance ratio from October 1966 to September 1967.

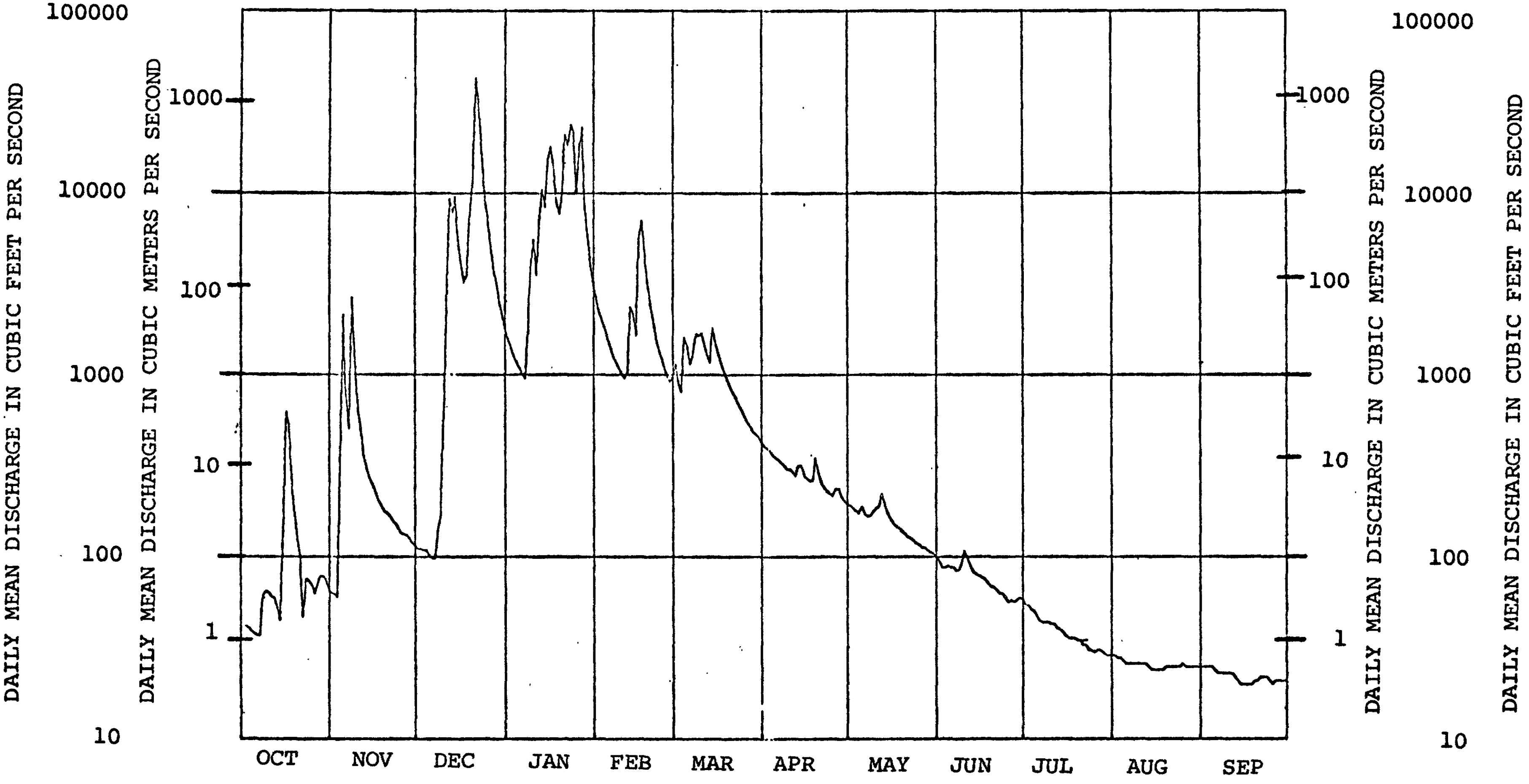

Figure 7. Graph of daily mean discharge of the Mattole River for the 1969-70 water year.

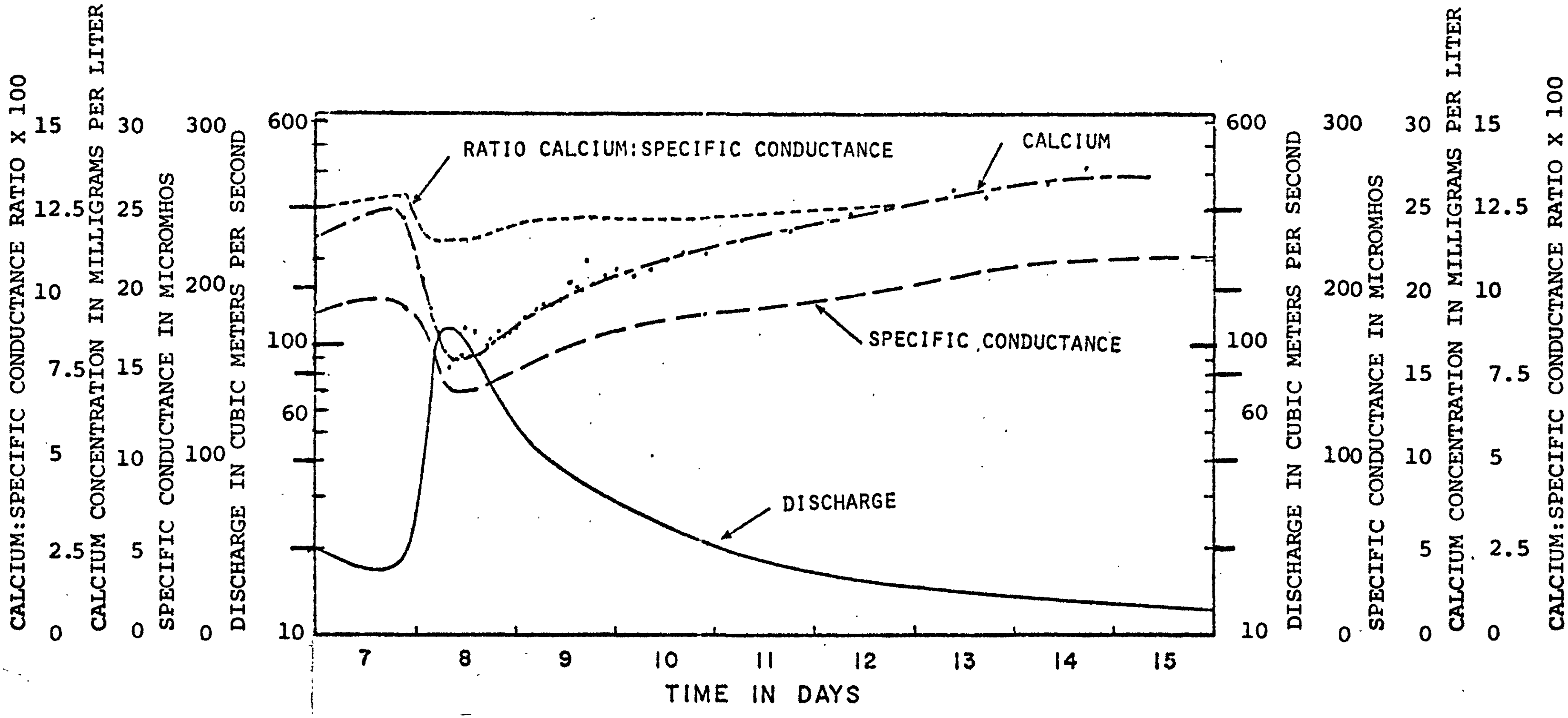

Figure 8. Graphs of discharge, calcium content, specific conductance and the calcium:specific conductance ratio of the Mattole River from November 7-15, 1969.

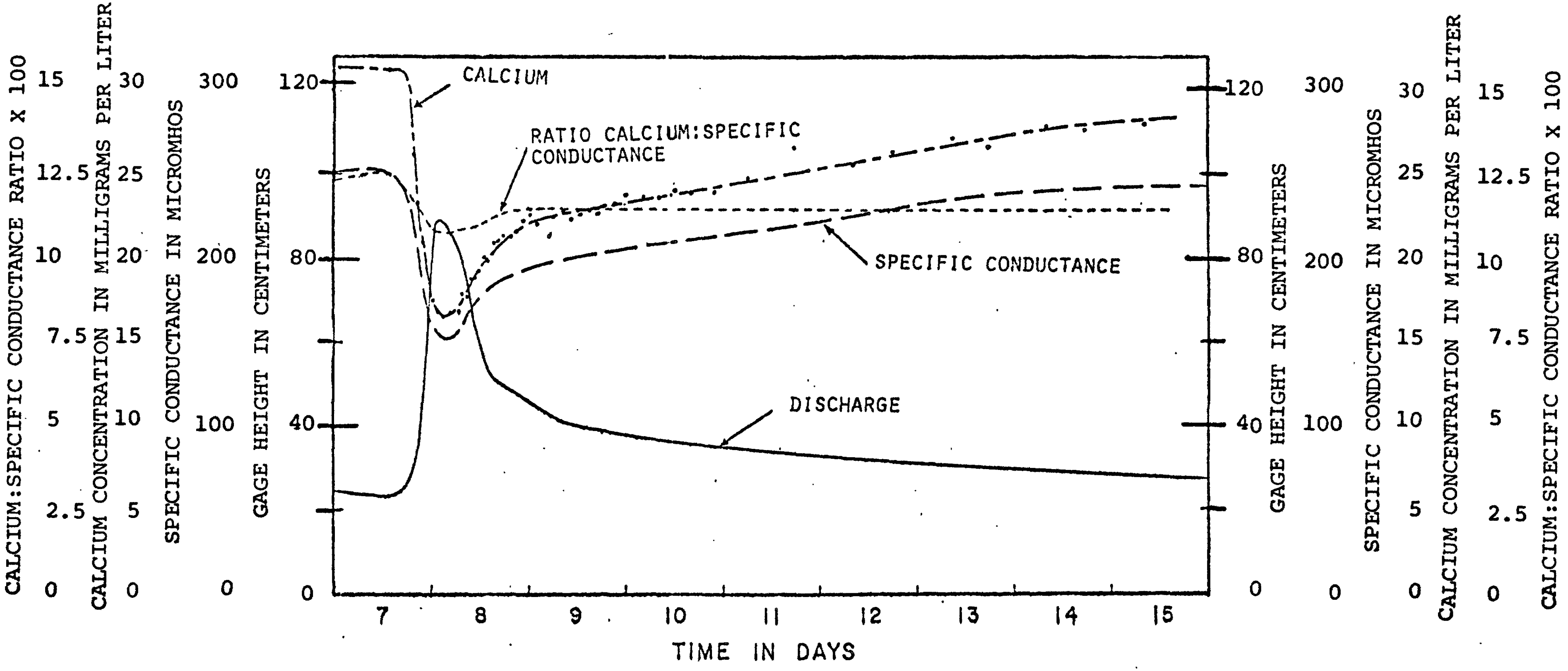

Figure 9. Graphs of discharge, calcium content, specific conductance and the calcium: specific conductance ratio of Conklin Creek from November 7-15, 1969.

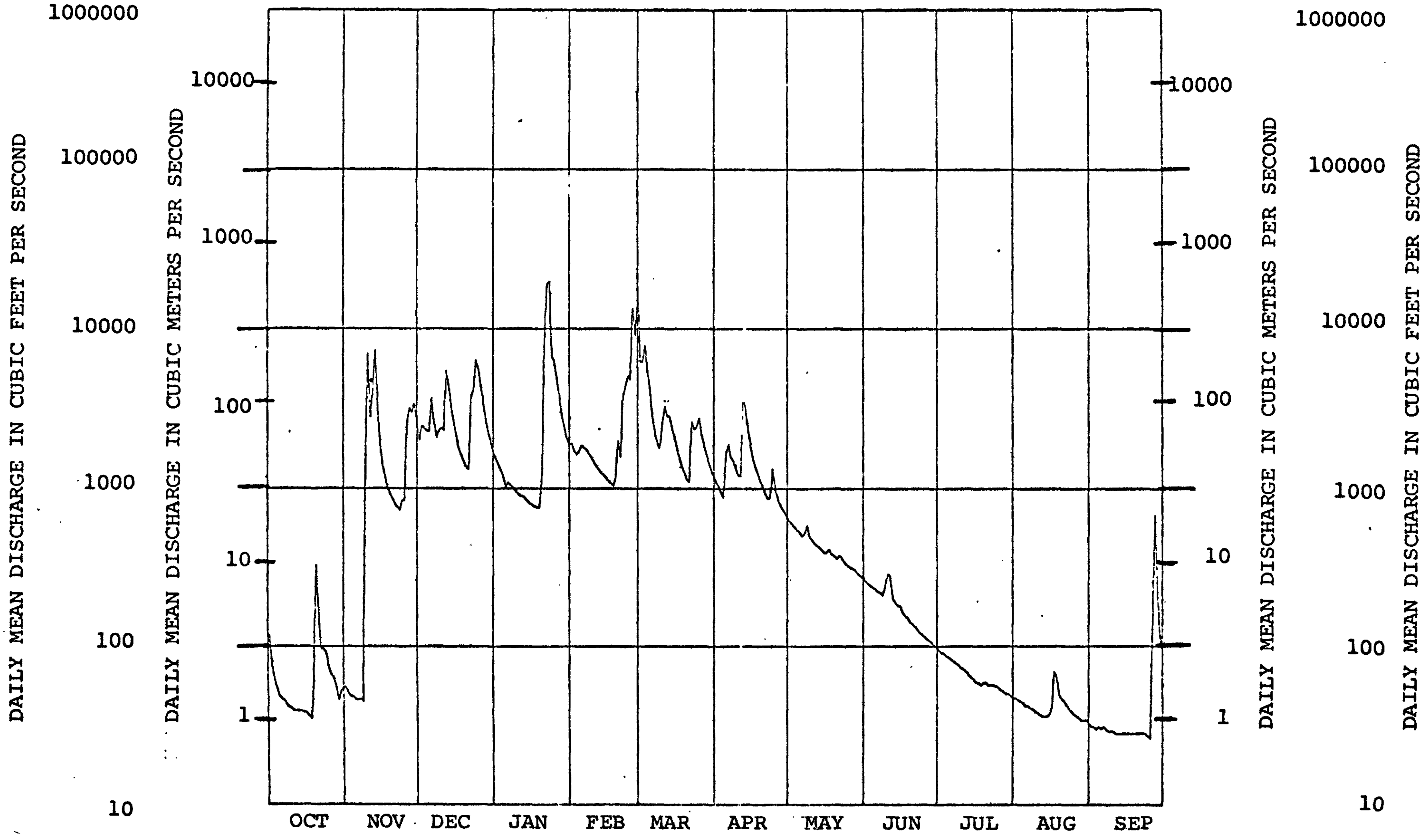

Figure 10. Graph of mean daily discharge of the Mattole River for the 1972 water year.

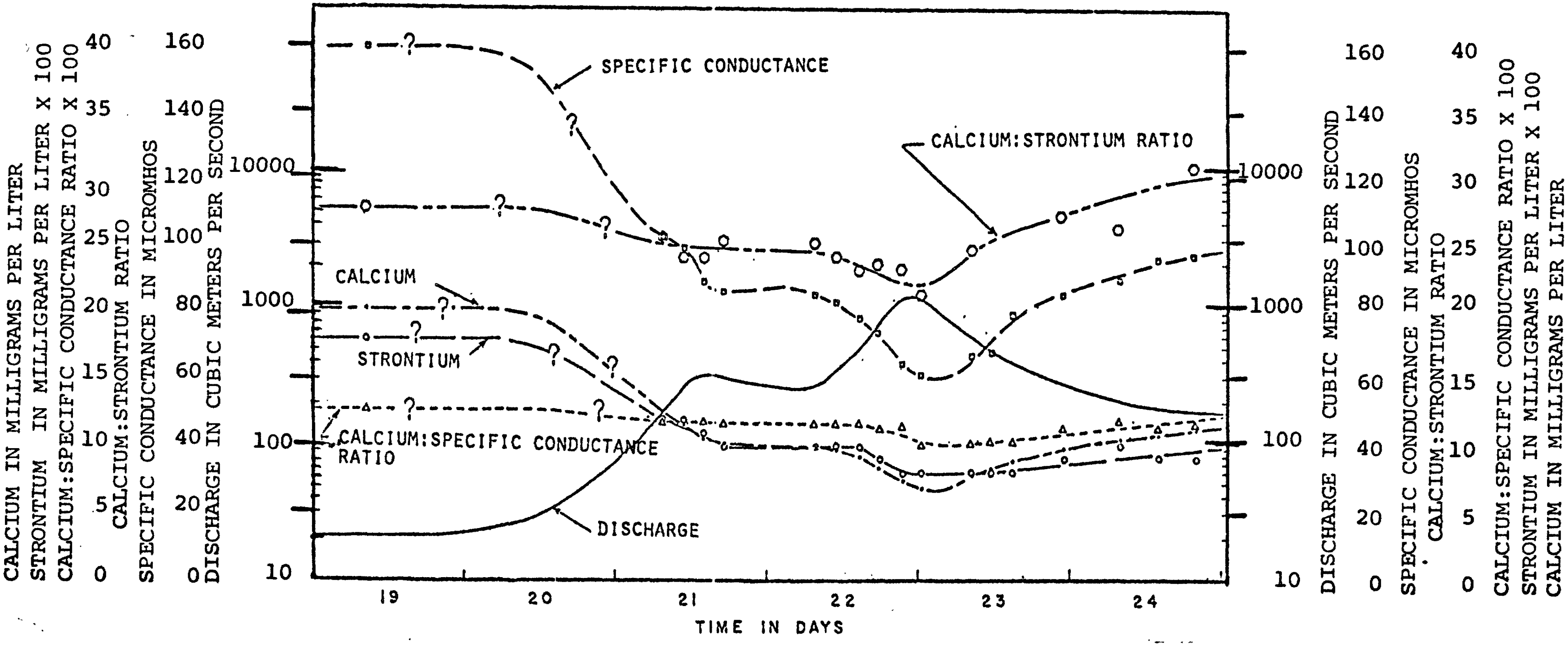

Figure 11. Graphs of discharge, calcium and strontium content, specific conductance, calcium: specific conductance and calcium:strontium ratio of the Mattole River from January 19-24, 1972.

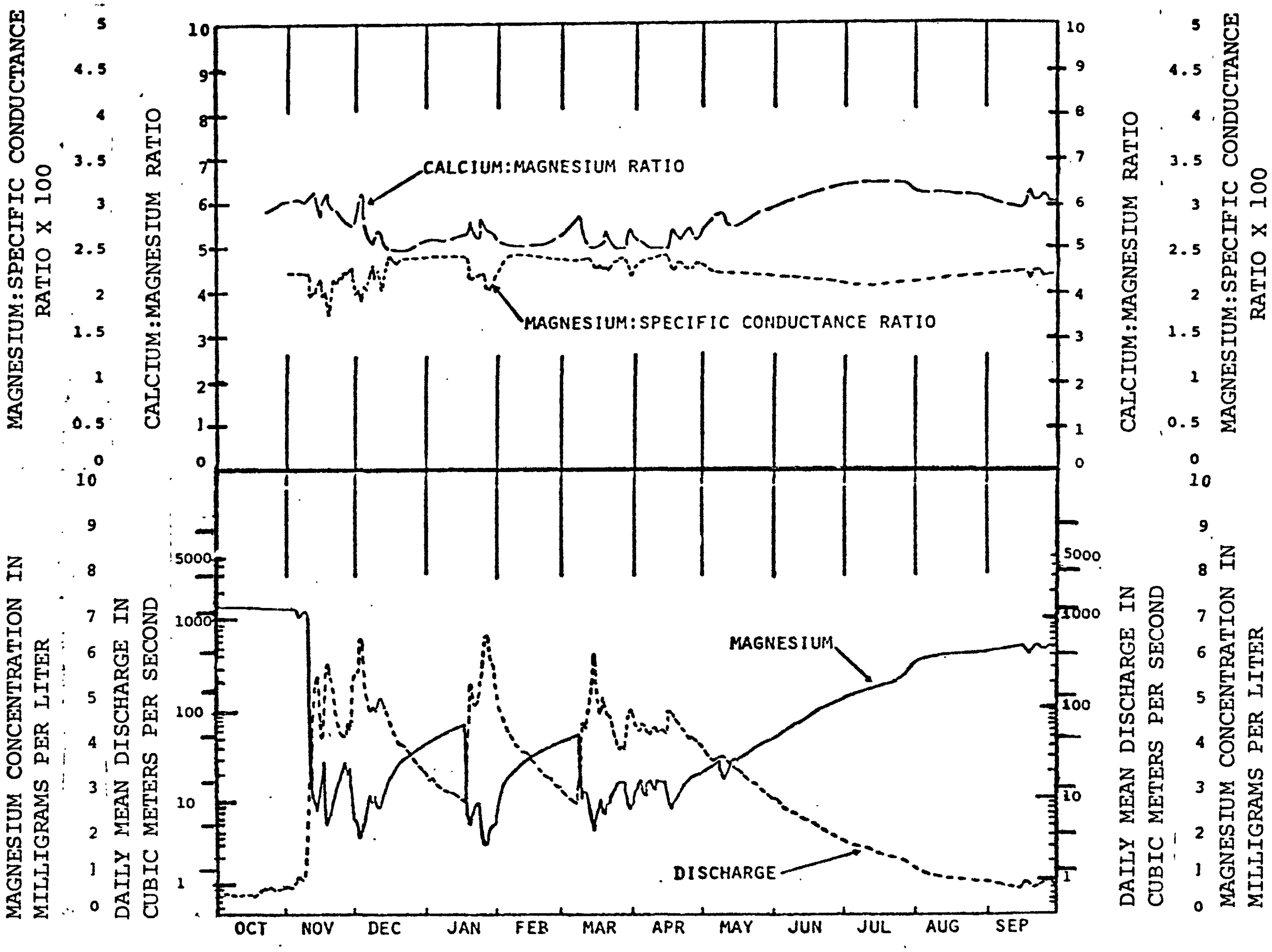

Figure 12. Graphs of daily mean discharge of the Mattole River, magnesium concentration and the ratios of magnesium:specific conductance and calcium:magnesium for the 1966-67 water year.

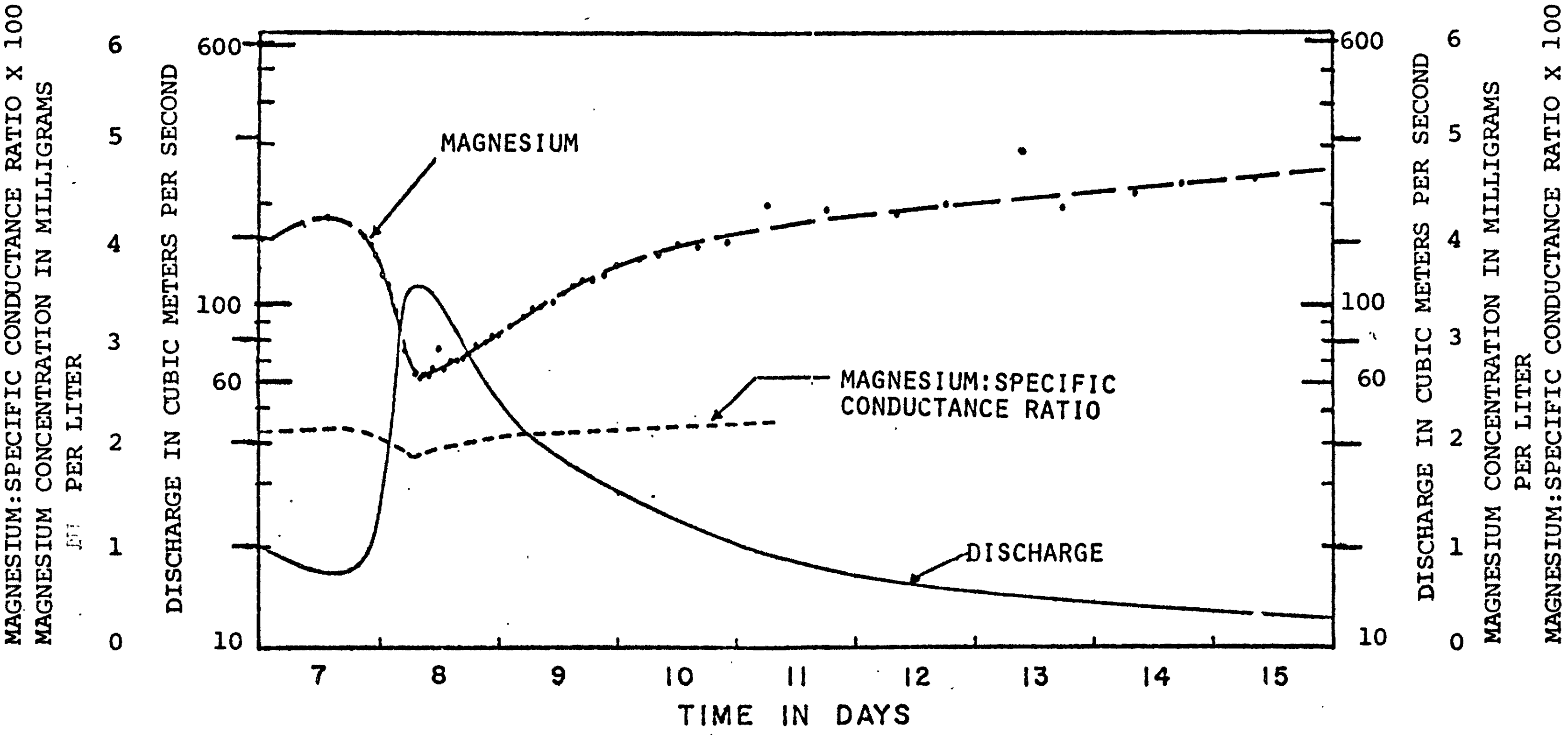

Figure 13. Graphs of discharge, magnesium content and magnesium:specific conductance ratio of the Mattole River from November 7-15, 1969.

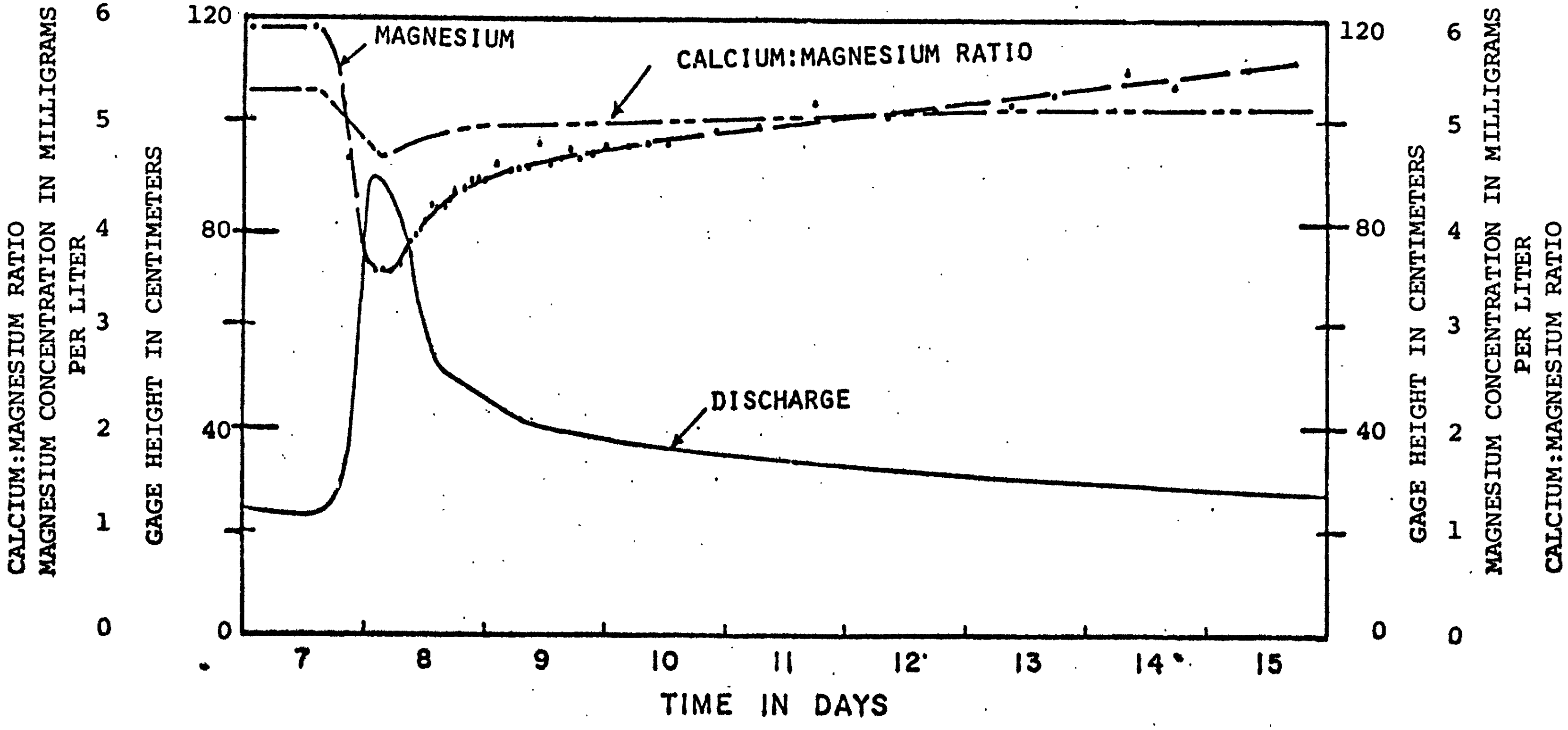

Figure 14. Graphs of discharge, magnesium content and calcium:magnesium ratio of Conklin Creek from November 7-15, 1969.

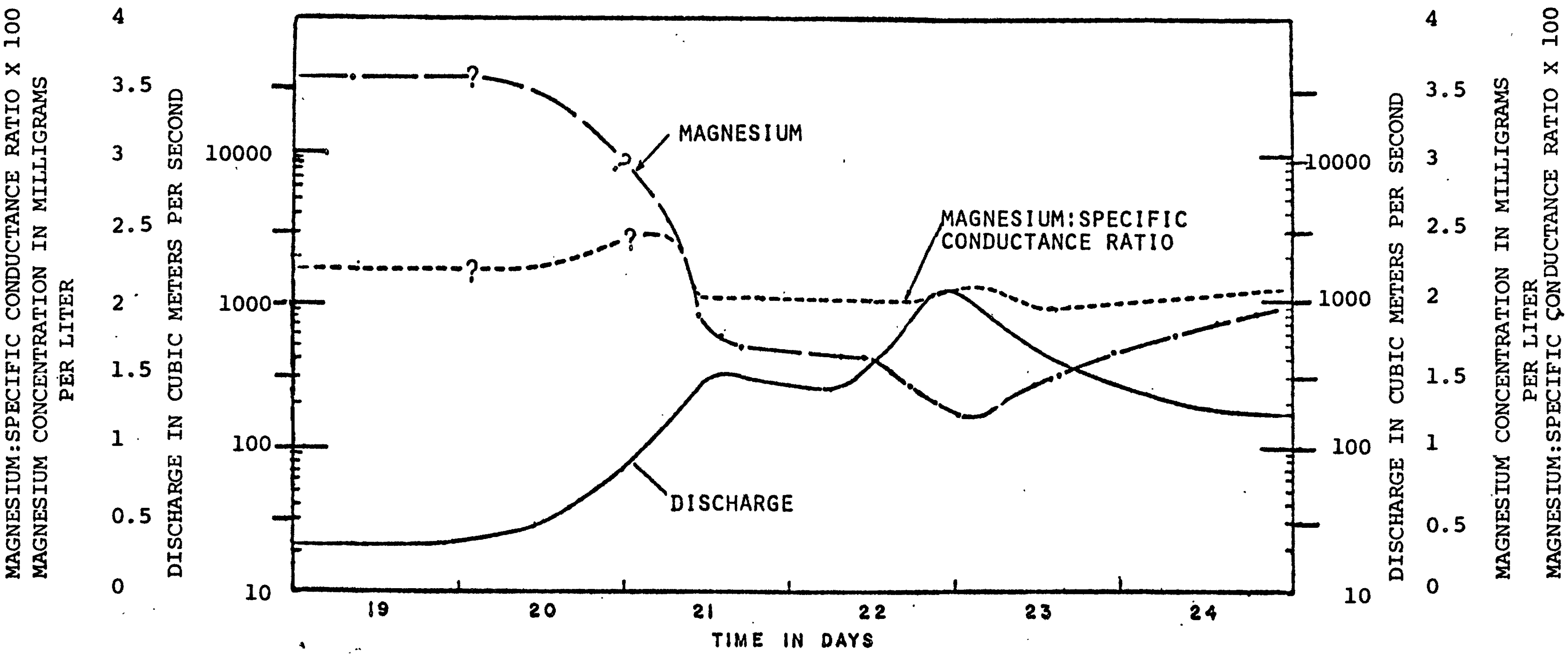

Figure 15. Graphs of discharge, magnesium content and magnesium:specific conductance ratio of the Mattole River from January 19-24, 1972.

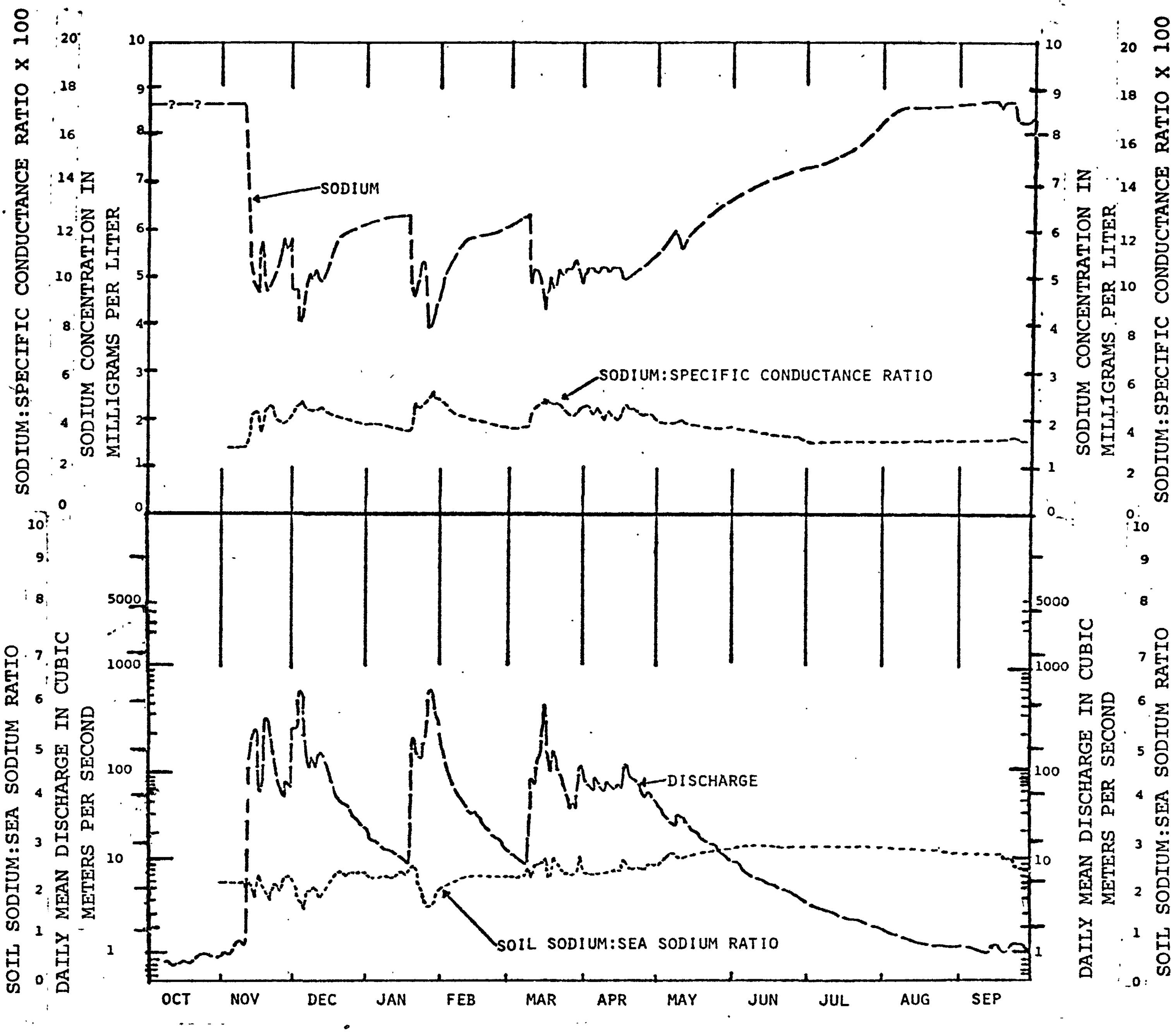

Figure 16. Graphs of daily mean discharge of the Mattole River, sodium concentration and the ratios of sodium:specific conductance and soil sodium:sea sodium for the 1966-67 water year.

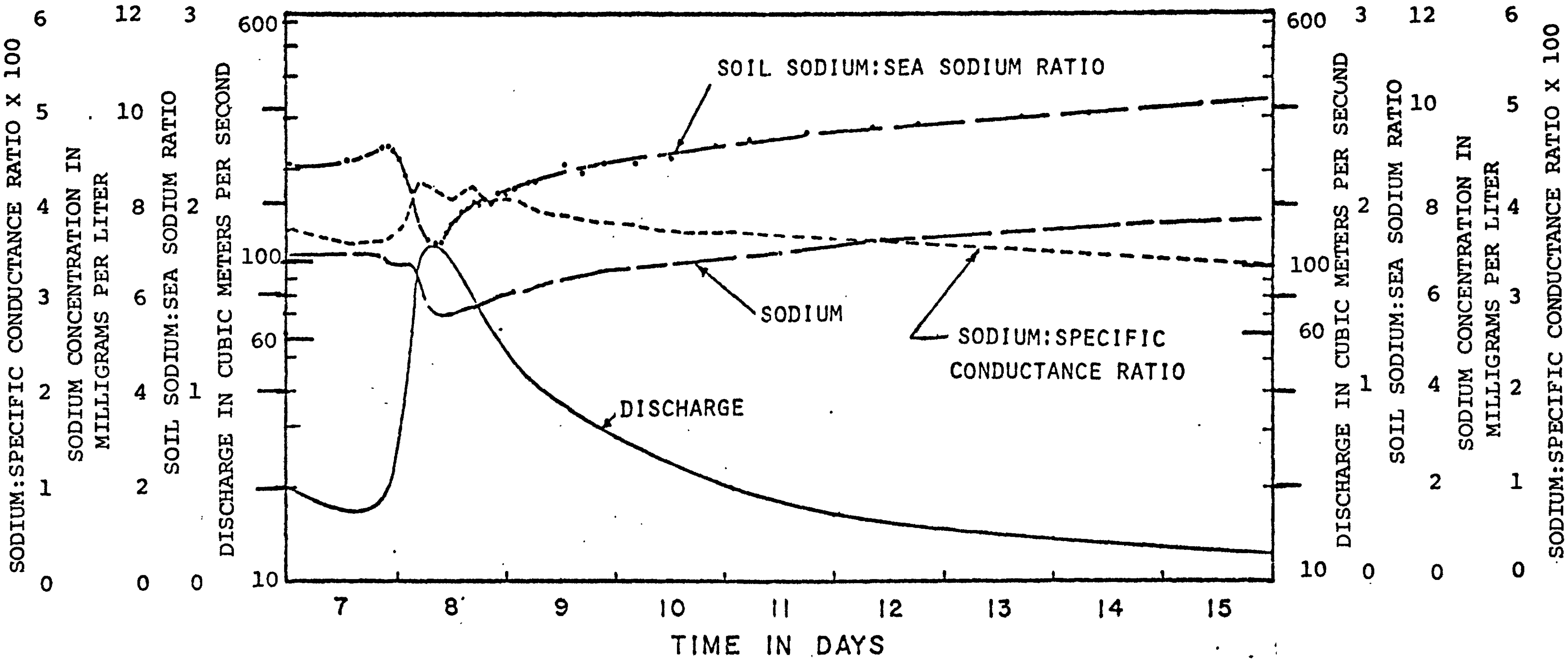

Figure 17. Graphs of discharge, sodium content, soil sodium:sea sodium ratio and sodium:specific conductance ratio of the Mattole River from November 7-15, 1969.

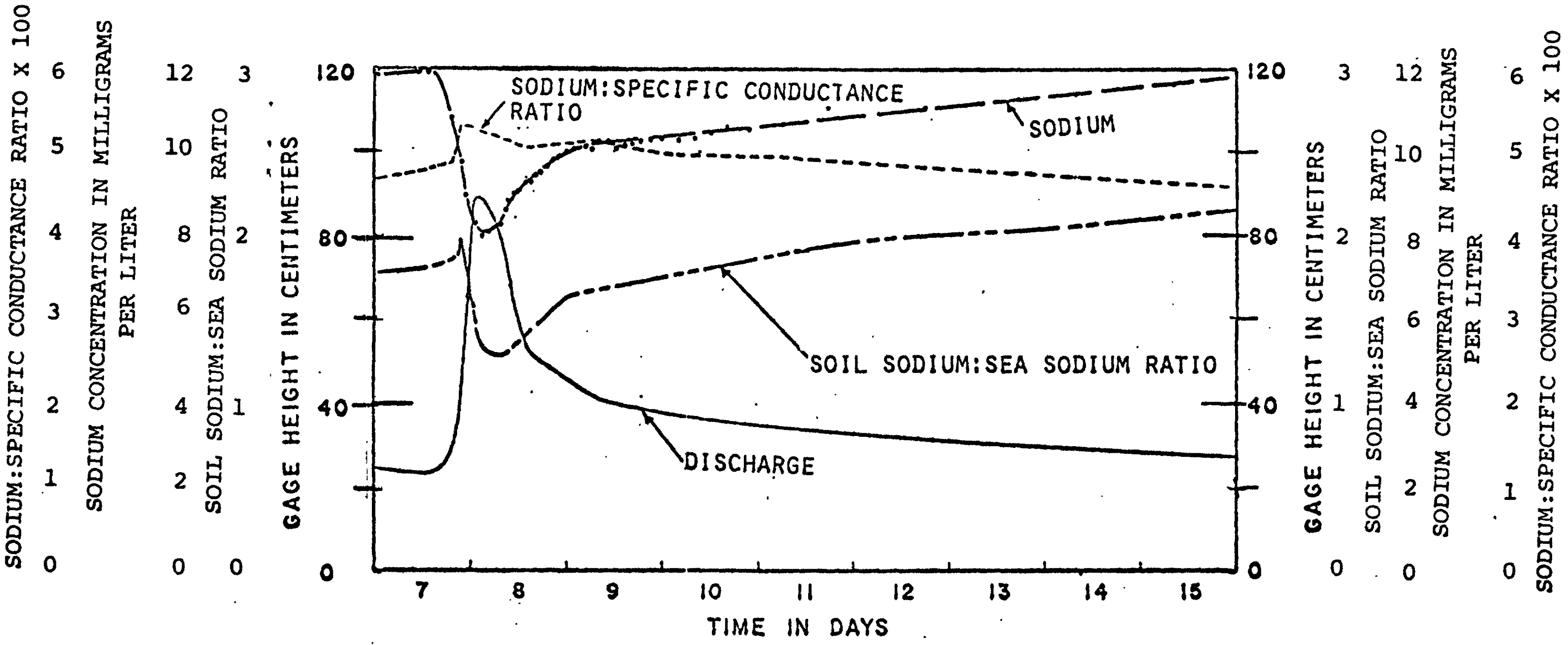

Figure 18. Graphs of discharge, sodium content, soil sodium:sea sodium ratio and sodium:specific conductance ratio of Conklin Creek from November 7-15, 1969.

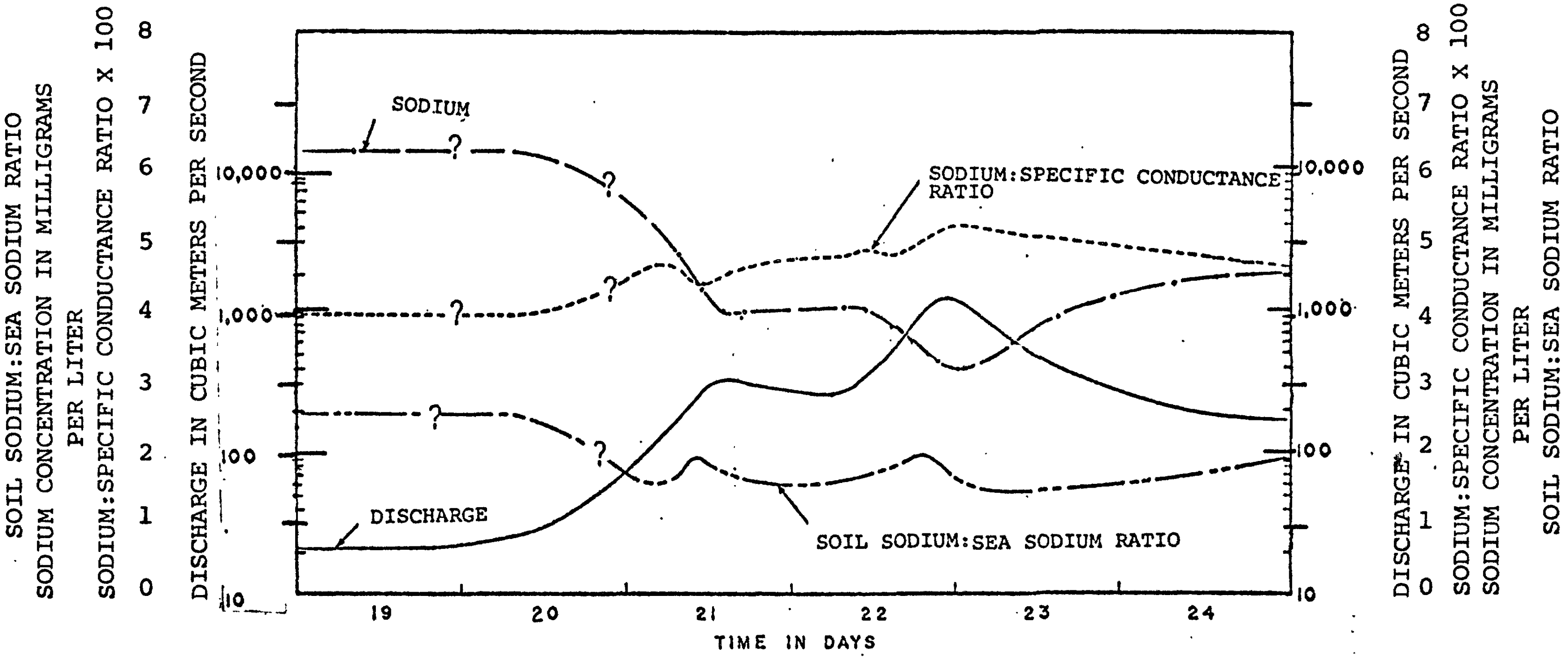

Figure 19. Graphs of discharge, sodium content, soil sodium:sea sodium ratio and sodium:specific conductance ratio of the Mattole River from January 19-24, 1972.

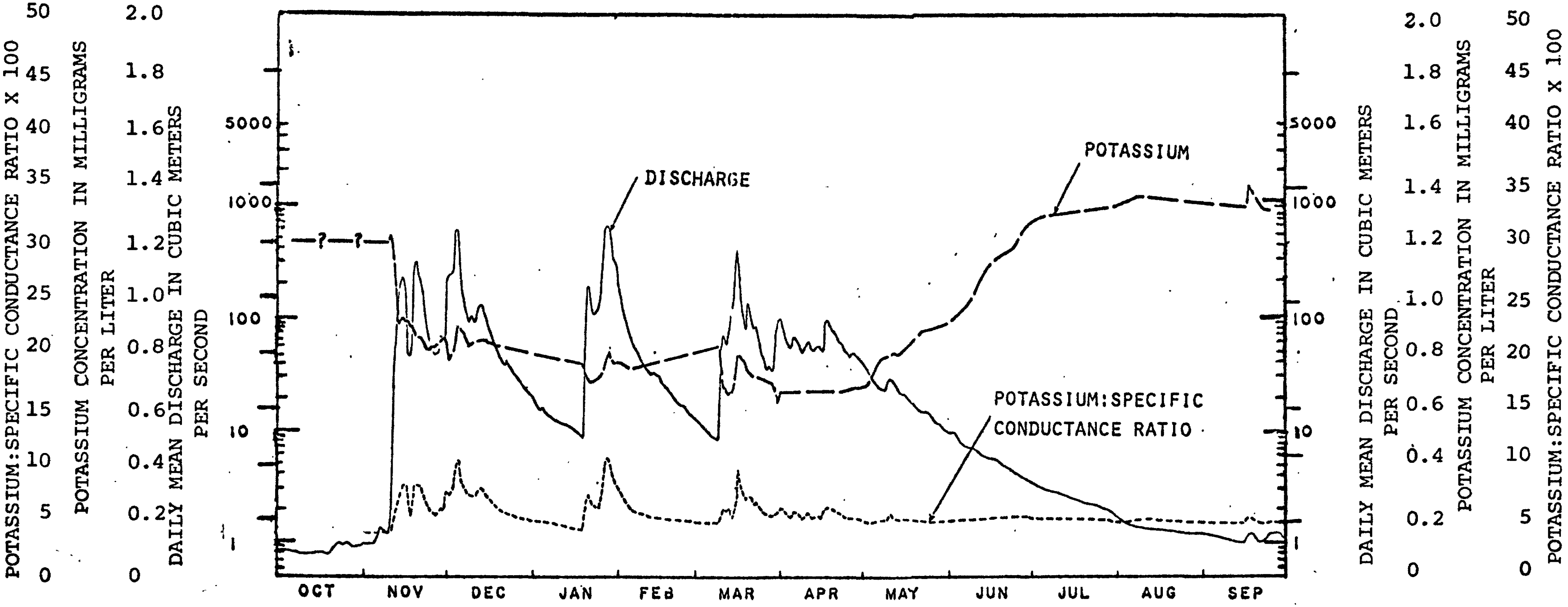

Figure 20. Graphs of daily mean discharge of the Mattole River, potassium concentration and the potassium:specific conductance ratio for the 1966-67 water year.

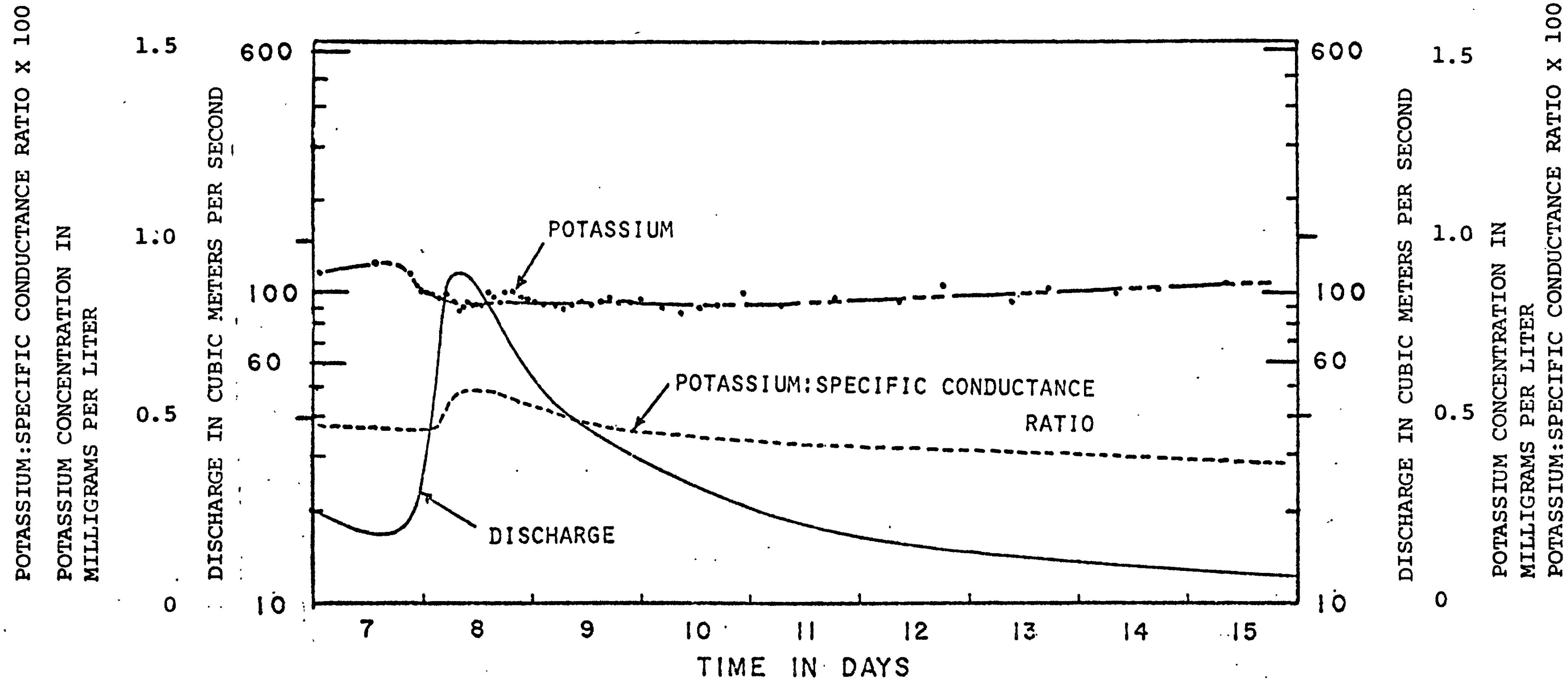

Figure 21. Graphs of discharge, potassium content and potassium:specific conductance ratio of the Mattole River from January 7-15, 1969.

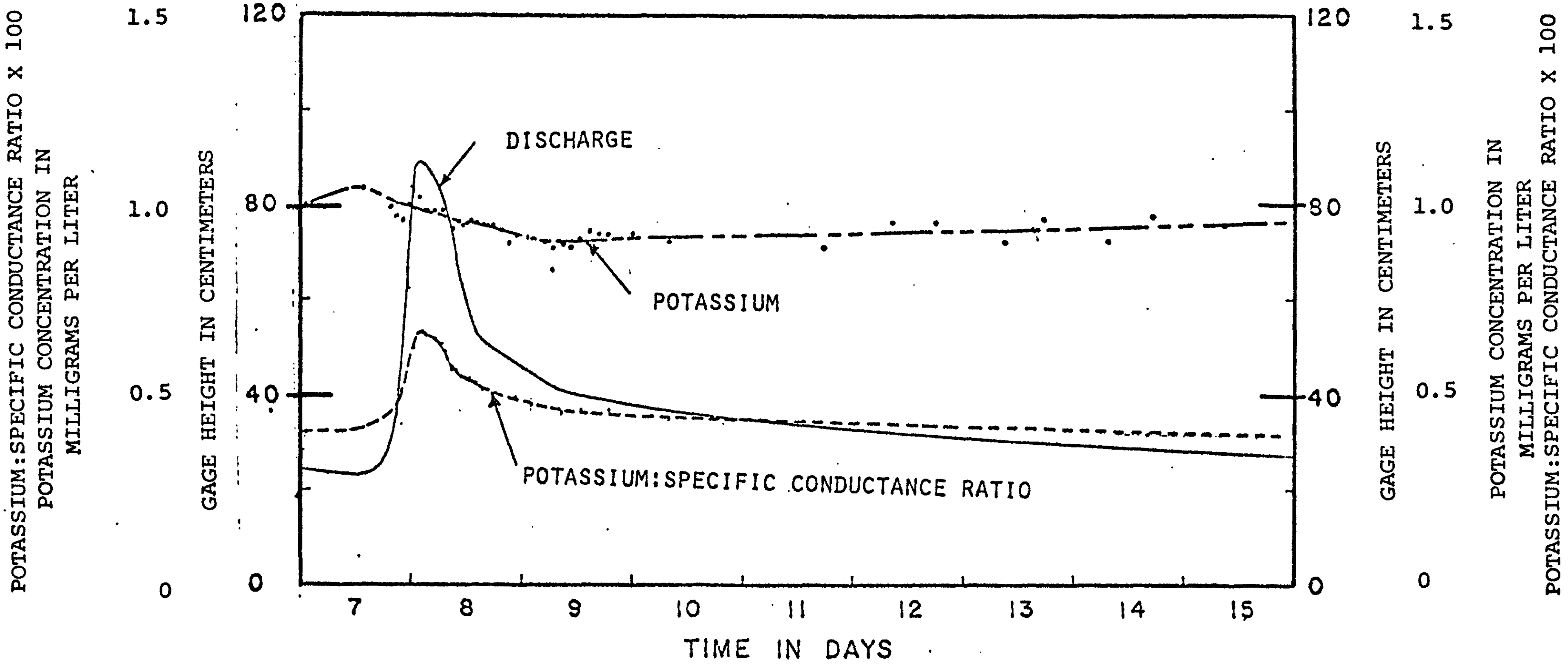

Figure 22. Graphs of discharge, potassium content and potassium:specific conductance ratio of Conklin Creek from November 7-15, 1969.

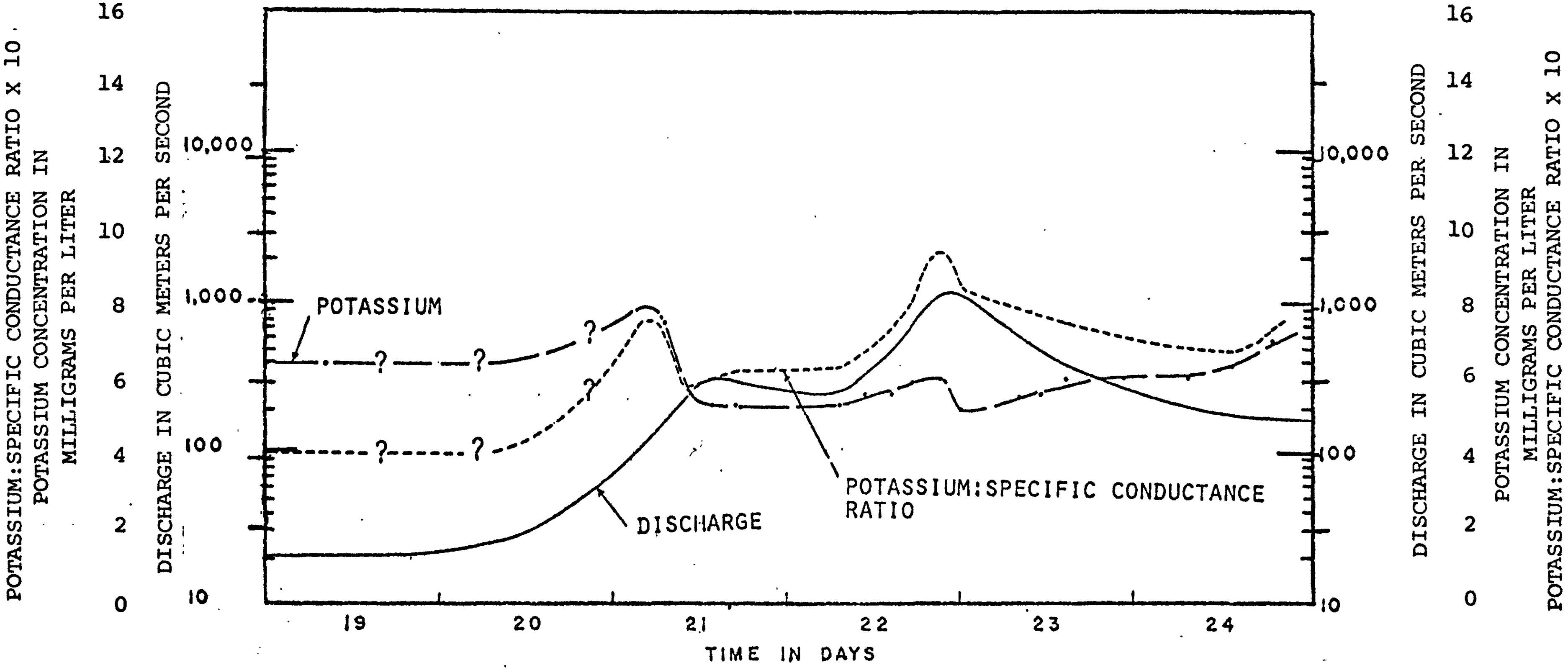

Figure 23. Graphs of discharge, potassium content and potassium:specific conductance ratio of the Mattole River from January 19-24, 1972.

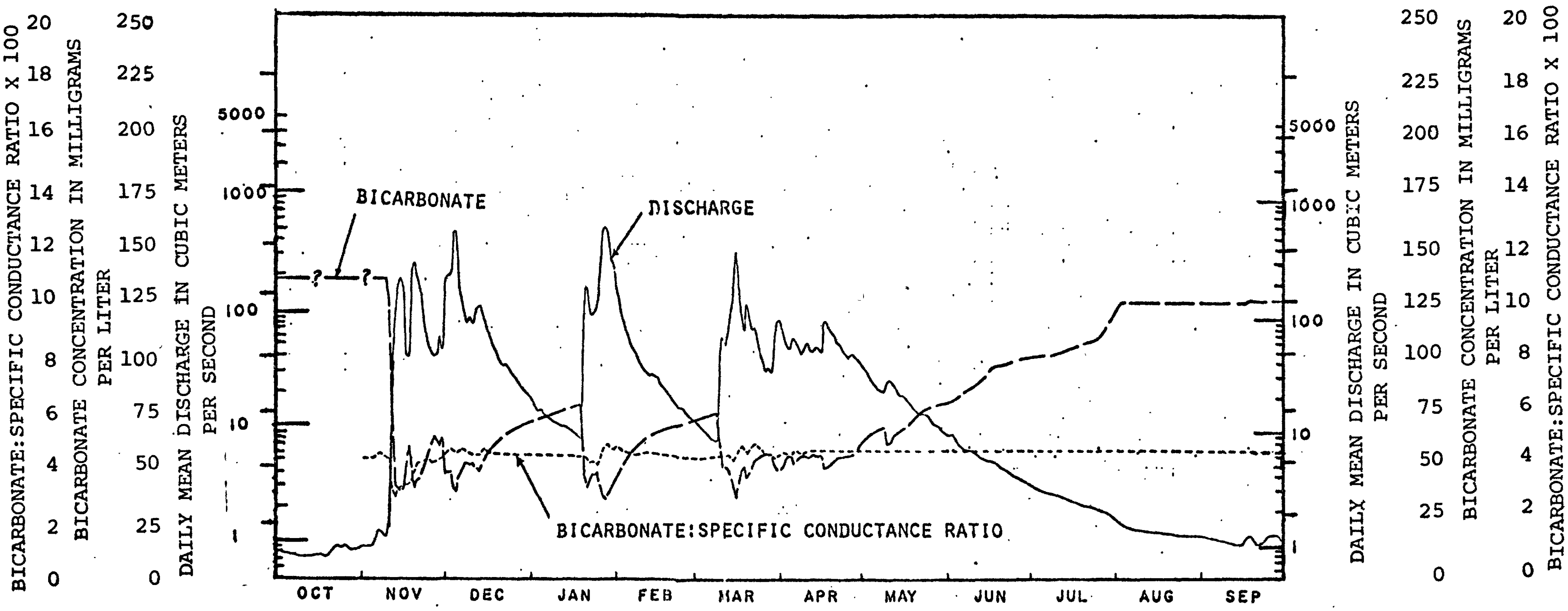

Figure 24. Graphs of daily mean discharge of the Mattole River, bicarbonate concentration and bicarbonate:specific conductance ratio for the 1966-67 water year.

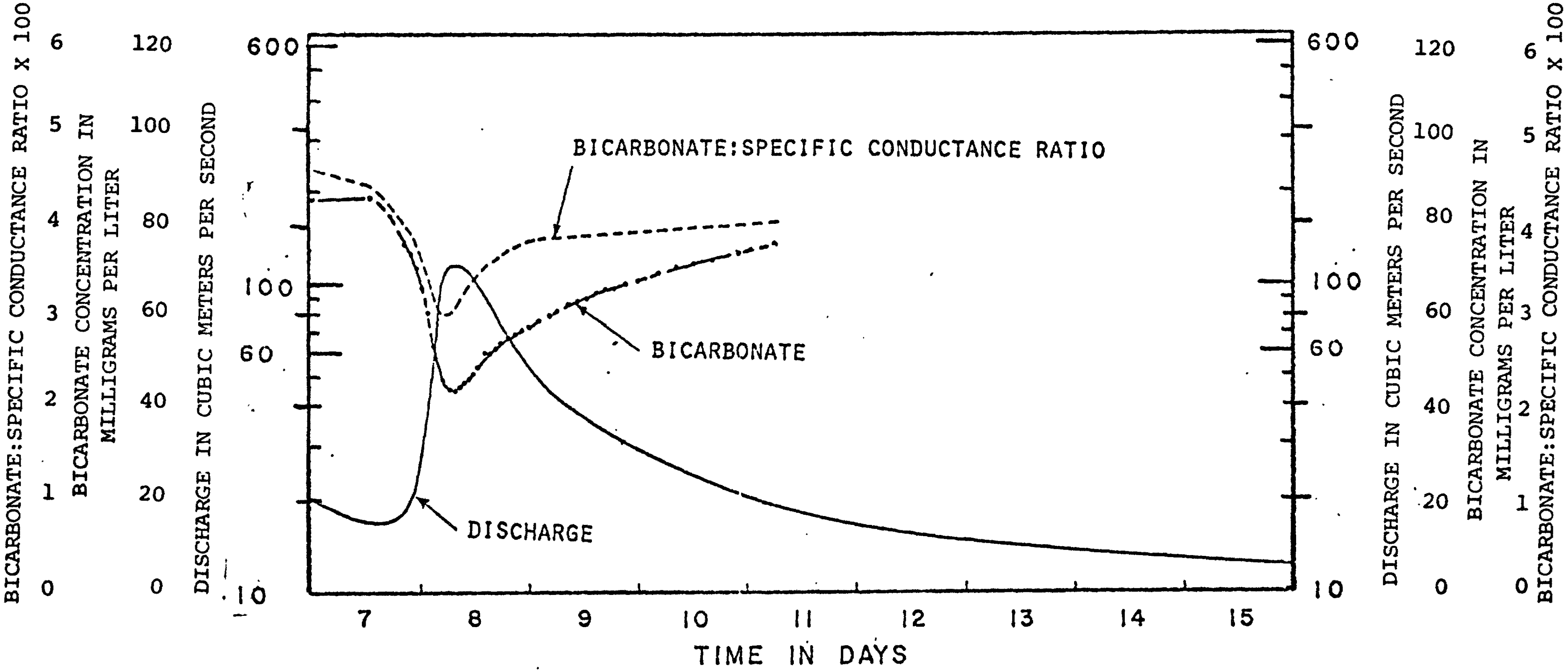

Figure 25. Graphs of discharge, bicarbonate content and bicarbonate:specific conductance ratio of the Mattole River from November 7-15, 1969.

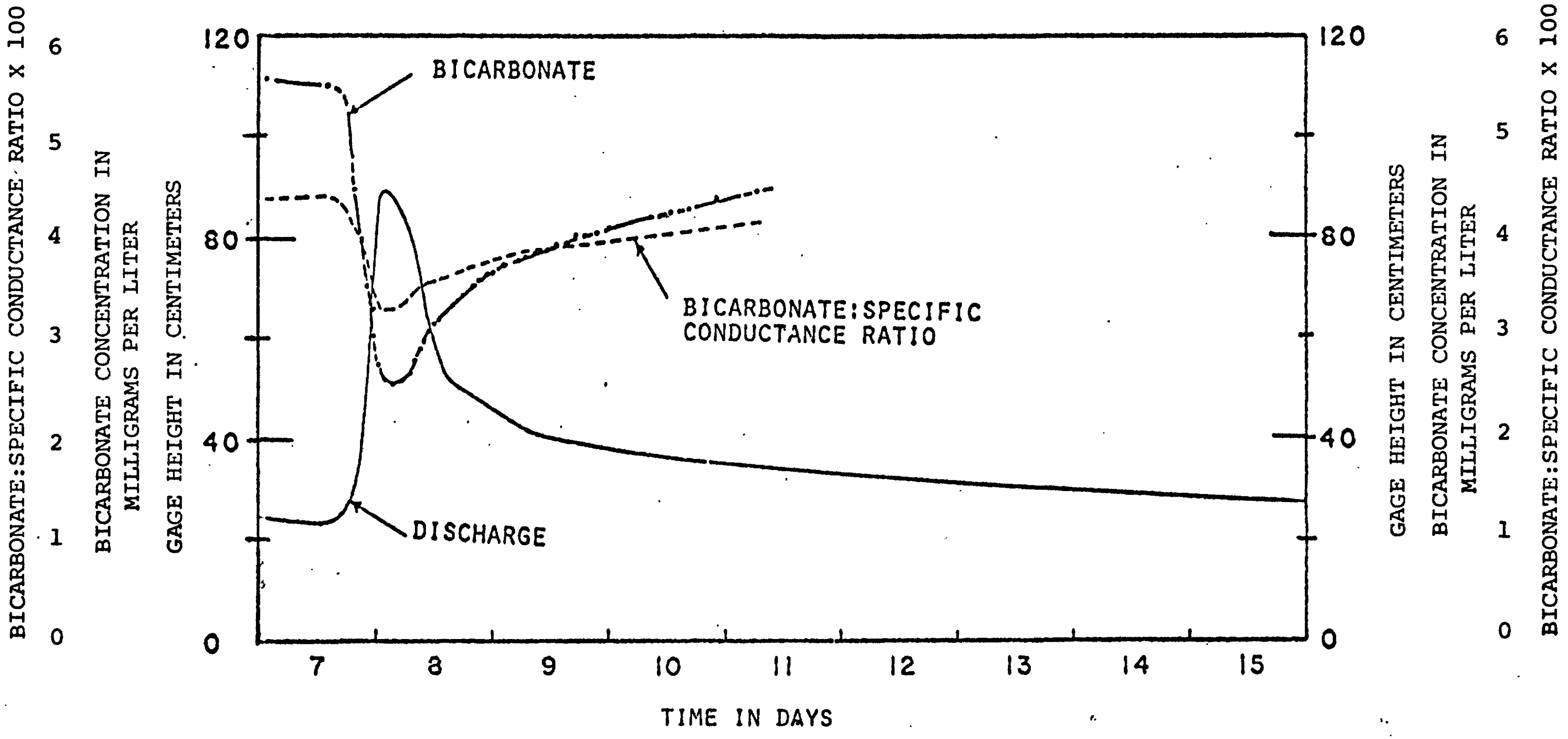

Figure 26. Graphs of discharge, bicarbonate content and bicarbonate:specific conductance ratio of Conklin Creek from November 7-15, 1969.

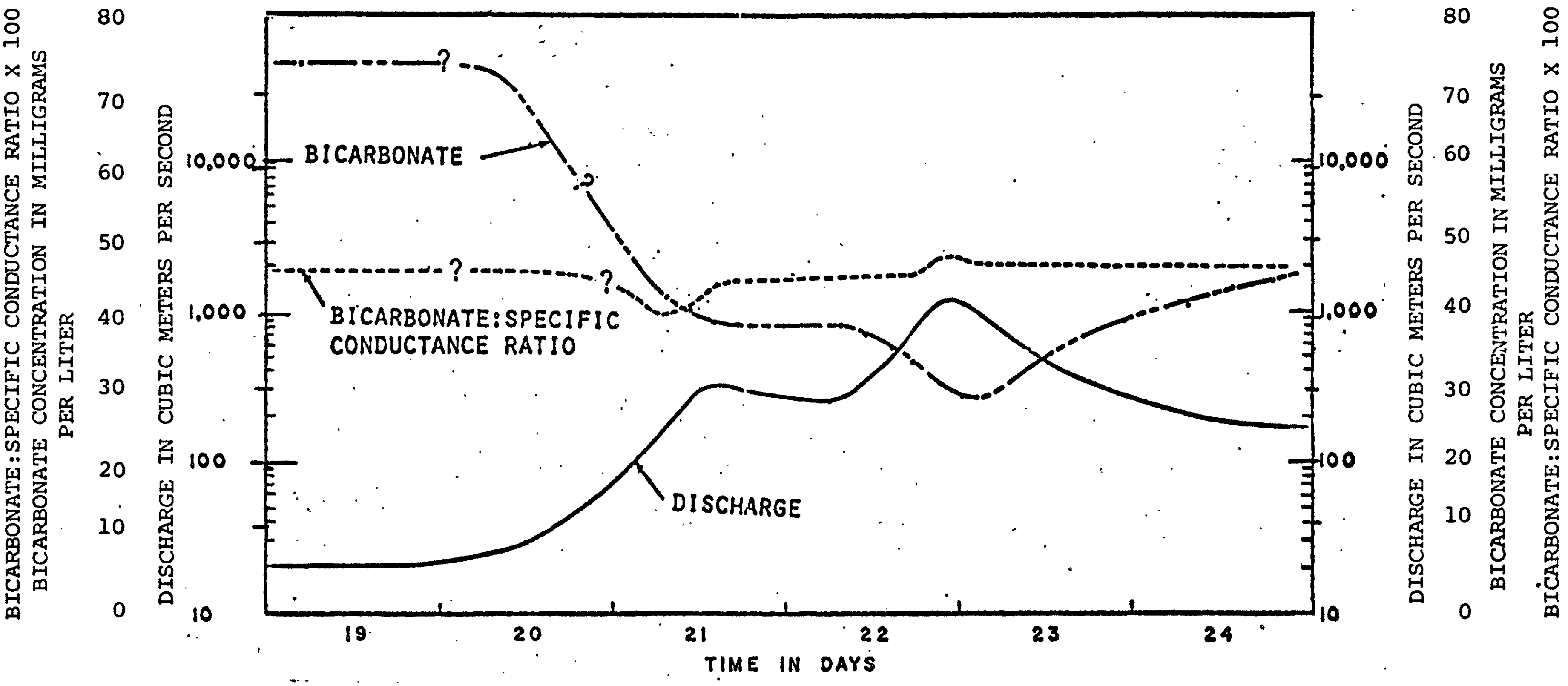

Figure 27. Graphs of discharge, bicarbonate content and bicarbonate:specific conductance ratio of the Mattole River from January 19-24, 1972.

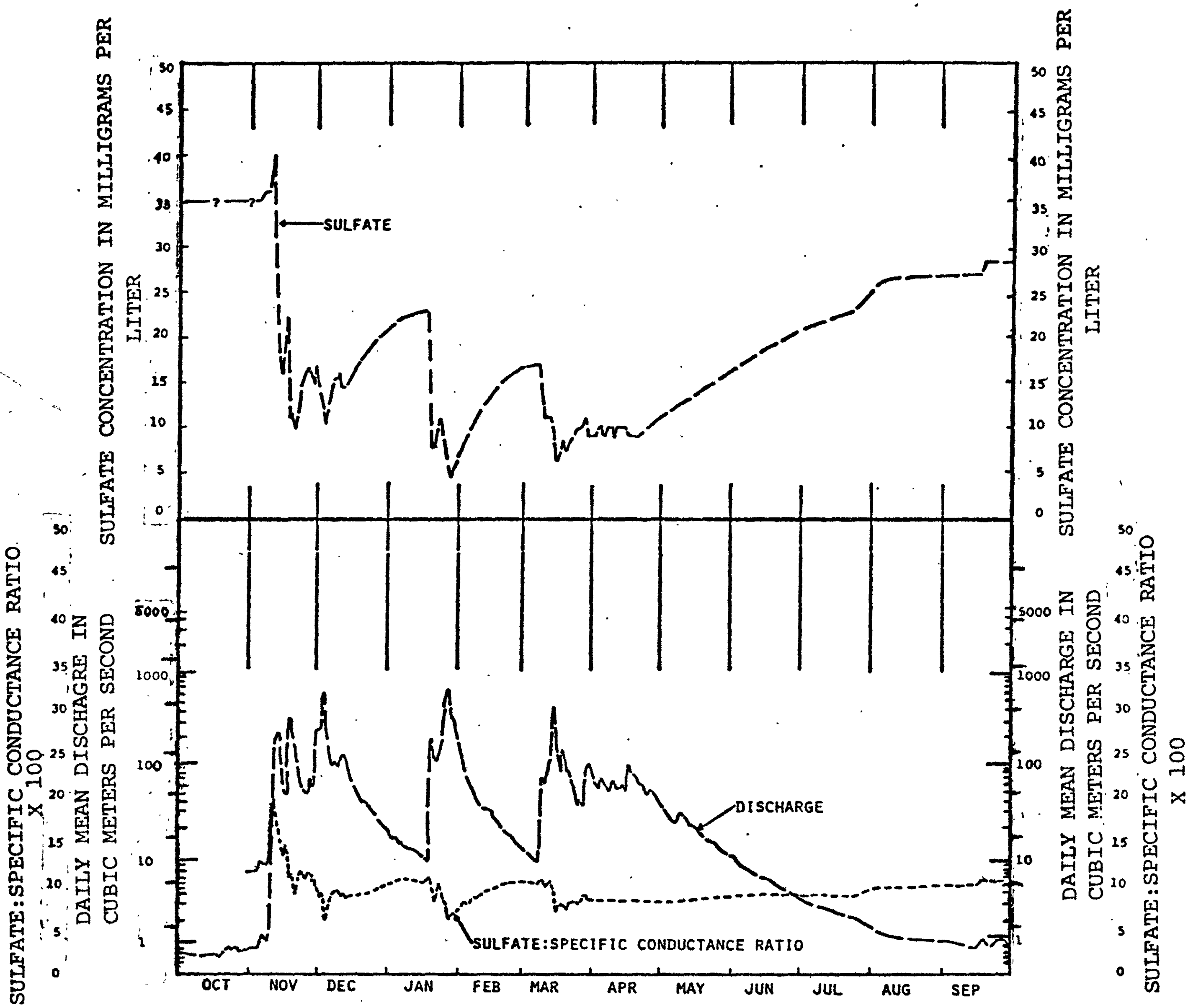

Figure 28. Graphs of daily mean discharge of the Mattole River, sulfate concentration and the sulfate:specific conductance ratio for the 1966-67 water year.

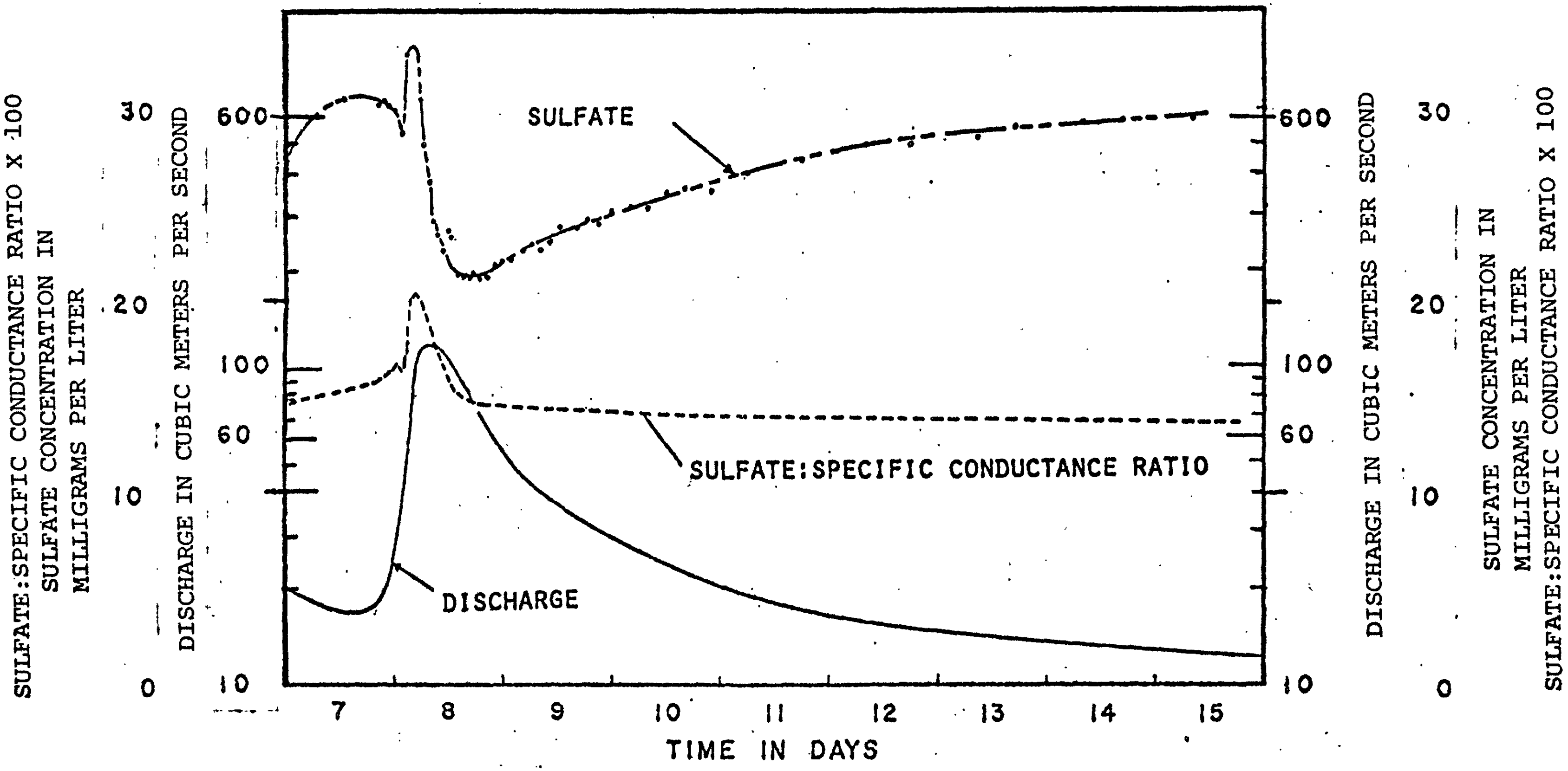

Figure 19. Graphs of discharge, sulfate content and sulfate:specific conductance ratio of the Mattole River from November 7-15, 1969.

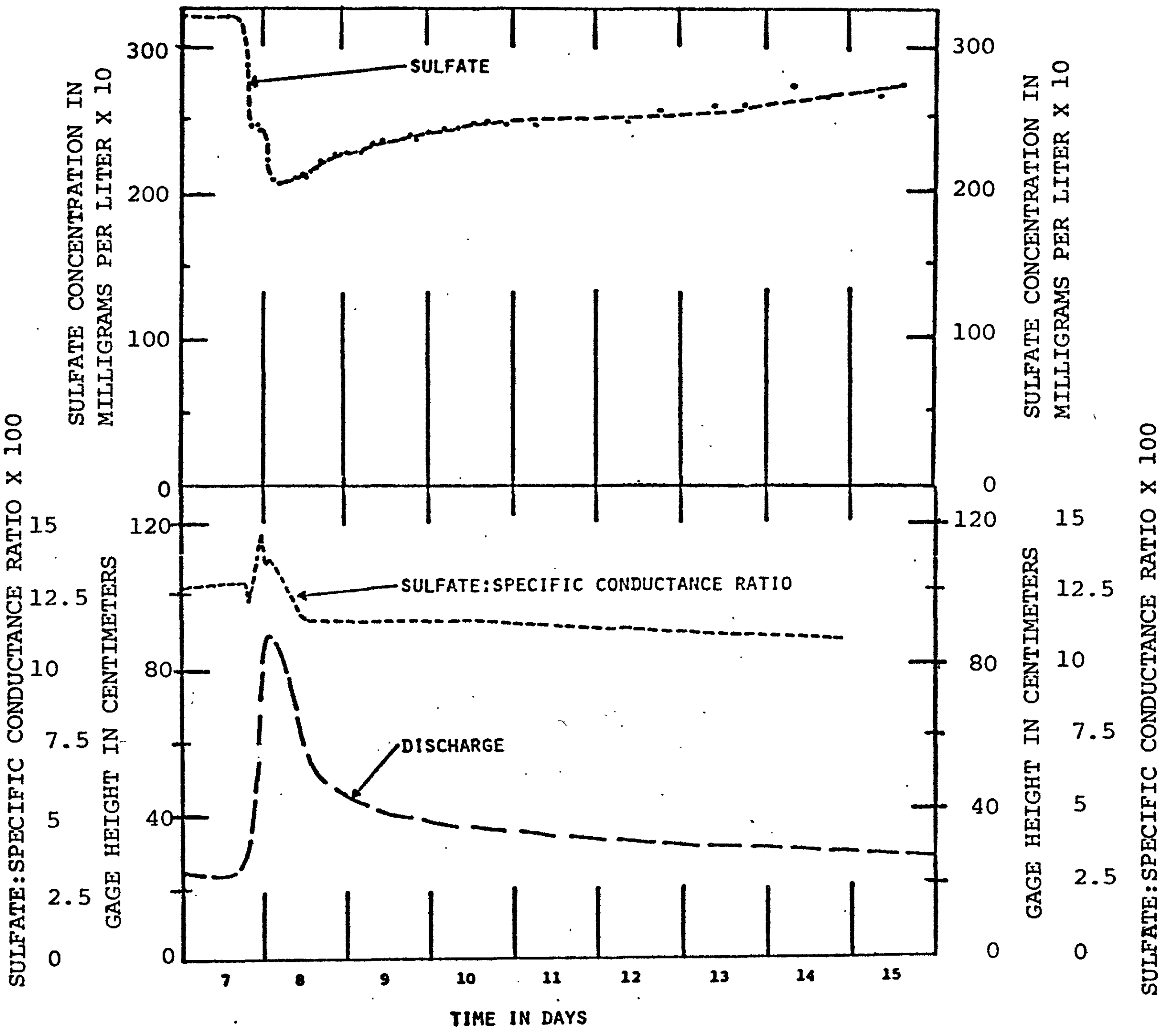

Figure 30. Graphs of discharge, sulfate content and sulfate:specific conductance ratio of Conklin Creek from November 7-15, 1969.

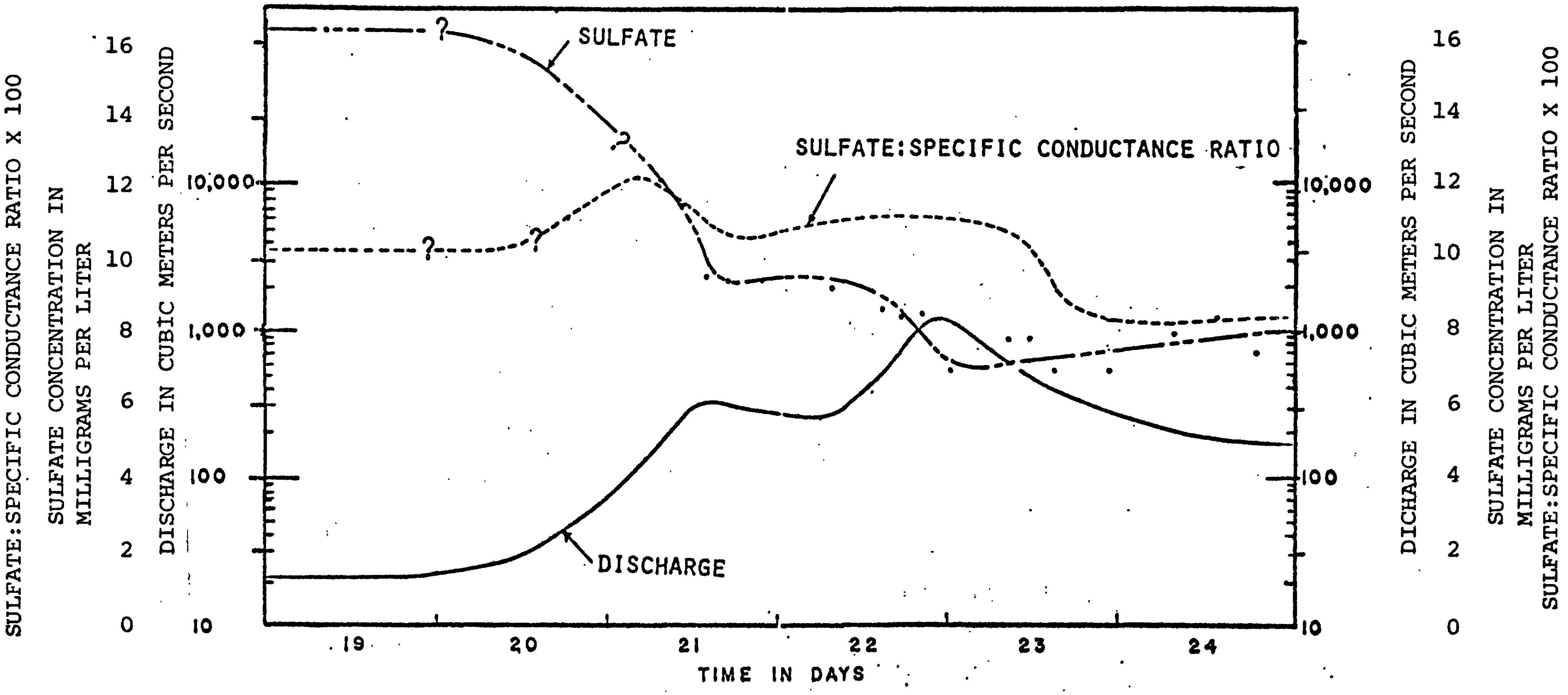

Figure 31. Graphs of discharge, sulfate content and sulfate:specific conductance ratio of the Mattole River from January 19-24, 1972.

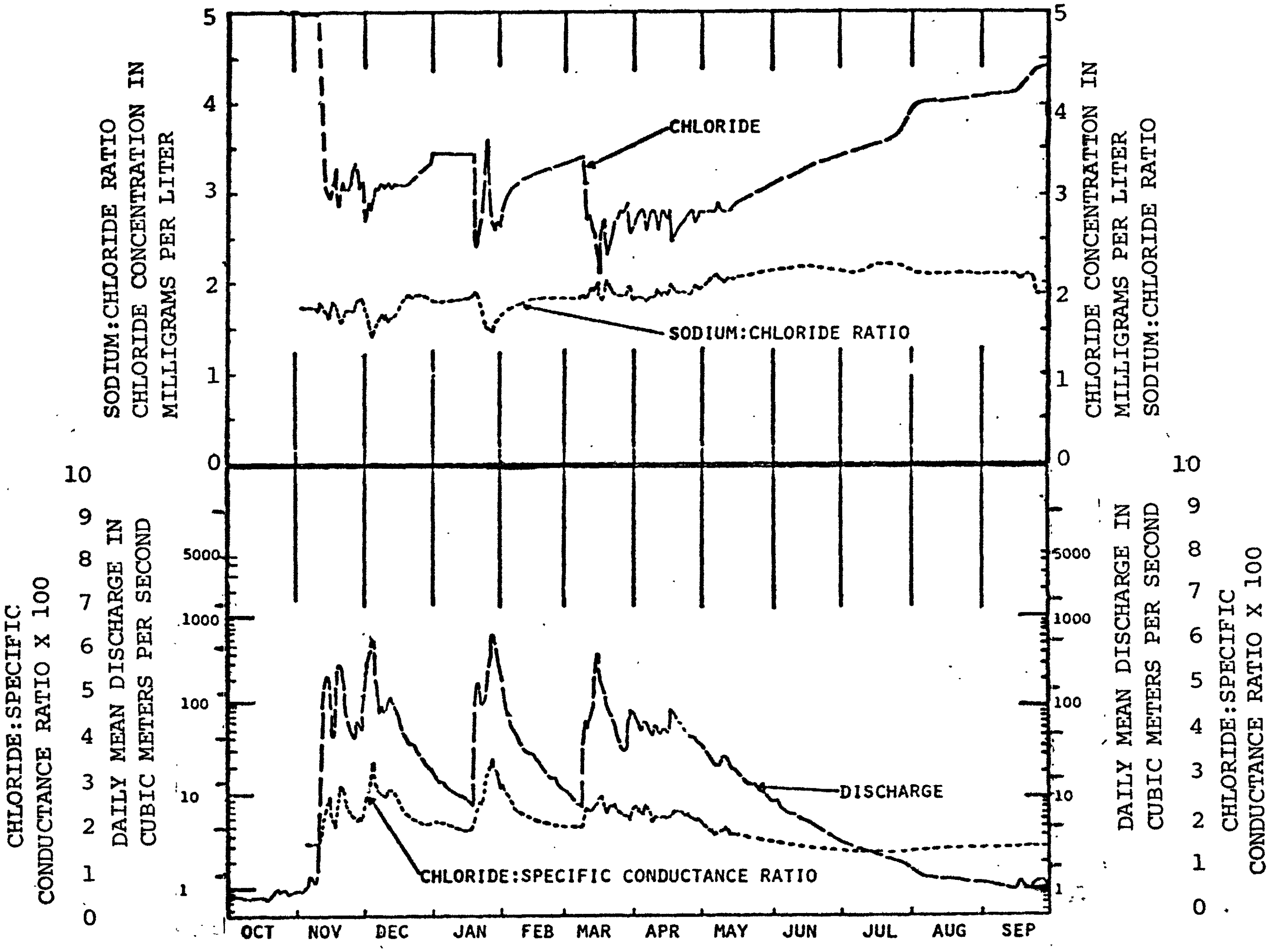

Figure 32. Variation of daily mean discharge of the Mattole River, chloride concentration and the ratios of sodium:chloride and chloride:specific conductance for the 1966-67 water year.

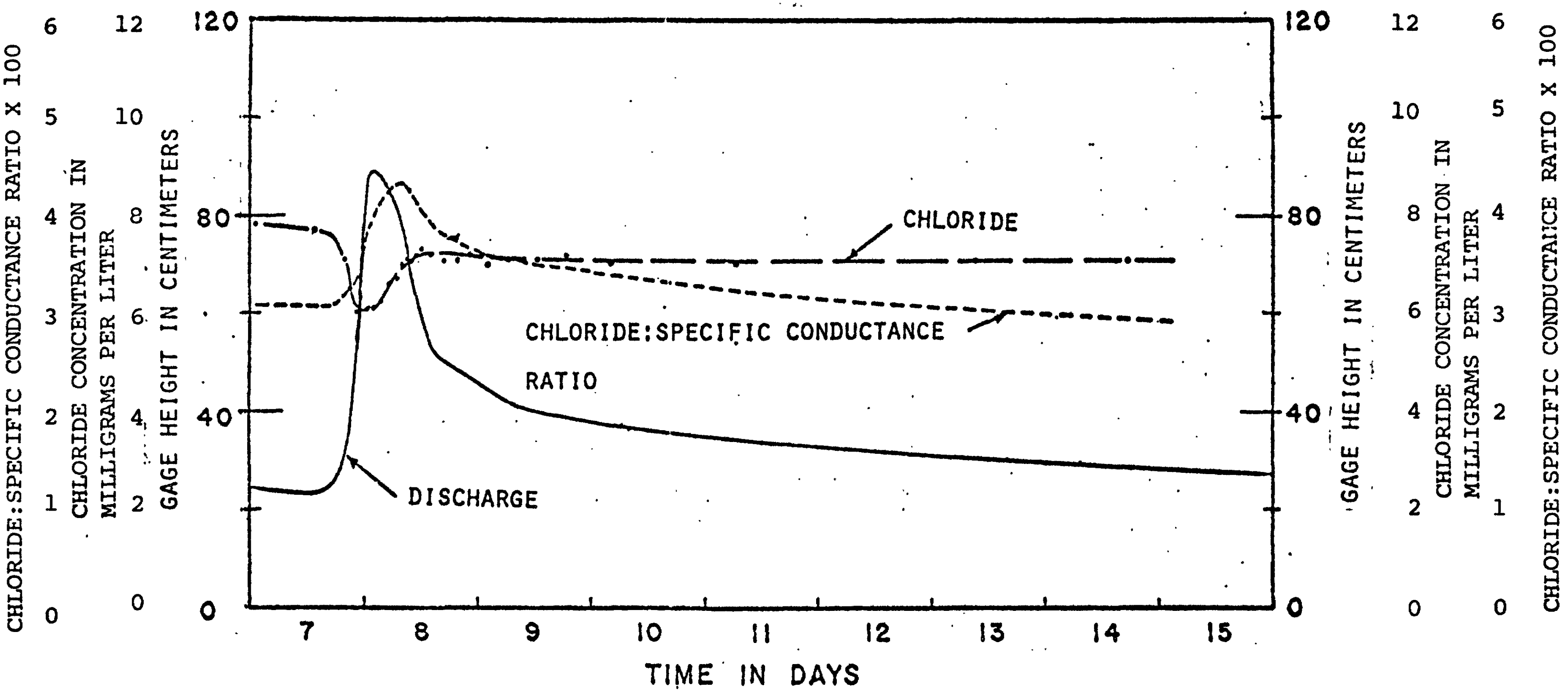

Figure 33. Graphs of discharge, chloride content and chloride:specific conductance ratio of Conklin Creek November 7-15, 1969.

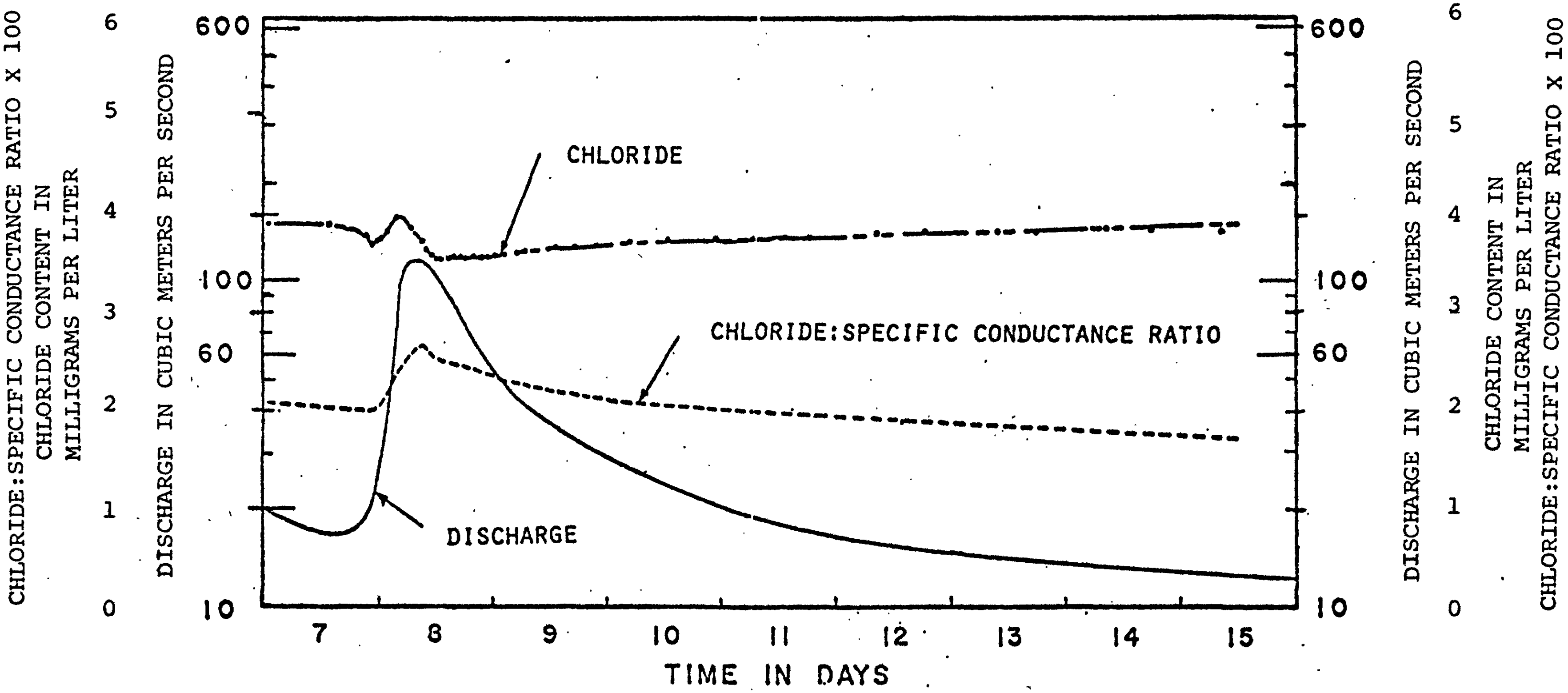

Figure 34. Graphs of discharge, chloride content and chloride:specific conductance ratio of the Mattole River from November 7-15, 1969.

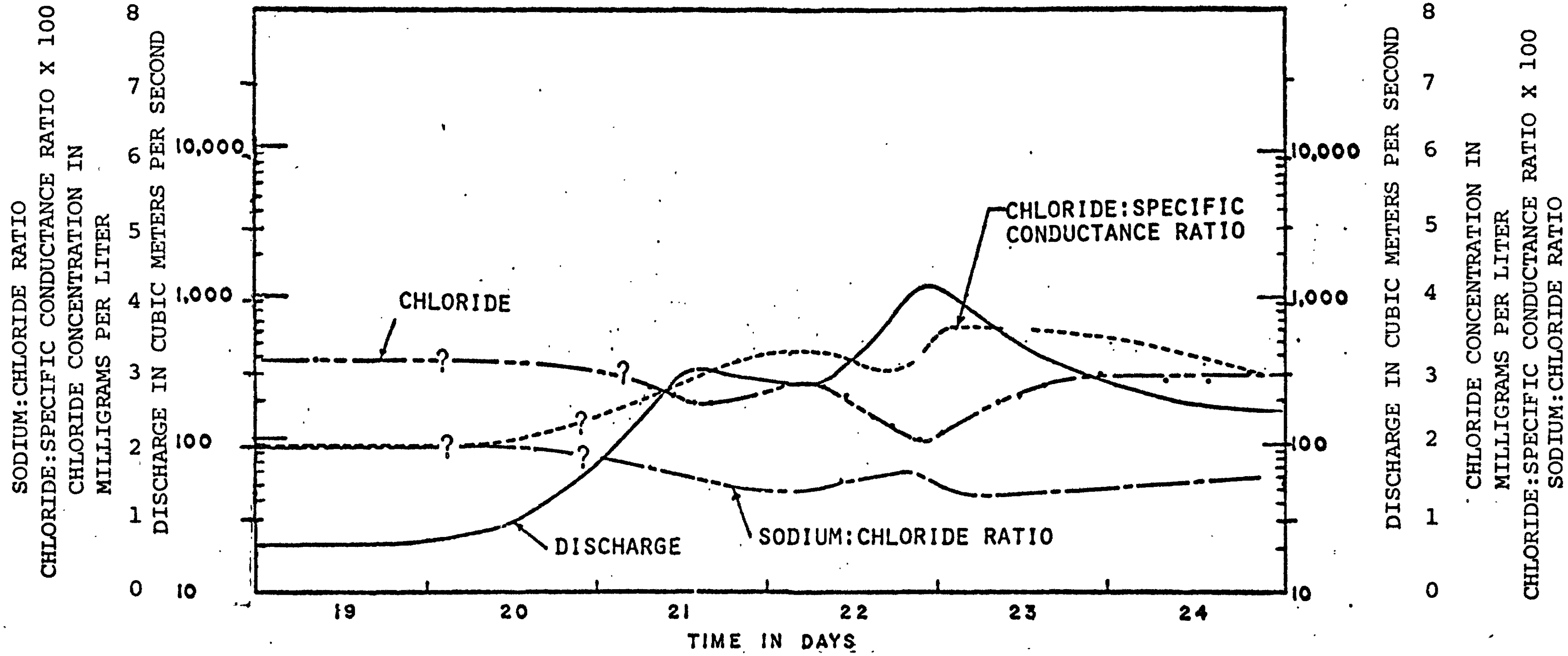

Figure 35. Graphs of discharge, chloride content and chloride:specific conductance ratio of the Mattole River from January 19-24, 1972.

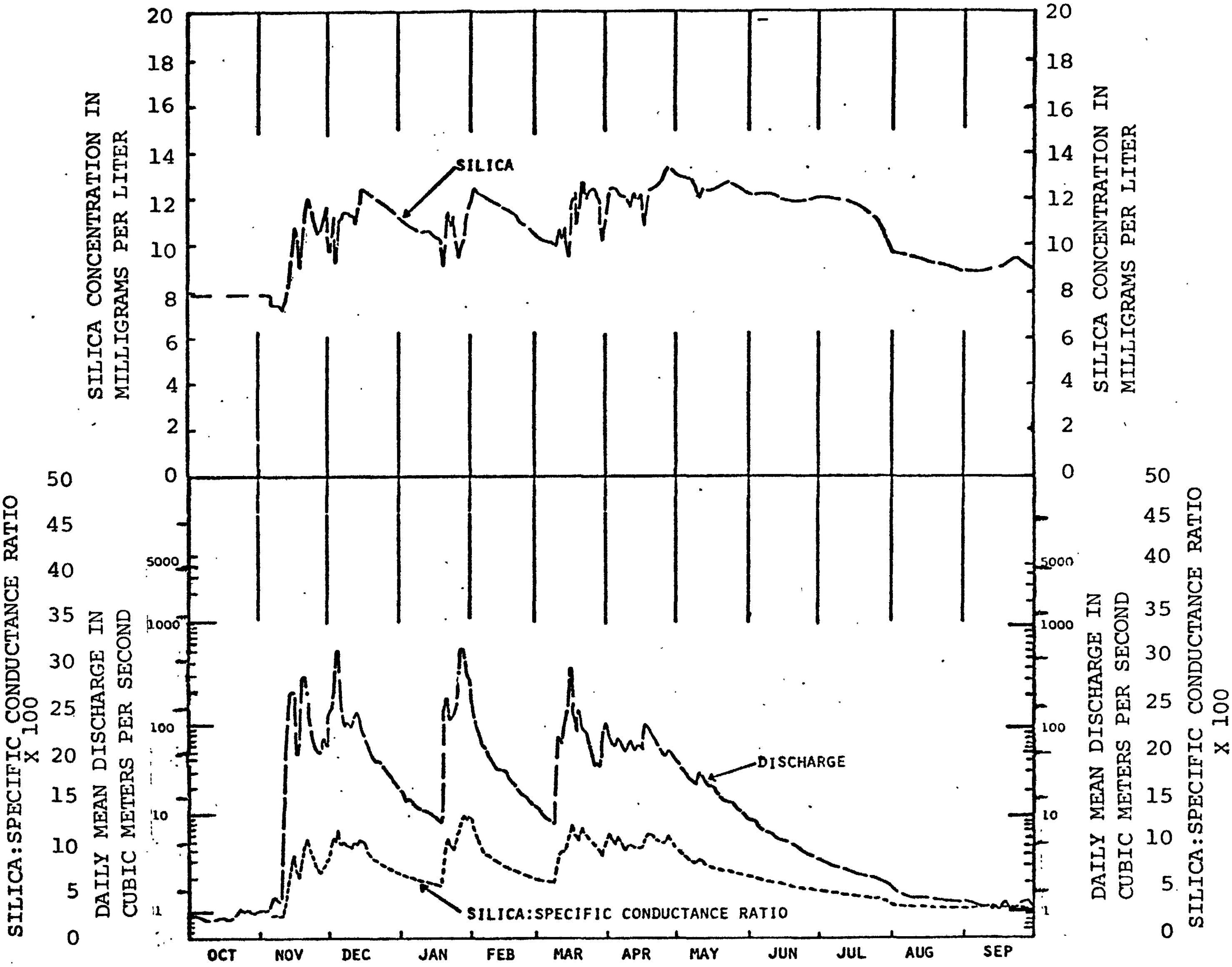

Figure 36. Graphs of daily mean discharge of the Mattole River, silica concentration and the silica:specific conductance ratio for the 1966-67 water year.

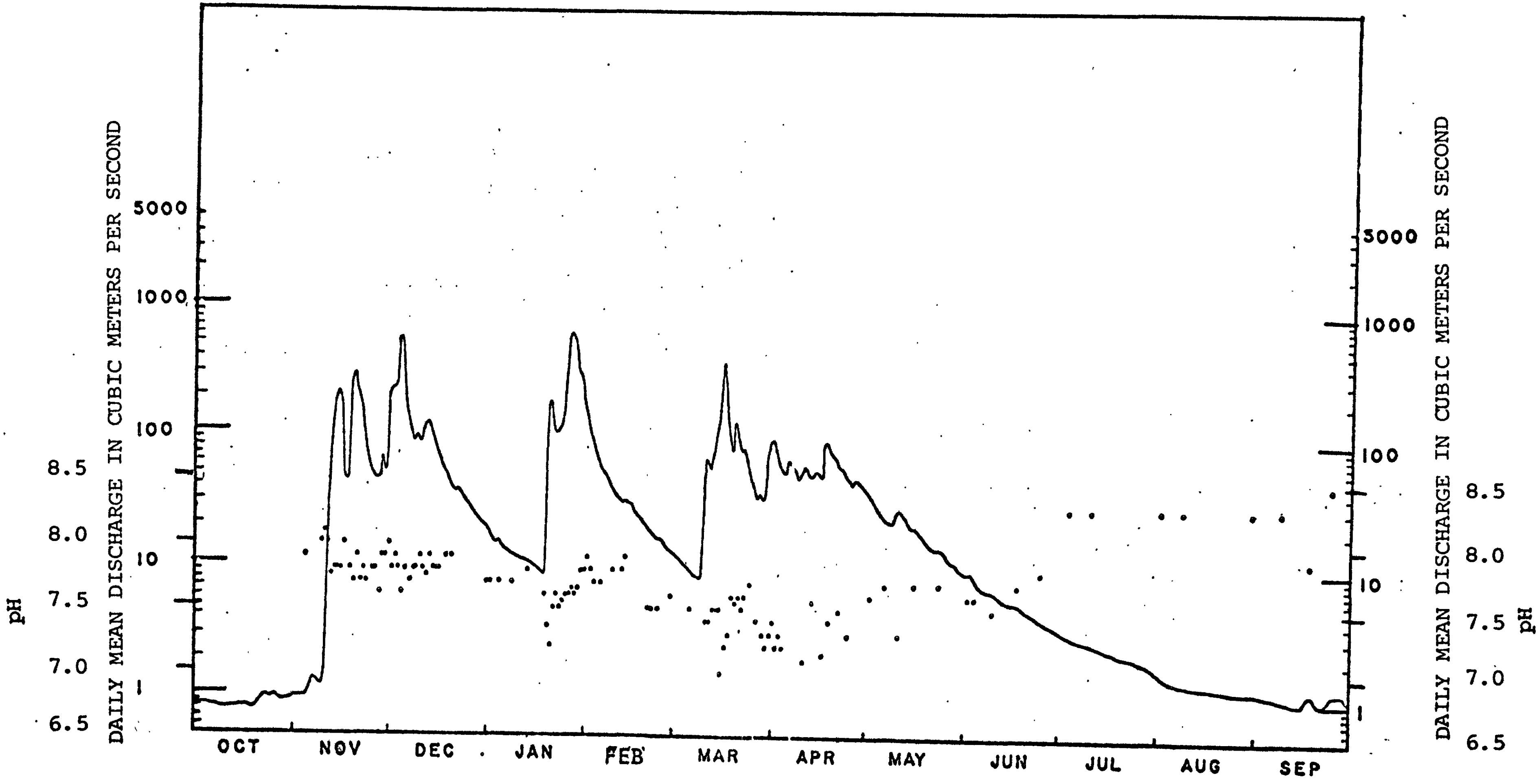

Figure 37. Graphs of pH and discharge of the Mattole River for the 1966-67 water year[1].

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[1] Each point represents an instantaneous sample instead of a composite value for a day, as reported for most other ions.

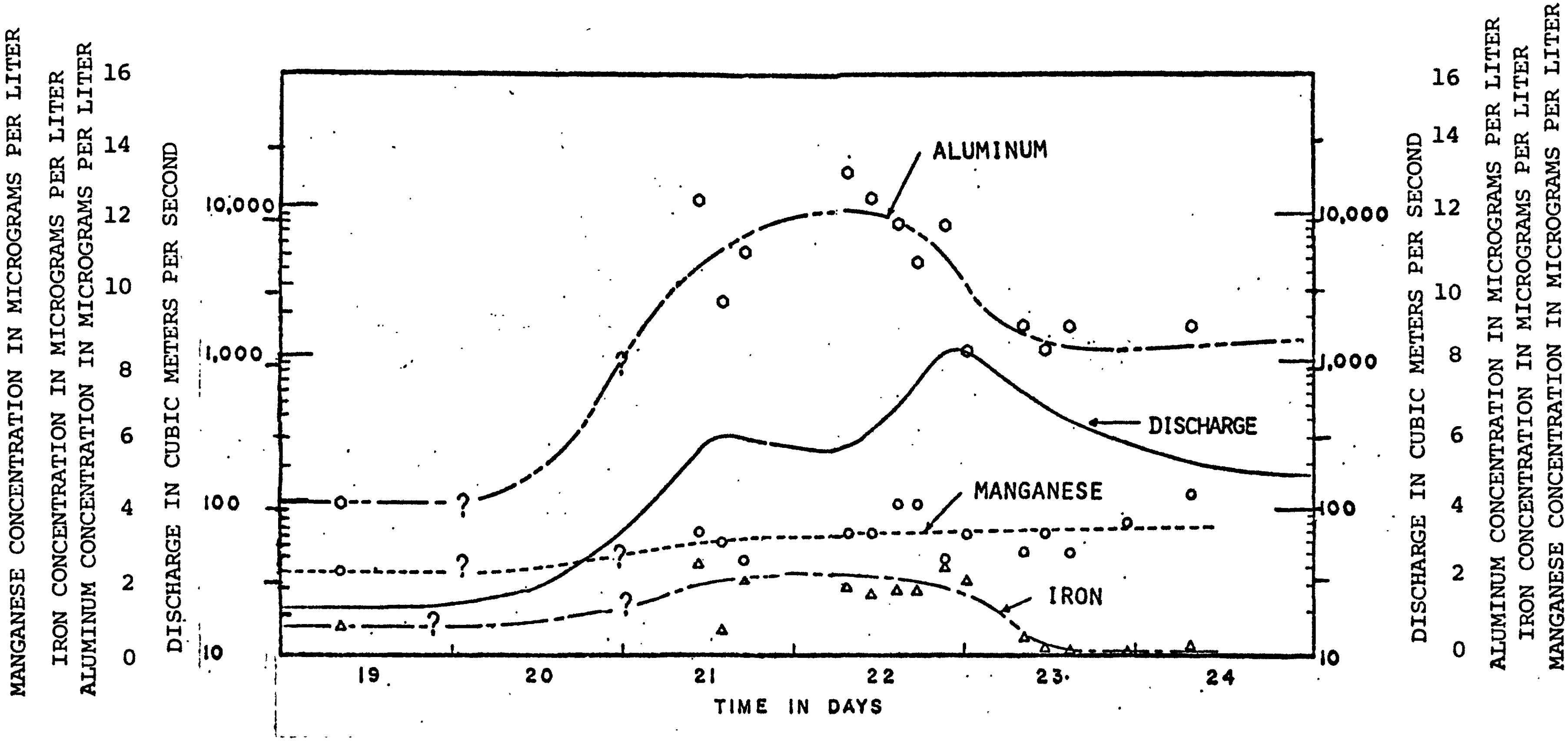

Figure 38. Graphs of discharge, aluminum content, iron content and manganese content of the Mattole River from January 19-24, 1972.

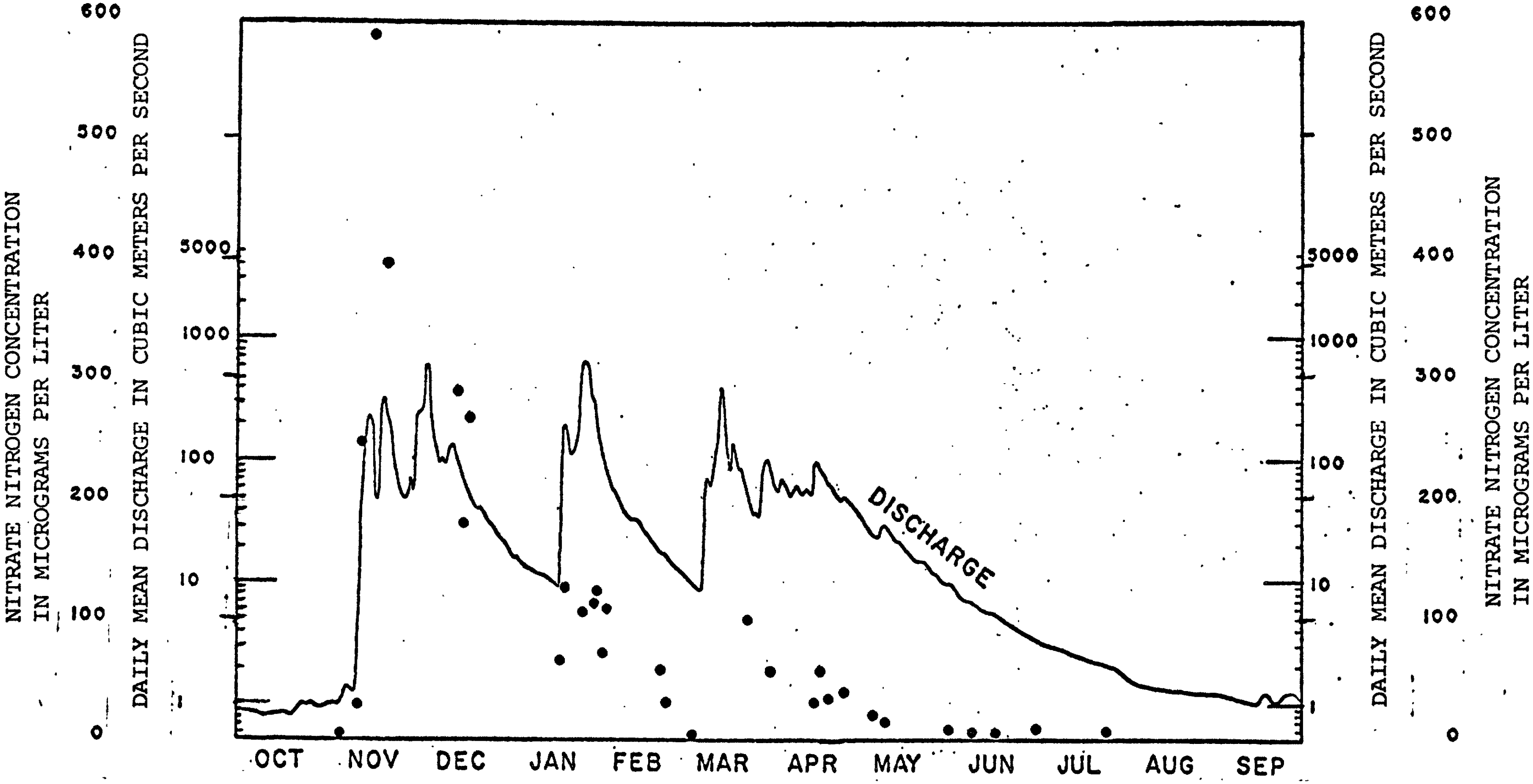

Figure 39. Graph of discharge and nitrate nitrogen in the Mattole River for the 1966-67 water year [1].

[1] Each point represents an instantaneous sample instead of a composite value for a day, as reported for most other ions.

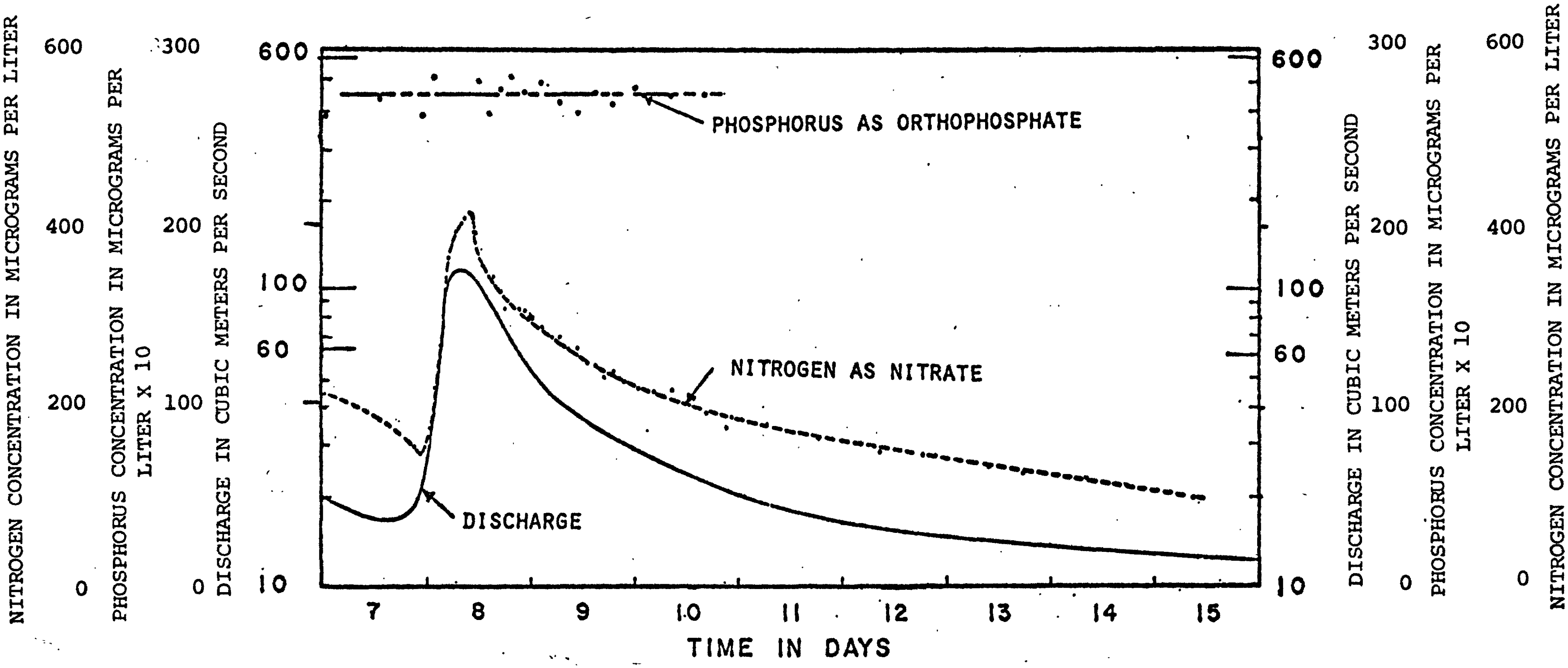

Figure 40. Graphs of discharge, nitrogen as nitrate and phosphorus as orthophosphate in the Mattole River from November 7-15, 1969.

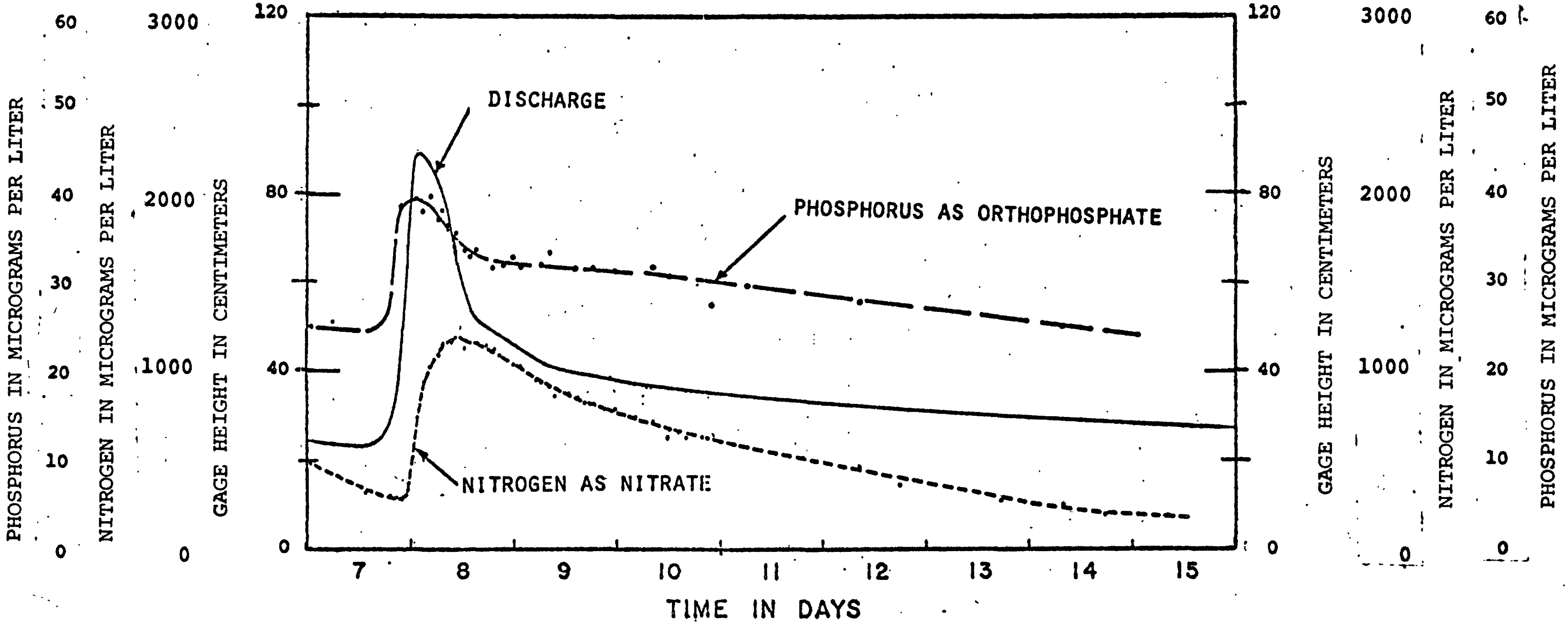

Figure 41. Graphs of discharge, nitrogen as nitrate and phosphorus as orthophosphate in Conklin Creek from November 7-15, 1969.

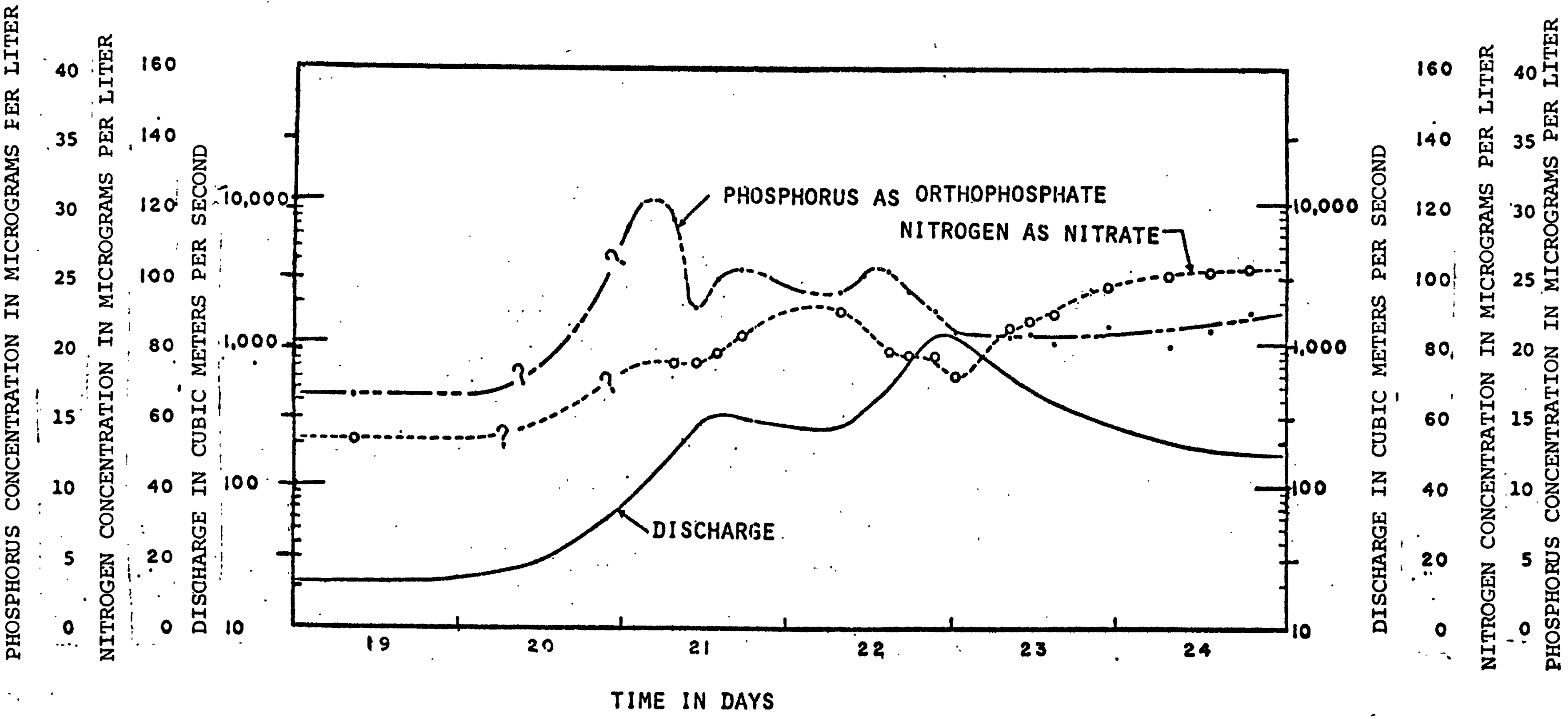

Figure 42. Graphs of discharge, nitrogen as nitrate and phosphorus as orthophosphate in the Mattole River from January 19-24, 1972.

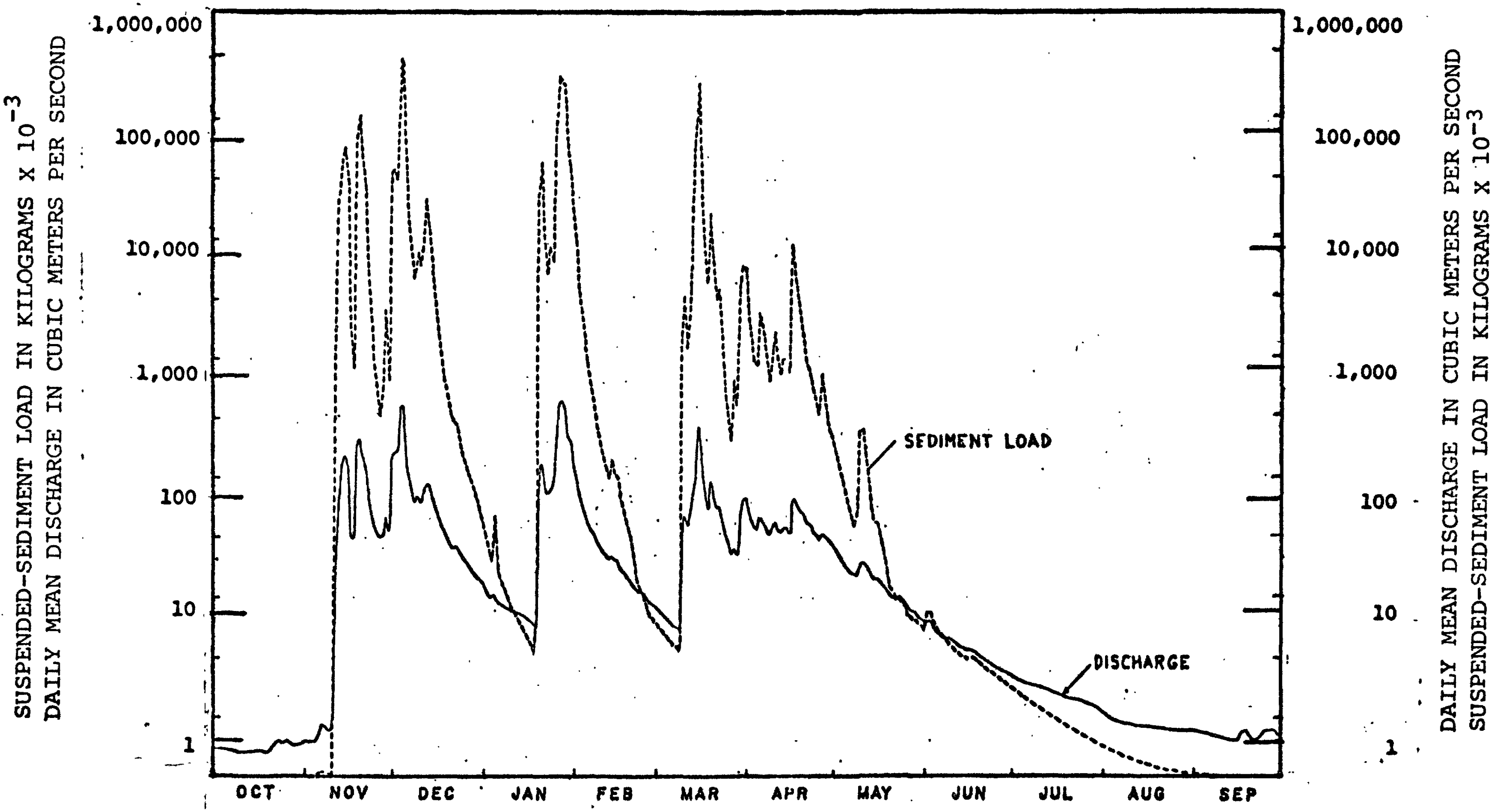

Figure 43. Graphs of daily mean discharge and suspended-sediment load of the Mattole River for the 1966-67 water year [1].

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[1] Only the upper 0.7 m of flow was sampled on December 4, 1966, so sediment loads are somewhat underestimated on that date.

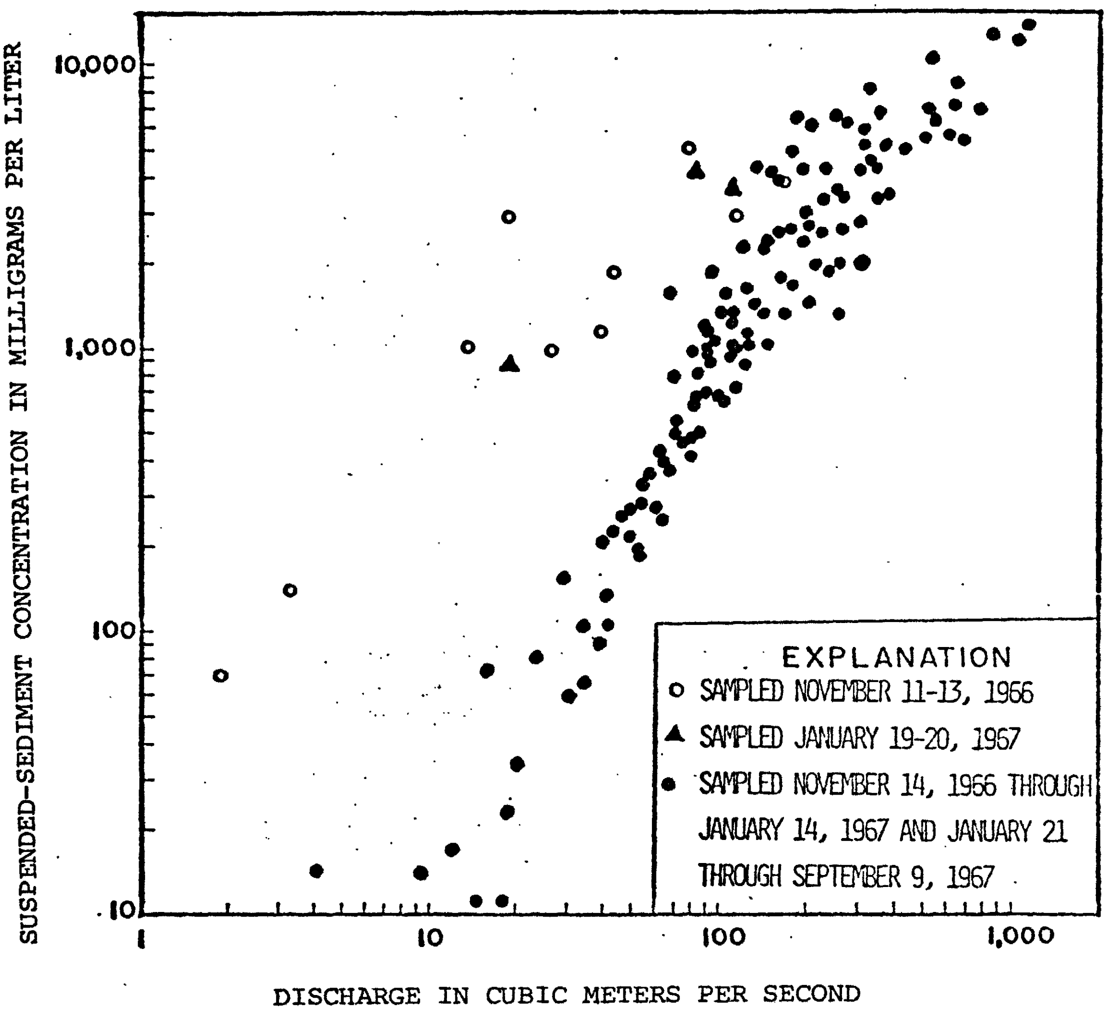

Figure 44. Suspended-sediment concentration plotted against stream discharge for the Mattole River during the 1966-67 water year.

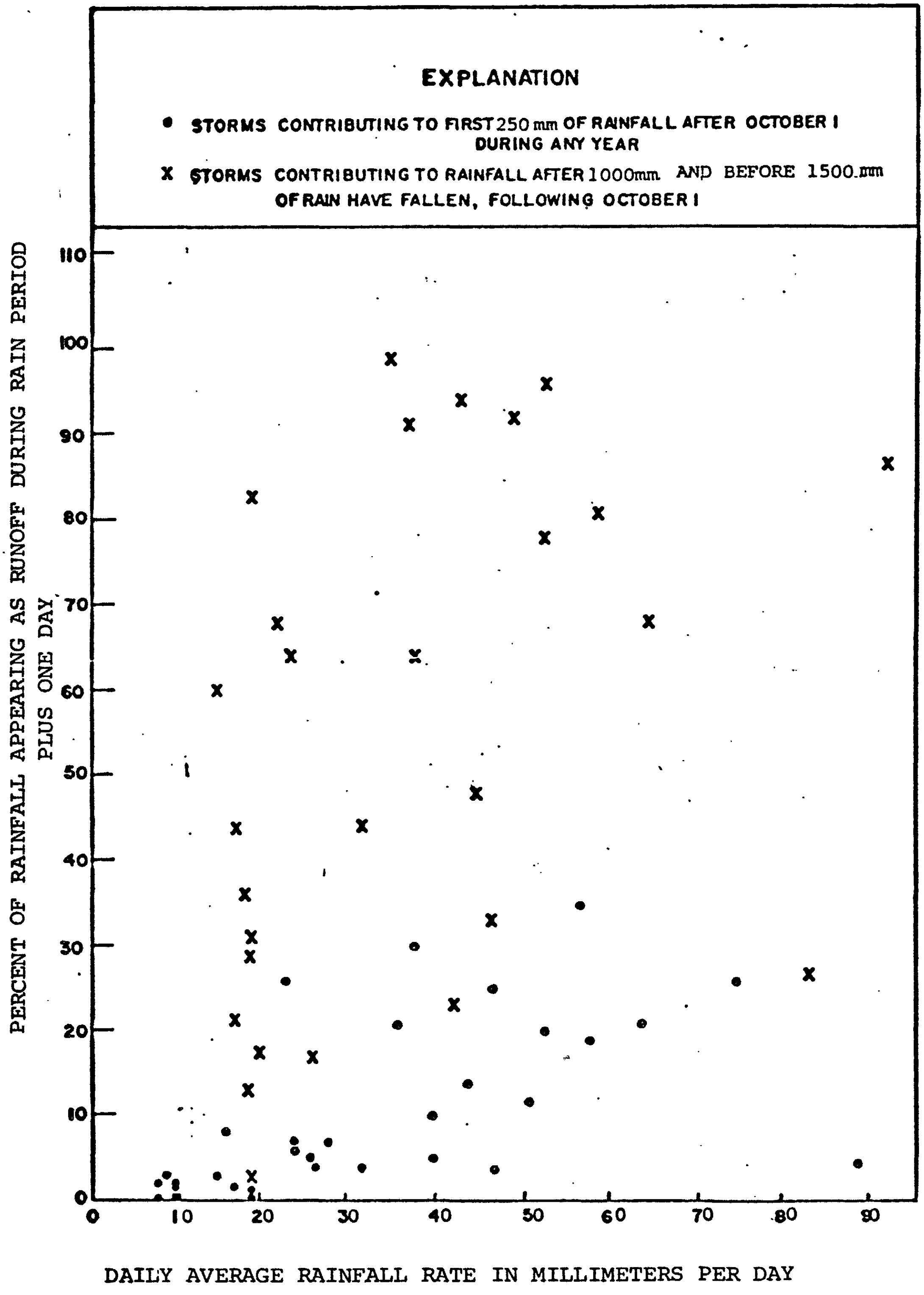

Figure 45. Graph showing relation of percent runoff to daily average rainfall rate during rainy seasons from October 1962 to December 1970.

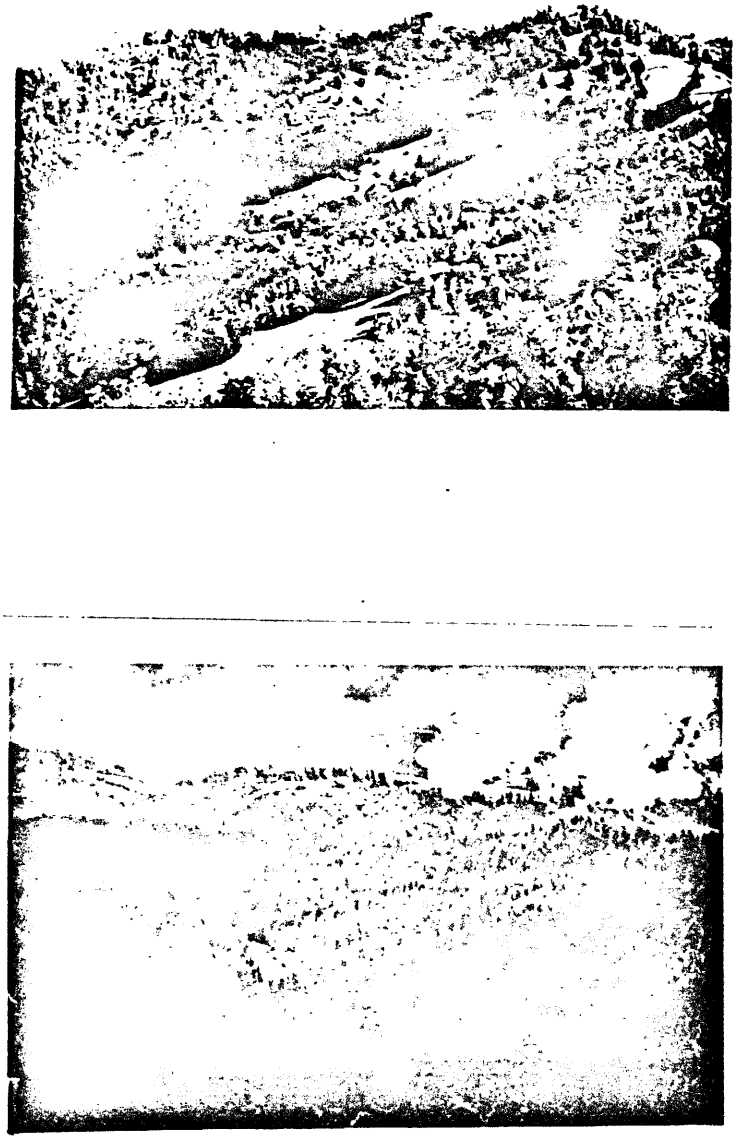

Figure 46 Views typical of vegetation in much of the upper part of the Mattole drainage basin.

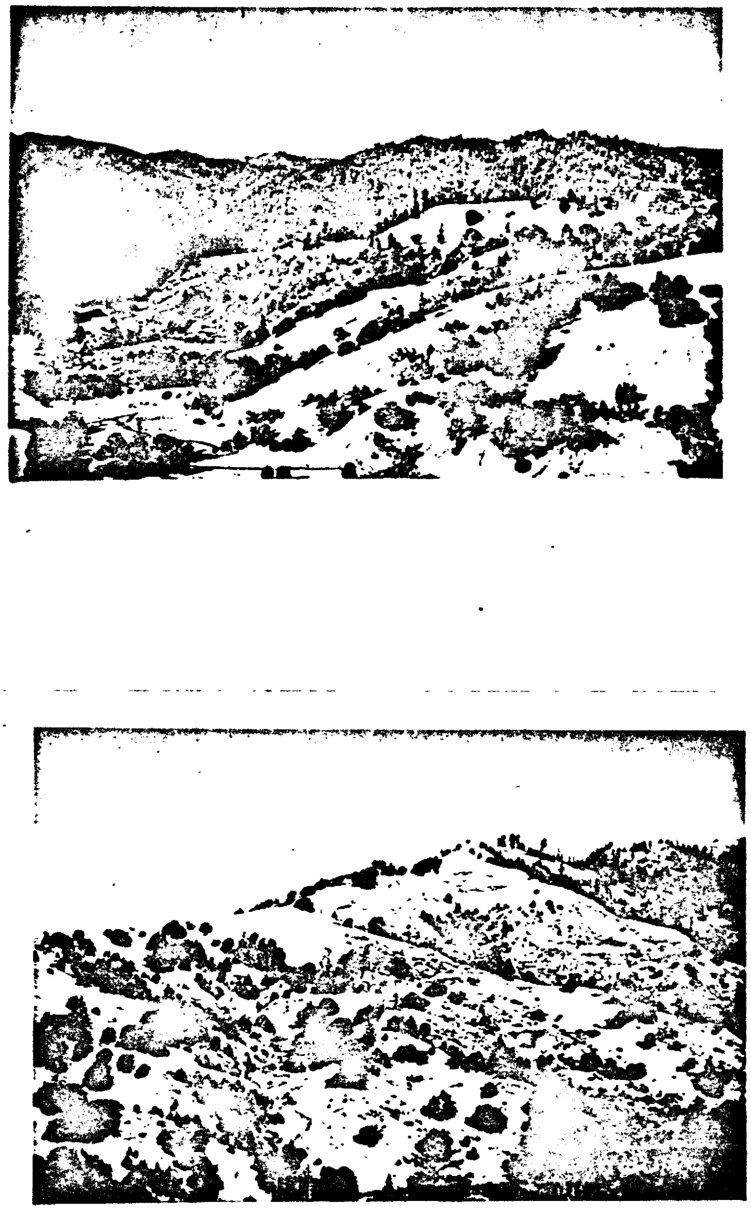

Figure 47 Views typical of the lower part of the Mattole drainage basin.

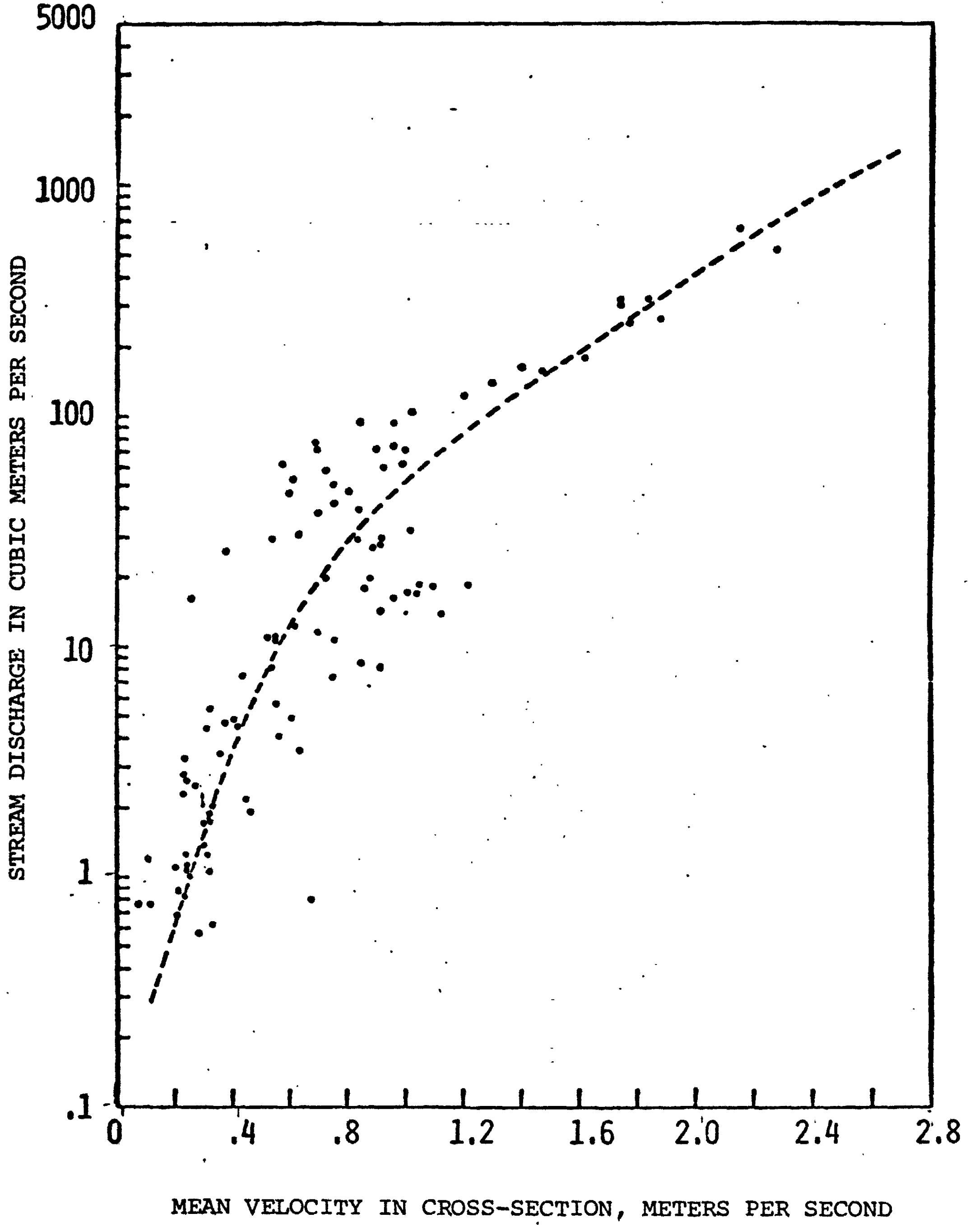

Figure 48. Graph showing relation between stream discharge and mean velocity, Mattole River.

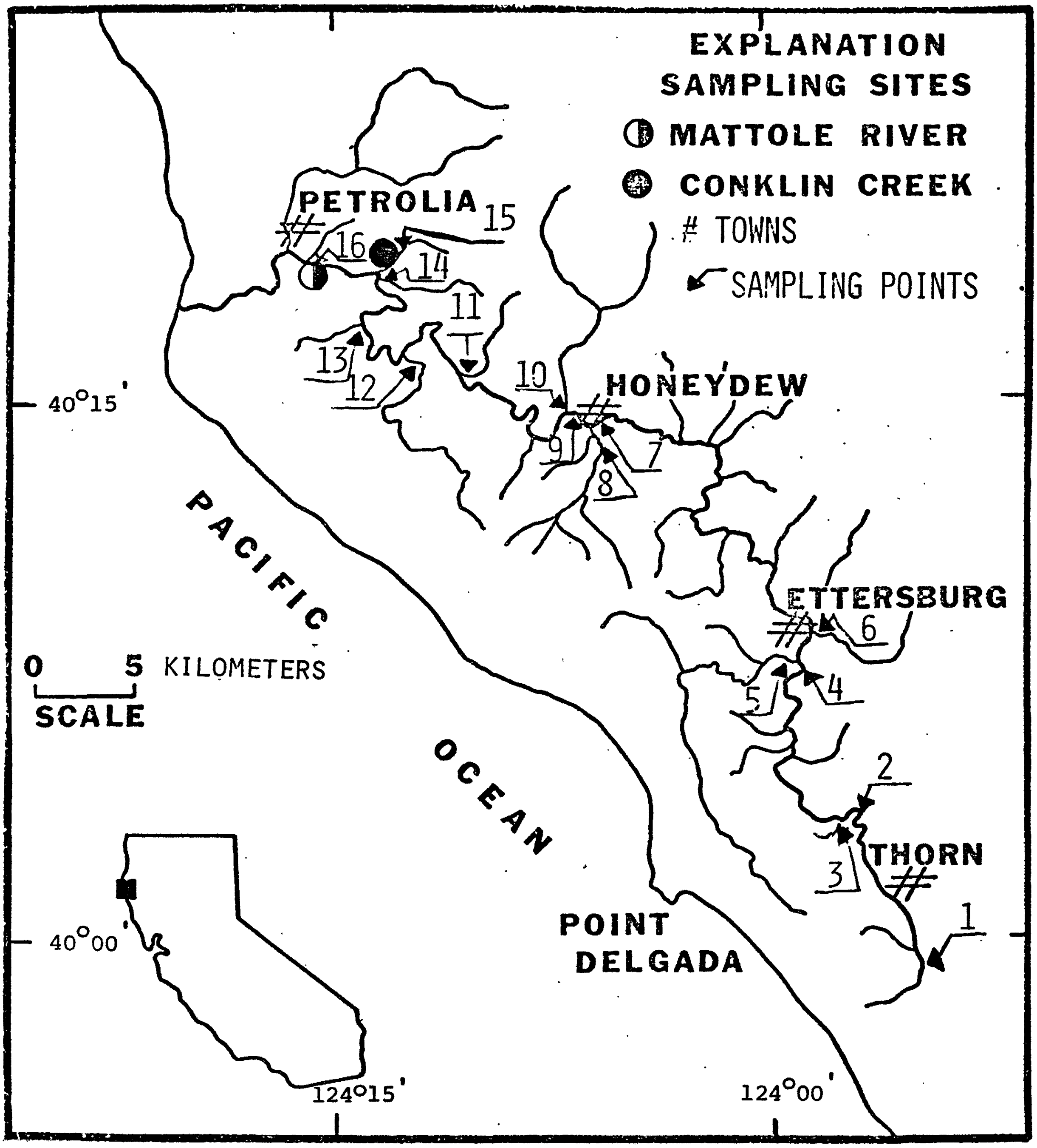

Figure 49. Map of Mattole River basin showing location of low-flow sampling points.

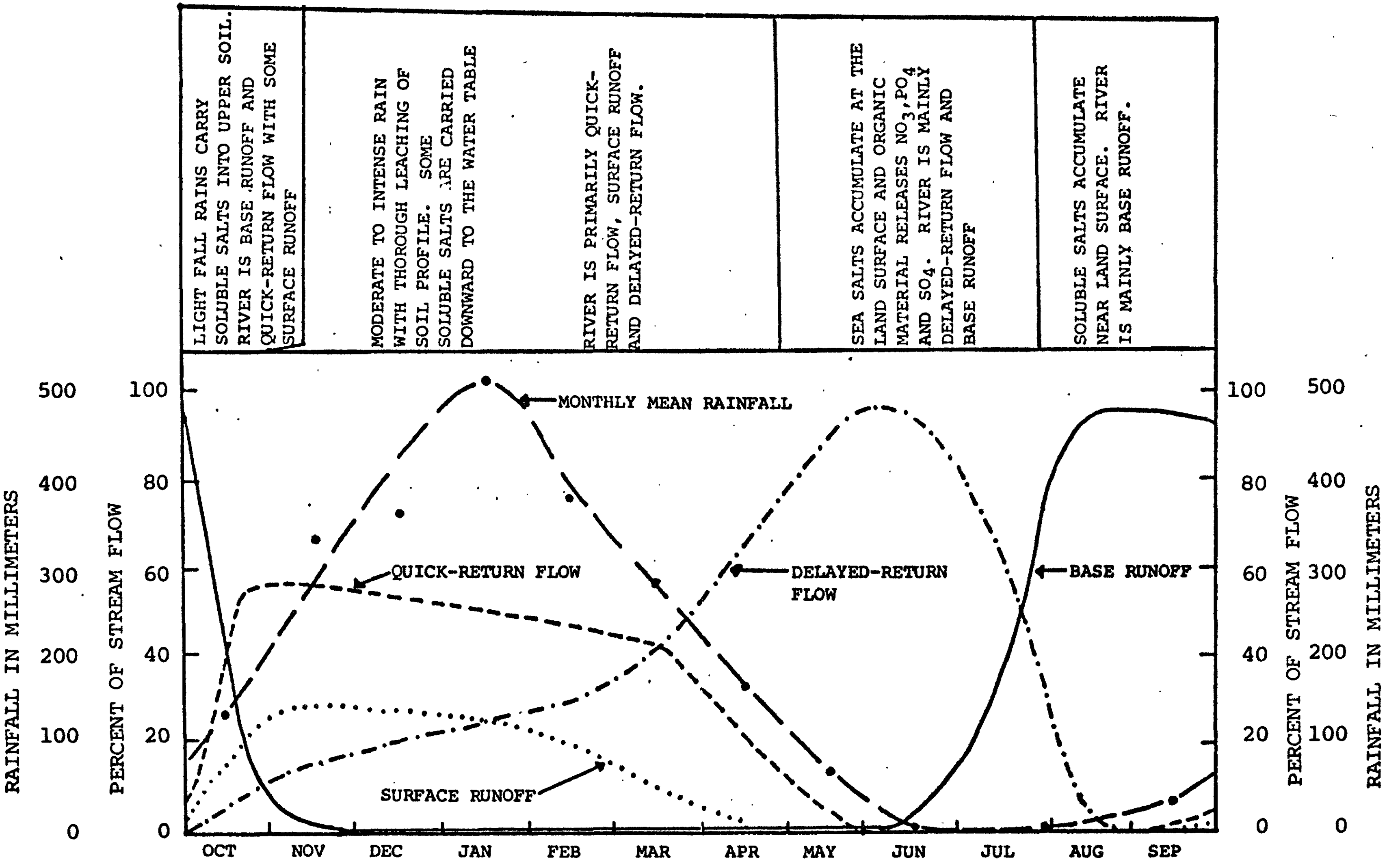

Figure 50. Graphs of ten-year monthly mean rainfall for the Mattole River basin, California and conceptual model of sources of stream flow.

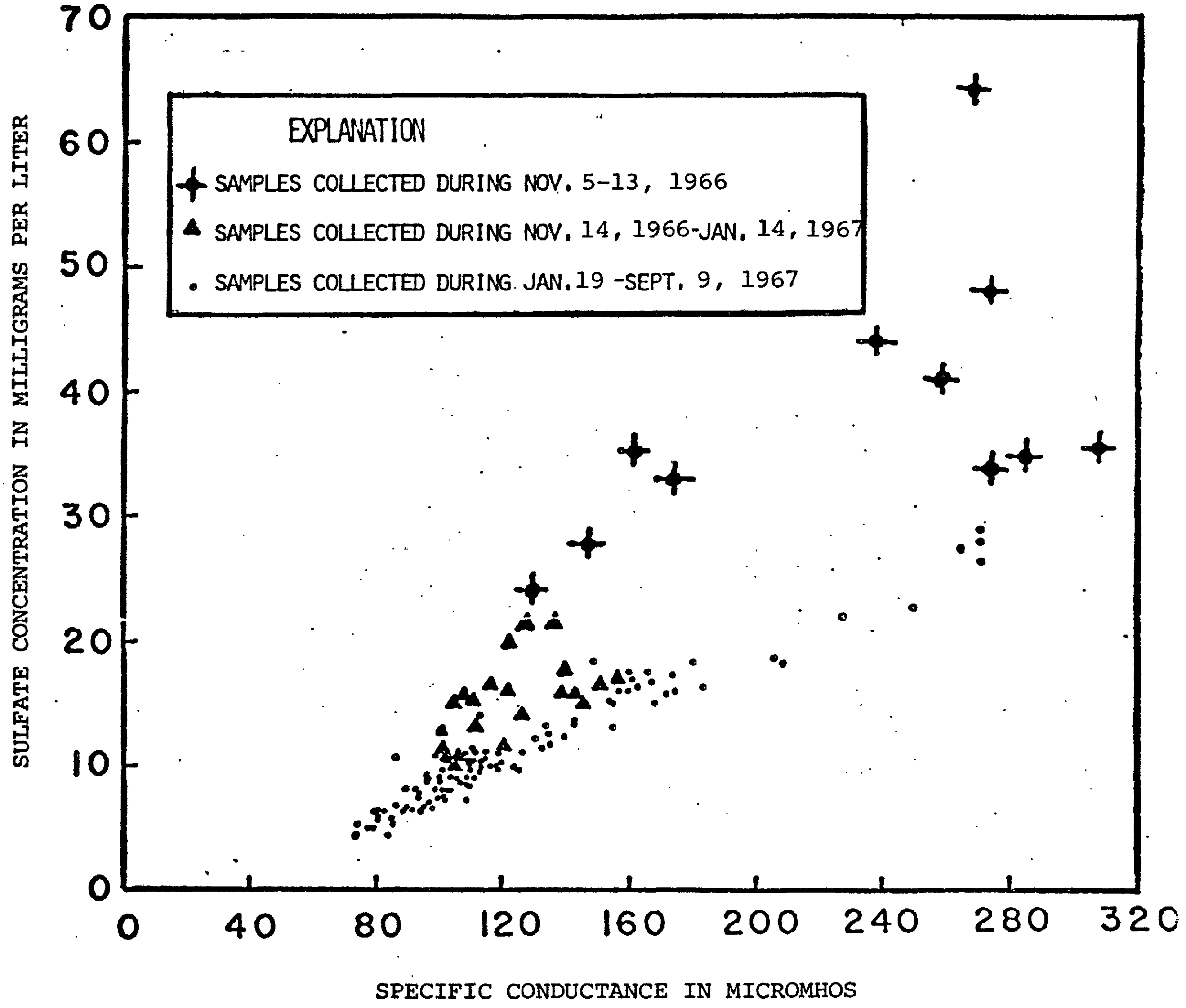

Figure 51. Graph showing relation of sulfate to specific conductance in the Mattole River for the 1966-67 water year.

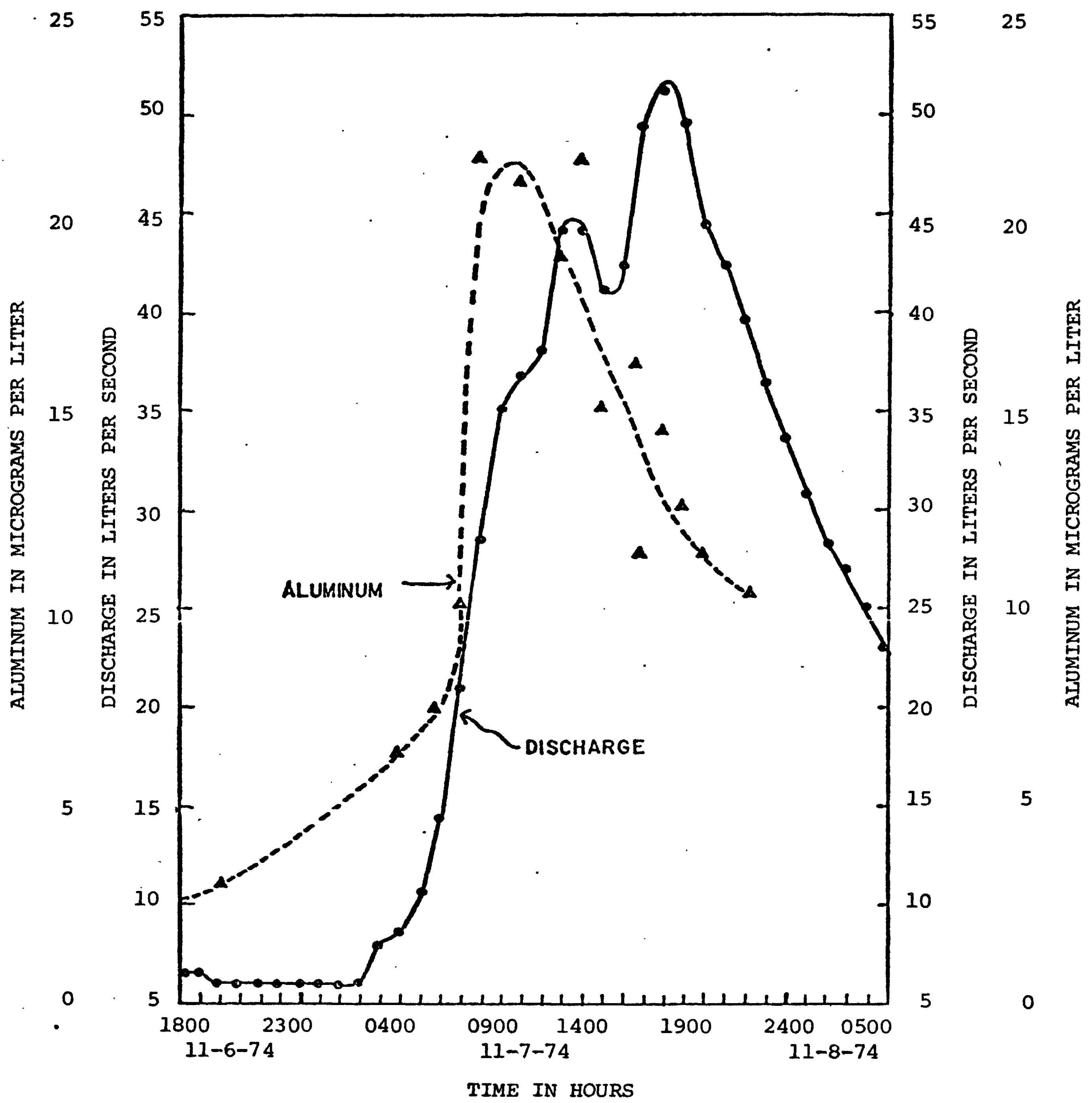

Figure 52. Graphs of aluminum concentration with discharge of Little Lost Men Creek for the period 1800, November 6 to 0500, November 8, 1974.

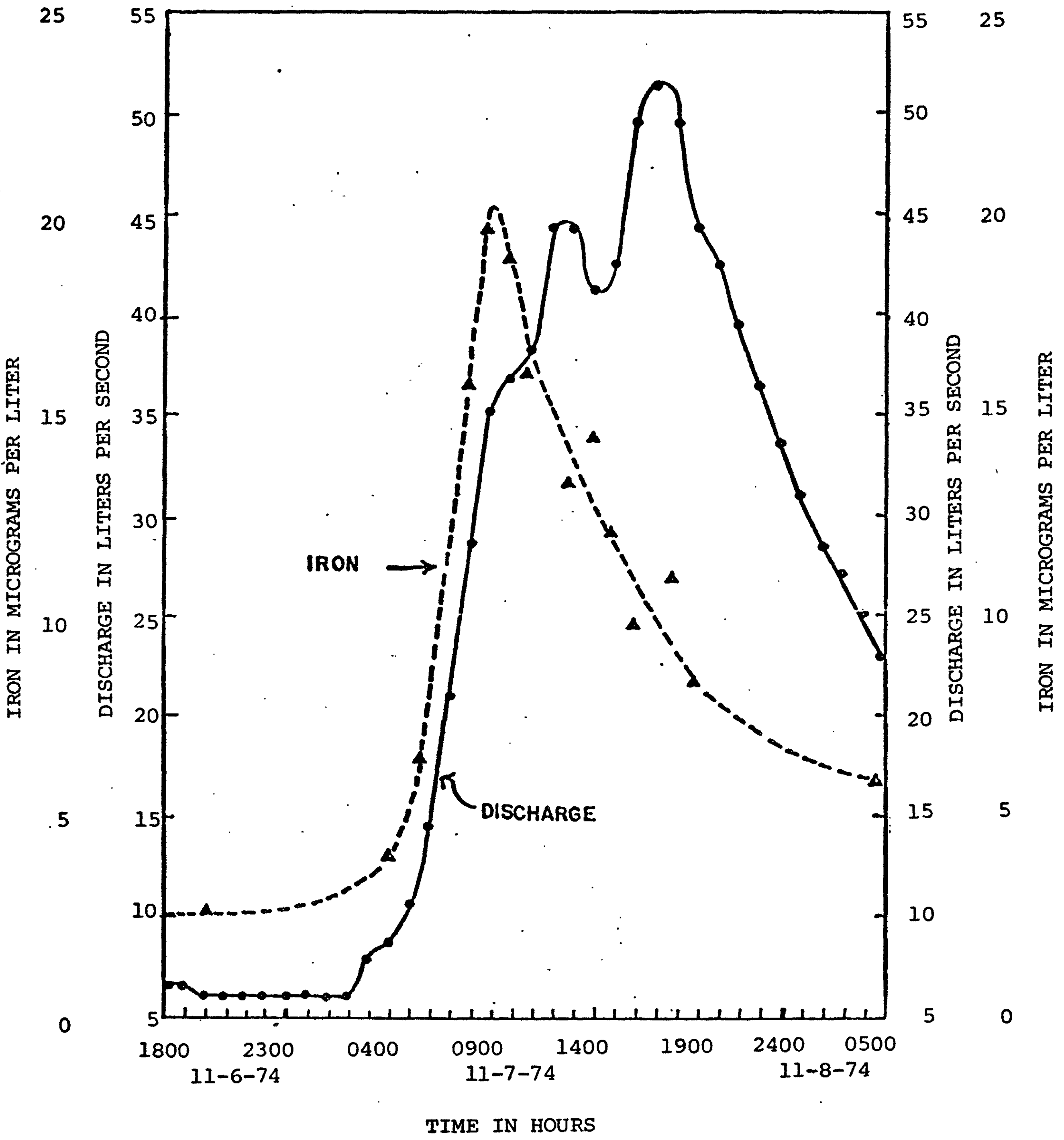

Figure 53. Graphs of iron concentration and discharge of Little Lost Man Creek for the period 1800, November 6 to 0500, November 8, 1974.

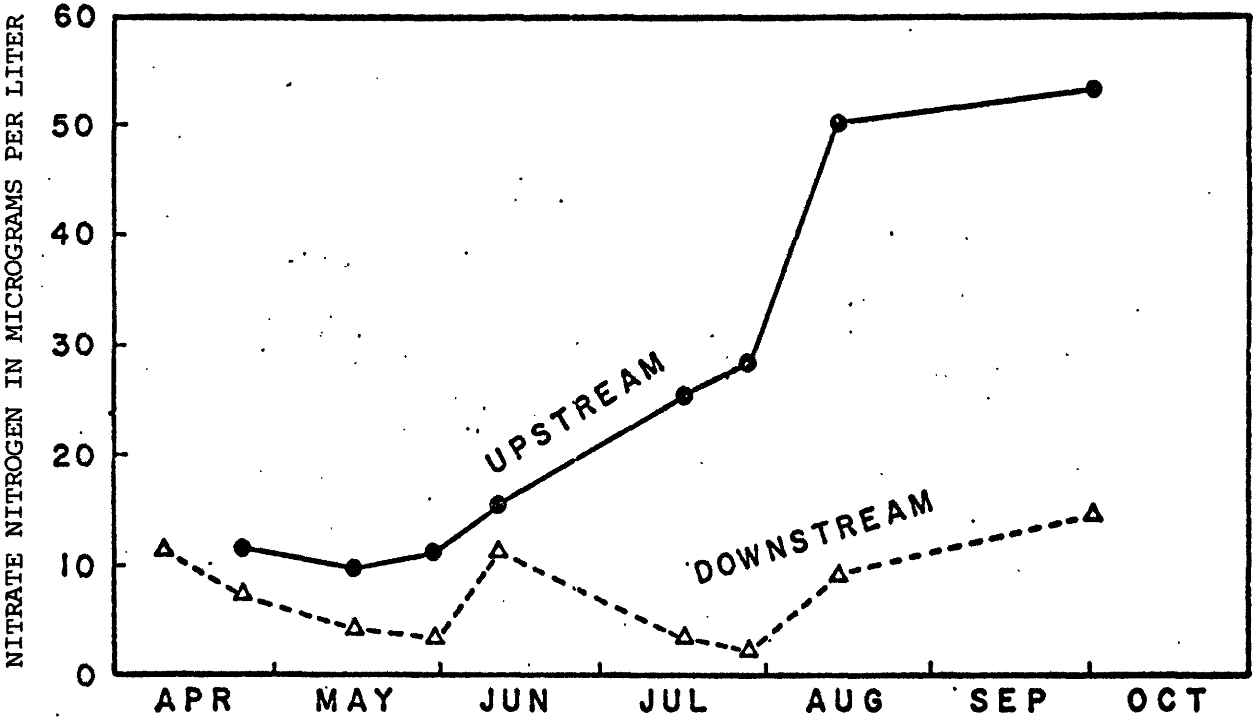

Figure 54. Graphs showing seasonal variation of nitrate nitrogen above and below a lighted stream reach in Little Lost Man Creek - 1974.

BASIC DATA SECTION

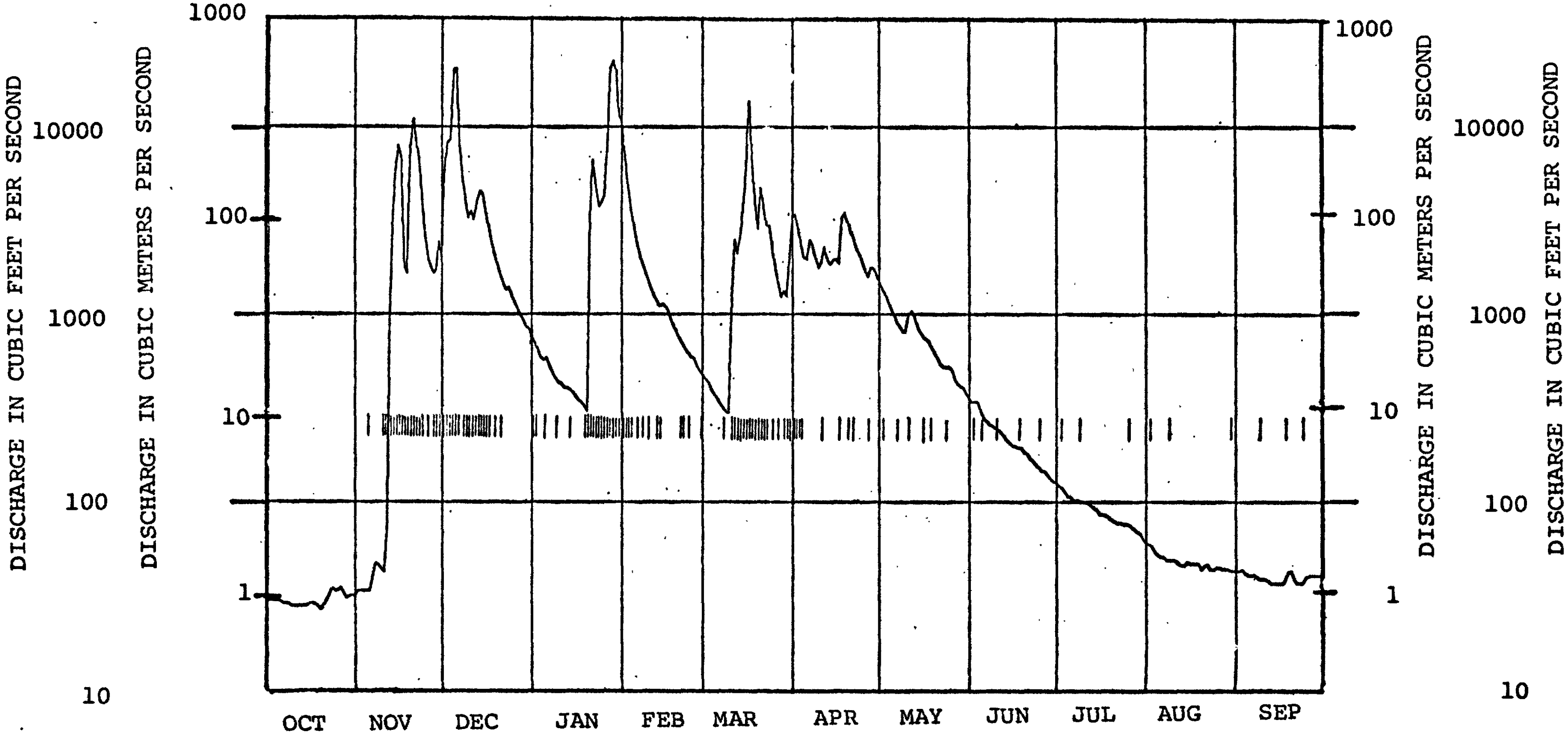

Figure 55. Daily mean discharge of the Mattole River for the 1966-67 water year with sampling days shown.

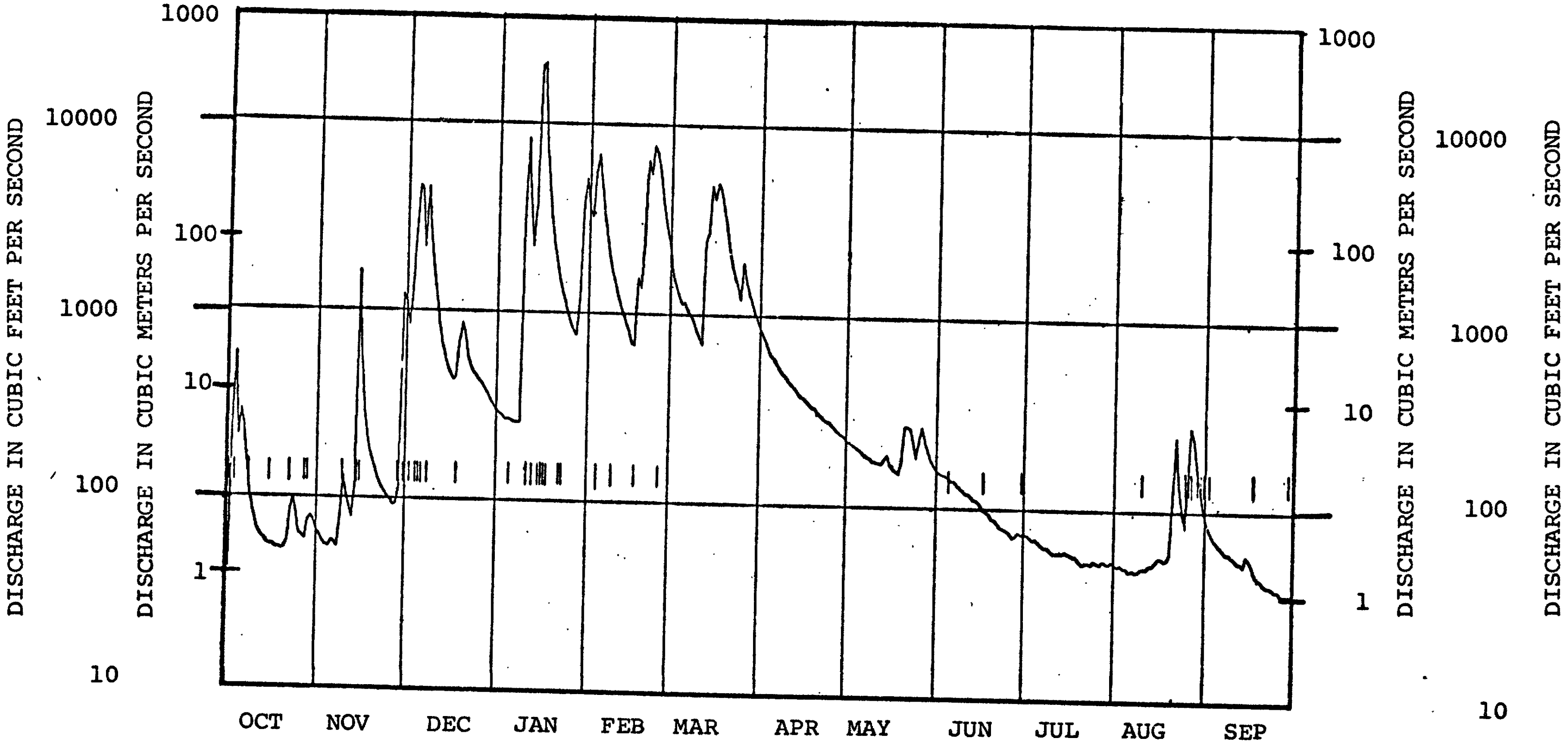

Figure 56. Daily mean discharge of the Mattole River for the 1968 water year with sampling days shown.

Table A. Composition of successive increments (1.35 mm) of rainfall at the MG building, U.S. Geological Survey, Menlo Park, CA Analysts were G. W. Zellweger and R. J. Avanzino.

Sample Number	Remarks	Time for sample collection (hours)	Conductivity (μmho/cm at 25°C	pH[1/]	Constituents in solution (milligrams per liter)[2/]													
					Na	Cl	Ca	SO_4	Mg	K	NO_3-N	Al	Cd	Cu	Fe	Mn	Pb	Zn
			Storm 1		1600 11-10-71 to 1100 11-13-71													
MG1-1		17	13	-	0.28	0.53	0.96	4.8	0.10	0.15	0.22	-	0.00022	0.0020	0.004	0.0057	0.003	0.010
1-2		22	13	-	.47	1.06	.89	0.4	.12	.15	.22	-	.00013	.0024	.004	.0053	.004	.013
1-3	2/3 bottle	9	9.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1-4		12	35	-	3.64	6.5	1.07	1.5	.43	.18	.21	-	.00009	.0014	.001	.0039	.012	.012
1-5		.8	5.0	-	-	.39	.21	<.2	.04	.03	.08	-	.00003	.0009	.001	.0005	.004	.004
1-6		.7	4.7	-	.11	.22	.25	<.2	.02	.04	.20	-	.00006	.0013	.001	.0004	.004	.005
1-7		.6	3.0	-	.09	.17	.18	<.2	.02	.02	.07	-	.00005	.0014	.002	.0005	.003	.006
1-8		.08	2.2	-	.05	.10	.08	<.2	.01	.03	.02	-	.00005	.0010	.004	.0002	.003	.004
1-9		.2	3.7	-	.23	.43	.09	<.2	.03	.02	.02	-	.00005	.0010	.001	.0002	.009	.003
1-10		.5	3.8	-	.23	.48	.08	<.2	.03	.01	.02	<0.002	.00013	.0010	<.001	.0001	.004	.002
1-11	3/4 bottle	4	65	-	8.2	15.0	.59	2.8	1.08	3.3	.11	-	-	.0029	.002	-	.035	.010
			Storm 2		1600 12-1-71 to 0930 12-3-71													
MG1-12	Includes dry fallout	12.6	13	5.8	0.71	1.39	0.94	0.3	0.13	0.09	0.25	-	0.00013	0.0017	0.004	0.008	0.010	0.010
-13		.5	3.0	5.3	.08	.16	.24	<.2	.02	.01	.12	-	-	.0009	.002	.0007	.004	.005
-14		.5	4.1	5.7	.09	.17	.23	<.2	.02	.01	.16	-	.00003	.0009	.002	.0007	.003	.005
-15		.6	2.9	5.6	.11	.16	.13	<.2	.02	.01	.23	-	.00007	.0012	.002	.0004	.005	.003
-16		.15	3.1	5.4	.14	.19	.08	<.2	.02	.07	.11	-	-	.0014	.002	.0002	.004	.002
-17		.15	4.0	5.4	.11	.20	.07	<.2	.02	.00	.11	-	.00002	.001	.002	.0003	.004	.002
-18		.5	4.7	5.4	.10	.16	.07	<.2	.02	.00	.05	-	.00006	.001	.002	.0004	.003	.002
-19		.3	7.9	5.4	.56	1.14	.10	.2	.10	.04	.06	-	-	.0014	.002	.0004	.005	.002
-20		3.8	21	4.5	2.1	4.8	.28	1.1	.29	.08	.20	0.004	.00012	.0012	.004	.0008	.023	.008
-21		.3	23	4.7	2.6	4.9	.23	1.3	.33	.09	.17	< .002	.00012	.0008	.005	.0006	.018	.008
-22		17.6	41	5.4	5.0	8.7	.40	1.9	.63	.19	.14	.004	-	.0008	.003	.0015	.013	.008
-23		4.5	18	5.5	-	3.2	-	-	-	-	.22	-	-	-	-			
			Storm 3		0800 12-10-71 to 1300 12-12-71													
MG1-25		0.5	6.5	5.7	0.26	0.53	0.17	0.1	0.05	0.04	0.07	0.002	-	0.0009	0.002	0.0009	0.014	0.005
-26		.15	4.1	5.6	.12	.21	.02	.1	.12	.02	.44	.002	-	.0019	.002	0.0005	.010	.0024
-27	Consider-able dry fallout	39	48	5.4	4.5	9.3	1.02	-	.68	.24	.12	-	-	-	-	-	-	-
-28		13.3	19	5.2	1.56	3.04	.60	-	.26	-	.20	.004	-	.0014	.002	0.004	.024	.017

Table A

Composition of successive increments (1.35 mm) of rainfall at the MG building, U.S. Geological Survey, Menlo Park, CA
Analysts were G. W. Zellweger and R. J. Avanzino (continued)

Sample Number	Remarks	Time for sample collection (hours)	Conductivity (μmho/cm at 25°C	pH 1/	Constituents in solution (milligrams per liter) 2/													
					Na	Cl	Ca	SO_4	Mg	K	NO_3-N	Al	Cd	Cu	Fe	Mn	Pb	Zn
			Storm 4		1600 12-21-71 to 2145 12-22-71													
MG1-29	Includes dry fallout	2.8	9.1	-	0.10	0.27	0.74	1.1	0.06	0.03	0.38	These elements were not determined in the remaining samples						
-30		.6	-	-	.04	.14	.20	1.0	.02	.03	.42	-	-	-	-	-	-	-
-31		.7	5.4	-	.02	.08	.07	<.2	<.01	-	.13	-	-	-	-	-	-	-
-32		.7	5.4	-	.07	.10	.08	<.2	<.01	-	.20	-	-	-	-	-	-	-
-33		.8	5.1	-	.01	.08	.03	<.2	<.01	-	.25	-	-	-	-	-	-	-
-34		.7	4.3	-	<.01	.06	.04	-	<.01	-	.16	-	-	-	-	-	-	-
-35		1.1	3.9	-	.01	.08	.05	-	.01	-	.18	-	-	-	-	-	-	-
-36	Includes dry fallout	21	11	-	.91	1.72	.22	-	.13	-	.16	-	-	-	-	-	-	-
-37		1	18	-	1.90	3.47	.21	-	.28	-	.26	-	-	-	-	-	-	-
-38		.4	21	-	2.35	4.27	.19	-	.18	-	.09	-	-	-	-	-	-	-
			Storm 5		1600 12-23-71 to 0900 12-25-71													
MG1-39	Includes dry fallout	19.5	16	-	1.34	2.43	0.42	-	-	0.04	0.16	-	-	-	-	-	-	-
-40		3	6.2	-	.27	.62	.09	-	.05	.02	.05	-	-	-	-	-	-	-
-41		2.5	4.0	5.5	.06	.11	.09	-	.01	-	.06	-	-	-	-	-	-	-
-42		.5	5.1	5.2	.07	.20	.08	-	.01	-	.09	-	-	-	-	-	-	-
-43		.3	7.8	4.9	.15	.39	.07	-	.03	-	.12	-	-	-	-	-	-	-
-44		.9	6.2	5.0	.10	.23	.05	-	.02	-	.08	-	-	-	-	-	-	-
-45		2	6.3	5.0	.12	.30	.04	-	.02	-	.08	-	-	-	-	-	-	-
-46		.8	6.9	4.9	.15	.29	.05	-	.02	-	.08	-	-	-	-	-	-	-
-47		1.5	10.4	4.7	.10	.19	.07	-	.01	-	.16	-	-	-	-	-	-	-
-48		1.2	8.2	4.7	.03	.10	.05	-	<.01	-	.14	-	-	-	-	-	-	-

Table A

Composition of successive increments (1.35 mm) of rainfall at the MG building, U.S. Geological Survey, Menlo Park, CA
Analysts were G. W. Zellweger and R. J. Avanzino (continued)

Sample Number	Remarks	Time for sample collection (hours)	Conductivity (μmho/cm at 25^{0}C	pH[1]	Constituents in solution (milligrams per liter)[2]													
					Na	Cl	Ca	SO_4	Mg	K	NO_3-N	Al	Cd	Cu	Fe	Mn	Pb	Zn
			Storm 5 (cont'd)															
MG1-49		1.5	5.4	5.0	0.02	0.10	0.05	-	<0.01	-	0.05	These elements were not determined in the remaining samples.						
-50		.6	3.5	5.3	.03	.09	.09	-	<.01	-	.06	-	-	-	-	-	-	-
-51		.3	2.6	5.8	.02	.06	.08	-	<.01	-	.05	-	-	-	-	-	-	-
-52		.8	3.0	5.5	.01	.06	.06	-	<.01	-	.05	-	-	-	-	-	-	-
-53		.9	3.3	5.3	.02	.07	.03	-	<.01	-	.05	-	-	-	-	-	-	-
-54		.5	3.3	5.5	.07	.15	.01	-	.01	-	.04	-	-	-	-	-	-	-
-55		.3	2.2	5.6	.02	.06	.04	-	.01	-	.03	-	-	-	-	-	-	-
-56		.5	2.6	5.5	.01	.05	.04	-	<.01	-	.03	-	-	-	-	-	-	-
-57		1.0	2.7	5.5	.01	.06	.04	-	<.01	-	.05	-	-	-	-	-	-	-
-58		2.4	3.9	5.4	.01	.08	.04	-	<.01	-	.05	-	-	-	-	-	-	-
			Storm 6		1130 12-25-71 to 1145 12-27-71													
MG1-59	Includes dry fallout	30.8	23	5.1	2.20	4.2	0.32	-	0.27	-	0.11	-	-	-	-	-	-	-
-60		1.3	6.4	5.3	.12	.34	0.14	-	.03	-	.15	-	-	-	-	-	-	-
-61		2.7	3.5	5.4	.03	.13	0.07	-	.01	-	.27	-	-	-	-	-	-	-
-62		3.5	2.9	5.4	.04	.12	0.05	-	.01	-	.04	-	-	-	-	-	-	-
-63		4.2	4.1	5.4	.04	.12	0.05	-	.01	-	.08	-	-	-	-	-	-	-
-64		1.2	4.0	5.4	.02	.08	0.08	-	.01	-	.09	-	-	-	-	-	-	-
-65		1.5	3.4	5.3	.00	.06	0.06	-	<.01	-	.15	-	-	-	-	-	-	-
-66	5/6 bottle	3.0	5.1	5.1	.00	.08	0.08	-	.01	-	.15	-	-	-	-	-	-	-

[1] Under these conditions of very low ionic strength pH measurements were unstable with a precision of 0.2. The procedure involved stirring the sample for 3 minutes with the pH electrode inserted, followed by no stirring for 2 minutes before recording the pH measurement. This procedure differed from that used for Mattole basin rain samples taken later.

[2] Precision of 0.02 mg/L for Na, Cl, Ca, Mg, K and NO_3-N; 0.2 for SO_4; 0.002 for Al; 0.001 for Fe, Pb and Zn; 0.0002 for Cu and Mn and 0.00002 for Cd.

Table B Composition of successive increments (2.64 mm) of rainfall at Building 3, U. S. Geological Survey, Menlo Park, CA
Analysts were G. W. Zellweger and R. J. Avanzino.

Sample Number	Remarks	Time for sample collection (hours)	Conductivity (µmho/cm at 25°C	pH[1/]	Constituents in solution (milligrams per liter)[2/]					
					Na	Cl	Ca	Mg	K	NO_3-N
		Storm 2		1600 12-1-71 to 0930 12-3-71						
B3-2-1		13	7.1	6.1	0.32	0.60	0.77	0.06	-	0.16
-2		1	2.5	5.3	.02	<.05	.13	.01	-	.11
-3		.5	3.2	5.3	.22	.19	.08	<.01	-	.14
-4		.8	2.8	5.4	.13	.20	.07	.01	-	.03
-5	2/3 bottle	2.7	3.7	5.3	.14	.34	.11	.01	-	.08
-6		.7	25	5.2	2.53	4.48	.31	.30	.07	.09
-7	1/2 bottle	22.8	42	5.4	4.42	8.5	.54	.56	.12	.20
		Storm 3		0830 12-9-71 to 1300 12-12-71						
B3-2-8		24	10.4	5.9	0.71	1.24	0.37	0.10	0.04	0.38
-9	1/2 bottle	0.3	3.3	5.7	.10	.17	.09	.02	.02	.08
-10		39	25	-	2.75	5.0	.51	.34	.08	.08
-11		0.7	4.6	-	.13	.22	.12	.02	.01	.09
-12	1/3 bottle	12.5	60	-	-	-	-	-	-	-
		Storm 4		1530 12-21-71 to 2145 12-22-71						
B3-2-13		-	7.7	5.6	0.05	0.13	0.47	0.03	-	0.54
-14		-	8.4	5.0	.03	.11	.13	.01	-	.25
-15		-	6.3	5.2	<.01	.06	.04	<.01	-	.07
-16		-	4.8	5.2	.01	.06	.06	<.01	-	-
-17		-	4.1	5.3	.00	.05	.07	<.01	-	.08
-18		-	9.4	5.3	.60	1.10	.03	.08	-	.15
-19		4	22	-	2.28	4.11	.21	.27	-	.07
-20		1.2	15	-	1.59	3.04	.13	.20	-	.04
		Storm 5		1600 12-23-71 to 1330 12-25-71						
B3-2-21		22	10.6	5.4	0.86	1.57	0.23	0.11	0.035	0.09
-22		3.5	3.3	5.4	.02	.08	.04	.01	-	.04
-23		1	2.5	5.4	.01	.06	.02	<.01	-	.10
-24		2.5	6.3	5.0	.10	.21	.03	<.02	-	.23
-25		1.5	8.3	4.8	.15	.31	.04	.02	-	.09
-26		3	7.0	4.8	.02	.10	.09	.01	-	.30
-27		1	5.0	5.0	.02	.09	.06	<.01	-	.06
-28		1	3.4	5.2	.00	<.05	.22	<.01	-	.06
-29		1.5	3.0	5.3	.00	<.05	.01	<.01	-	.08
-30		.8	3.4	5.3	.00	.05	.22	<.01	-	.25
-31		3.5	2.5	5.4	.01	<.05	.03	<.01	-	.07
-32	1/2 bottle	4.2	4.0	5.2	.02	.05	.04	<.01	-	.06
		Storm 6		1330 12-25-71 to 1030 12-27-71						
B3-2-33		30	14	5.2	1.16	2.3	0.17	0.15	-	0.02
-34		2.5	5.7	5.1	.03	.08	.05	.01	-	.22
-35		4	3.2	5.3	.05	.08	.03	.01	-	.05
-36		4.5	3.1	5.3	.04	<.05	.03	<.01	-	.05
-37		2.5	5.3	5.3	.00	.11	.06	<.01	-	.14
-38	1/2 bottle	1.5	9.6	5.8	.07	.29	.15	.01	-	.39

[1/] Under these conditions of very low ionic strength pH measurements were unstable with a precision of 0.2. The procedure involved stirring the sample for 3 minutes with pH electrode inserted followed by no stirring for 2 minutes before recording the pH measurement. This procedure differed from that used for Mattole basin rain samples taken later.

[2/] A precision of approximately 0.02 mg/L is appropriate for these constituents at the lower concentrations shown.

Table C - Chemical Analyses in mg/L of water samples from the Mattole River near Petrolia, California 1966-67 Water Year

Date and time of collection	Instantaneous Discharge M^3 Sec^{-1}	Silica	Ca	Mg	Sr	Na	K	HCO_3	SO_4	Cl	NO_3	Suspended Sediment	Specific conductance (micromhos at 25°C)	pH	T°C
Nov.-1966															
5- 1155	0.96	7.9	41	6.8	.34	8.7	1.3	134	35	5.0	<.01	50	-	7.9	13
10-1000	1.2	7.4	41	6.7	.34	8.7	1.2	134	36	5.1	-	50	-	8.0	12
11-1750	1.9	7.3	40	6.6	.32	8.7	1.2	127	35	5.0	-	70	286	8.3	12
11-2300	3.3	6.7	37	6.0	.31	8.1	1.2	113	34	5.0	.03	140	275	8.0	12
12-0430	14.	6.8	35	5.6	.30	8.1	1.3	94	41	4.8	-	1000	259	8.0	12
12-0630	19	6.1	33	5.2	.29	8.9	1.4	68	64	5.0	-	2890	269	8.1	12
12-0845	27	7.0	35	5.6	.33	8.5	1.3	97	48	4.7	-	980	274	8.2	12
12-1330	43	7.2	28	4.5	.24	7.2	1.1	82	44	3.9	-	1830	238	8.1	12
12-1750	39	7.2	22	3.5	.20	6.0	1.0	56	33	3.2	.25	1150	175	7.8	12
13-1030	79	7.0	21	3.4	.20	6.2	1.0	47	36	3.3	-	5020	-	7.7	12
13-1700	115	7.5	18	2.9	-	5.7	1.0	44	28	3.1		2900	148	7.8	12
13-2300	169	7.5	16	2.6	-	5.3	.9	38	25	3.1	-	3400	130	7.7	12
14-1000	180	8.5	16	2.5	-	5.0	.9	41	22	2.9	-	4850	128	7.9	12
14-1130	143	9.0	16	2.7	-	5.2	.9	47	21	3.1	-	2220	137	7.7	12
15-0930	161	9.6	16	2.5	-	5.0	.9	41	20	3.1	-	-	123	7.8	12
15-2130	312	8.7	13	2.1	-	4.6	.9	36	15	2.9	-	5140	105	7.7	12
16-0900	204	10.2	14	2.2	-	4.7	1.0	40	16	2.9	.58	2570	109	7.8	12
16-2130	126	10.6	15	2.6	-	5.1	.9	46	16	3.0	-	1060	122	7.8	12
17-0945	77	10.7	18	2.9	-	5.6	.9	51	18	3.1	-	560	140	8.0	12
18-2130	47	10.3	21	3.5	-	6.1	1.0	-	22	3.3	-	250	-		
19-0900	179	9.0	14	2.4	-	5.1	1.0	42	17	2.8	-	2590	117	7.8	12
19-1500	276	9.7	14	2.1	-	5.0	1.0	-	13	2.9	-	6140	-	-	12
20-1015	315	9.7	12	2.1	-	4.7	.9	41	11	2.9	-	5780	101	7.7	12
20-1500	355	10.0	13	2.0	-	4.6	.9	-	11	3.2	-	6690	-	-	12
21-1030	228	11.0	13	2.2	-	4.9	.9	45	11	3.2	.40	2510	106	7.9	12
21-2115	235	11.9	13	2.3	-	4.8	.9	-	12	3.2	-	-	-	-	12
22-0930	217	11.5	13	2.3	-	4.7	.9	45	10	3.1	-	1940	106	7.7	12
23-0945	122	11.9	15	2.6	-	5.1	.9	-	12	3.1	-	860	-	-	12
24-0930	81	11.8	16	2.8	-	5.2	.8	54	14	3.0	-	410	127	-	12
26-0930	53	10.9	18	3.2	-	5.5	.8	61	16	3.2	-	190	143	-	12
28-0945	42	10.8	19	3.4	-	5.8	.8	64	17	3.2	-	105	151	-	12
29-0945	72	10.7	17	3.1	-	5.5	.6	58	16	3.0	-	540	139	-	12
30-1100	54	11.7	18	3.3	-	-	.9	-	15	3.2	-	180	-	-	12
Dec.-1966															
1-0700	208	8.6	14	2.4	-	5.0	.9	43	15	2.5	-	6000	111	8.0	12
1-1310	228	9.4	12	2.2	-	4.6	.8	48	11	2.5	-	4120	106	8.0	12
2-1010	176	10.0	12	2.2	-	4.7	.7	46	11	2.8	-	3480	105	7.8	12
2-2200	253	11.3	13	2.0	-	4.8	.8	48	9	2.8	-	1950	104	7.8	12
3-0945	231	11.3	12	2.1	-	4.8	.7	48	9	2.9	-	1850	106	8.0	12
3-2130	263	10.8	12	2.1	-	4.7	.8	45	9	2.9	-	2670	100	7.9	12
4-0900	364	10.2	11	1.9	-	4.5	.7	42	9	3.0	-	5100	96	7.8	11
4-1630	646	9.2	11	1.6	-	4.0	.9	41	8	2.8	-	8440	89	7.9	12
4-2130	1165	8.2	8.5	1.5	-	3.9	.9	36	6	2.7	-	[illegible]	80	7.7	11
5-0130	1049	8.8	9.0	1.6	-	3.9	.9	38	6	2.7	-	12000	80	7.7	11
5-1030	533	10.7	9.7	1.8	-	4.2	.9	38	4.5	3.0	-	6530	84	7.6	11
5-1530	421	10.9	9.7	1.9	-	4.4	.9	40	6	3.2	-	4950	90	7.5	12
6-0915	222	11.0	11	2.1	-	4.7	.9	46	8	3.0	-	3220	102	7.8	12
8-0700	125	11.4	13	2.6	-	5.0	.9	52	10	3.1	-	1040	-	-	13

Table C (con't)

Date and time of collection	Instantaneous Discharge M^3 Sec^{-1}	Silica	Ca	Mg	Sr	Na	K	HCO_3	SO_4	Cl	NO_3	Suspended Sediment	Specific conductance (micromhos at 25°C)	pH	T°C
Dec.-1966															
9-1800	87	11.6	14	2.7	-	5.1	.8	52	11	3.1	-	860	115	7.8	13
10-1000	109	11.2	13	2.5	-	5.0	.8	51	10	3.0	-	1580	114	7.8	13
11-1700	93	11.3	14	2.6	-	5.2	.8	54	12	3.1	-	1160	120	7.9	13
12-1315	113	11.4	13	2.4	-	4.9	.8	49	9	3.1	-	1230	110	7.8	13
13-1030	119	10.9	12	2.4	-	4.9	.8	47	11	3.0	-	2270	109	7.7	13
13-1730	149	10.4	12	2.4	-	5.1	.8	48	9	2.9	-	4200	107	7.8	13
14-1415	122	12.0	14	2.4	-	5.0	.8	51	10	3.0	-	1150	111	7.9	13
15-1420	97	12.4	14	2.7	-	5.1	.8	54	10	3.1	.29	880	117	7.8	13
16-1300	82	12.5	14	2.8	-	5.3	.8	55	10	3.1	-	470	120	7.8	13
17-1205	69	12.4	15	3.0	-	5.5	.8	57	11	3.1	.17	360	127	7.8	13
19-0945	51	12.3	16	3.2	-	5.7	.8	61	12	3.1	-	210	135	7.9	13
21-1005	42	12.2	17	3.4	-	5.9	.8	63	13	-	-	130	141	7.9	13
Jan.-1967															
1-1600	19	11.2	20	3.8	-	6.2	.8	71	16	3.4	-	2	160	7.7	11
2-1300	18	11.1	20	3.9	-	6.2	.8	73	16	3.3	-	-	160	7.7	11
5-1500	17	10.9	20	3.9	-	6.2	.8	72	17	3.4	-	73	161	7.7	7
9-1215	12	10.6	21	4.0	-	6.2	.8	74	18	3.4	-	17	166	7.7	6
14-0945	11	10.6	22	4.1	.21	6.3	.8	77	18	3.4	-	10	174	7.8	6
19-1100	8	10.2	24	4.2	-	6.3	.8	79	18	3.4	-	7	180	-	6
19-2200	10	9.3	21	3.9	-	6.2	.8	70	18	3.4	.04	-	160	7.6	6
20-0140	19	8.8	19	3.4	-	6.1	.8	61	18	3.2	-	860	149	7.5	6
20-0930	86	8.2	14	2.5	-	4.9	.7	45	14	2.6	-	4200	113	7.4	6
20-1620	114	8.8	13	2.2	-	4.8	.7	-	11	2.4	-	3490	-	-	6
20-2355	160	9.4	12	2.1	-	4.7	.7	44	9	2.4	-	3890	100	7.2	6
21-0930	190	9.7	11	2.0	-	4.5	.7	41	8	2.3	.13	4230	94	7.0	6
21-1900	200	10.4	11	2.1	-	4.6	.7	42	8	2.4	-	3110	94	7.4	7
22-0945	140	11.3	12	2.2	-	4.7	.7	44	8	2.7	-	1330	103	7.5	7
23-0915	110	11.2	12	2.4	-	5.0	.7	46	10	2.8	-	930	108	7.4	7
23-1745	102	11.3	13	2.5	-	5.0	.7	49	10	2.8	-	650	111	-	7
24-1000	105	10.6	13	2.5	-	[illegible]	.7	46	11	3.2	-	1360	112	7.5	7
25-1010	124	11.2	14	2.6	-	5.3	.7	48	10	3.7	-	860	114	7.5	7
25-2305	115	11.7	14	2.6	-	5.4	.7	50	10	3.4	-	720	116	7.6	7
26-1050	252	9.5	11	2.1	-	4.6	.7	40	9	3.1	-	6420	96	7.5	7
26-1415	316	9.3	11	2.0	-	4.4	.7	41	8	3.0	-	8000	92	7.6	7
26-2340	306	10.2	10	1.9	-	4.3	.7	40	7	3.0	.11	4110	86	7.8	7
27-0945	511	9.5	9.6	1.7	.09	4.1	.7	37	6	2.8	-	6780	82	7.7	7
27-1530	633	9.2	9.1	1.6	-	3.9	.8	36	6	2.6	-	7150	78	7.6	7
27-2310	789	9.2	8.5	1.5	-	3.8	.8	35	5	2.5	-	7000	74	7.5	7
28-1045	663	9.9	8.4	1.6	-	3.8	.8	35	4	2.6	-	5360	73	7.6	7
28-2325	501	10.4	9.0	1.7	-	4.1	.8	38	5	2.7	-	5500	79	7.7	7
29-1140	609	10.1	8.6	1.7	-	4.0	.8	36	5	2.5	-	5720	77	7.5	7
29-2225	380	11.4	9.5	1.9	-	4.3	.8	41	5	2.8	-	3380	85	7.7	7
30-1030	306	11.6	10	1.9	-	4.5	.8	41	6	2.8	-	2780	89	7.7	7
30-2240	343	10.7	10	1.9	-	4.4	.8	42	7	2.7	-	3300	90	7.6	7
31-1055	302	11.6	10	1.9	-	4.5	.8	44	6	2.7	.11	1940	91	7.8	7
31-2100	255	12.1	11	2.0	-	4.5	.8	45	6	2.8	-	[illegible]	94	-	7

Table C (con't)

Date and time of collection	Instantaneous Discharge M^3 Sec^{-1}	Silica	Ca	Mg	Sr	Na	K	HCO$_3$	SO$_4$	Cl	NO$_3$	Suspended Sediment	Specific conductance (micromhos at 25°C)	pH	T°C
Feb.-1967															
1-0955	203	12.2	11	2.1	-	4.7	.8	46	7	2.8	.12	1450	97	7.8	8
1-2305	166	12.3	12	2.2	-	4.8	.7	47	7	2.9	-	1300	100	7.8	8
2-1035	146	12.4	12	2.3	-	5.0	.8	49	8	2.9	-	1000	104	7.9	9
3-1000	108	12.5	13	2.5	.14	5.1	.7	52	8	3.0	.07	650	110	7.8	10
4-0930	88	12.3	13	2.7	-	5.2	.7	52	9	-	.11	490	113	7.7	10
6-0945	62	12.2	15	3.0	-	5.4	.7	57	10	3.1	-	270	126	7.7	10
8-1045	49	12.1	16	3.1	-	5.6	.7	59	11	3.1	-	-	133	-	10
10-1000	40	-	17	3.3	-	5.7	.7	62	12	3.2	-	91	136	7.8	10
13-0945	32	11.8	18	3.5	-	5.9	.8	65	13	3.2	-	59	143	7.8	10
14-0900	35	11.5	17	3.5	-	5.9	.7	65	14	3.2	-	104	143	7.9	9
21-1500	20	11.2	19	3.7	-	5.9	.8	68	15	3.2	-	23	154	7.5	9
22-1400	18	11.0	19	3.7	-	5.9	.7	68	15	3.2	.06	11	155	7.5	9
24-1500	17	10.8	20	3.7	-	5.9	.8	69	16	3.2	-	-	157	7.5	9
28-0930	13	10.7	20	3.9	-	6.0	.8	71	16	3.3	.03	9	163	7.6	8
March-1967															
6-1030	9	10.2	22	4.0	.20	6.3	.8	74	17	3.4	<.01	9	167	7.5	8
11-1100	72	10.0	13	2.5	-	4.8	.6	48	11	2.6	-	770	109	7.4	10
12-1055	57	10.6	14	2.8	-	5.2	.6	51	11	2.8	-	320	119	7.4	10
13-0945	73	10.6	14	2.7	-	5.2	.6	50	11	2.6	-	490	114	7.5	10
14-1000	94	10.8	13	2.6	-	5.1	.6	48	11	2.6	-	680	111	7.4	10
14-2015	131	9.6	12	2.3	-	5.0	.6	44	11	2.6	-	4320	102	7.6	11
15-0955	181	10.6	12	2.3	-	4.8	.7	44	9	2.5	-	6380	100	7.5	11
16-0930	528	8.4	9	1.8	-	4.1	.8	37	6	1.9	-	10660	79	6.9	11
16-2030	325	10.6	10	1.9	-	4.4	.8	40	6	2.3	-	4550	85	7.1	11
17-0945	195	11.4	11	2.1	-	4.7	.7	44	7	2.6	-	2360	95	7.2	11
17-2305	161	11.6	12	2.2	-	4.7	.7	45	7	2.6	-	1730	98	7.3	11
18-1055	115	11.8	12	2.3	-	5.0	.7	48	8	2.6	-	1340	101	7.3	11
19-0630	85	12.2	13	2.5	-	5.0	.7	52	8	2.7	-	940	109	7.6	11
20-0930	147	10.3	12	2.2	-	4.6	.7	46	8	2.2	-	2420	99	7.6	12
20-2135	129	11.3	12	2.2	-	4.7	.7	47	7	2.3	-	1450	102	7.5	12
21-0945	113	12.0	12	2.3	-	4.8	.7	48	7	2.5	-	990	102	7.6	12
22-1000	86	12.7	13	2.5	-	5.1	.8	53	7	2.7	-	620	109	7.5	12
23-0830	94	11.9	13	2.4	-	5.1	.8	52	9	2.6	-	920	107	7.6	12
25-0945	59	12.4	14	2.8	-	5.2	.8	56	10	2.8	.10	360	119	7.7	12
27-0830	44	12.4	15	3.0	-	5.2	.8	57	10	2.8	-	220	124	7.4	12
29-1000	40	12.3	15	3.0	-	5.4	.7	56	11	2.9	-	210	127	7.3	12
30-1420	69	10.2	14	2.5	-	5.2	.7	49	11	2.5	-	1580	116	7.2	12
31-0300	92	11.0	13	2.4	-	5.0	.7	49	9	2.6	-	1150	109	7.3	12
April-1967															
1-0910	99	11.6	13	2.4	-	5.1	.7	49	9	2.7	-	1070	109	7.4	11
2-1410	77	12.5	14	2.6	-	5.1	.7	51	9	2.7	.06	450	111	7.2	11
3-1010	66	12.4	14	2.7	-	5.1	.7	53	9	2.8	-	390	116	7.3	11
4-1130	56	12.5	15	2.9	-	5.2	.7	55	9	2.8	-	280	-	7.2	11
11-1300	64	11.6	14	2.7	-	5.1	.8	55	9	2.6	-	420	114	7.1	11

Table C (con't)

Date and time of collection	Instantaneous Discharge M^3 Sec^{-1}	Silica	Ca	Mg	Sr	Na	K	HCO$_3$	SO$_4$	Cl	NO$_3$	Suspended Sediment	Specific conductance (micromhos at 25°C)	pH	T°C
April-1967															
17-1210	97	10.8	13	2.4	-	4.9	.7	50	9	2.4	.03	1970	106	7.2	9
19-1030	85	12.4	13	2.5	-	5.0	.7	51	9	2.6	.06	640	106	7.4	9
22-1440	63	12.5	14	2.7	-	5.2	.7	55	10	2.7	.04	250	114	7.5	9
27-1350	51	13.4	15	2.9	-	5.3	.7	56	10	2.6	.04	260	119	7.3	9
May-1967															
2-1310	36	13.0	17	3.2	-	5.8	.7	63	12	2.8	-	60	131	7.6	13
7-1315	24	12.9	19	3.4	-	6.0	.8	67	12	2.8	.02	80	140	7.7	13
11-1400	30	12.1	17	3.1	-	5.6	.8	60	13	2.8	.015	150	134	7.3	14
16-1300	21	12.4	19	3.5	-	6.0	.9	67	13	2.9	-	30	-	7.7	13
24-1200	15	12.7	22	3.8	-	6.3	.9	78	15	3.0	-	11	168	7.7	16
June-1967															
2-1140	9.6	12.2	22	4.0	-	6.6	.9	79	16	3.1	<.01	14	172	7.6	16
4-0930	8.6	12.2	24	4.0	-	6.8	1.0	81	16	3.1	-	-	176	7.6	16
10-1215	6.8	12.2	26	4.3	-	6.9	1.1	86	16	3.2	<.01	-	184	7.5	18
18-1100	5.1	11.9	28	4.6	-	7.2	1.2	96	19	3.3	<.01	-	206	7.7	19
25-1330	4.1	11.9	29	4.6	-	7.2	1.2	97	19	3.3	-	14	209	7.8	20
July-1967															
2-1100	3.3	12.1	32	5.0	-	7.3	1.3	100	22	3.5	.01	-	228	8.3	21
9-1140	2.9	12.0	32	5.3	-	7.5	1.3	101	22	3.5	-	-	228	8.3	21
26-1130	2.0	11.0	34	5.6	-	8.0	1.4	110	23	3.6	<.01	-	-	-	21
Aug.-1967															
2-1300	1.6	9.6	36	5.8	-	8.4	1.4	124	27	4.0	-	-	271	8.3	21
9-1130	1.4	9.6	36	5.8	-	8.6	1.4	-	28	4.0	-	4	265	8.3	21
30-1030	1.2	8.9	36	5.9	-	8.6	1.4	-	29	4.1	-	6	271	8.3	21
Sept.-1967															
9-1010	1.1	8.9	36	5.9	-	8.6	1.4	-	29	4.1	-	-	271	8.3	21
18-0005	1.1	9.1	36	5.9	-	8.4	1.3	122	27	4.1	-	-	-	8.0	22
18-0200	1.2	9.1	36	5.8	-	8.5	1.4	124	29	4.1	-	-	261	7.9	22
18-0700	1.2	9.1	38	6.0	-	8.6	1.4	127	28	4.2	-	-	270	7.9	22
18-0930	1.2	9.2	37	5.9	-	8.7	1.4	127	29	4.3	-	-	268	8.1	22
24-1100	1.1	9.5	37	6.0	-	9.1	1.4	125	29	4.4	-	-	278	8.5	22

Table D - Chemical analyses in mg/L of water samples from the Mattole River near Petrolia, California, 1967-68 water year.

Date and time of collection	Instantaneous Discharge M^3 Sec^{-1}	Silica	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	Specific conductance (micromhos at 25°C)	pH	T°C
Oct.-1967													
1-1100	1.2	9.1	37	5.8	8.2	1.4	-	29	4.4	-	266	8.1	21
3-1030	17	9.0	29	5.0	8.1	1.3	113	40	4.6	.32	228	8.1	20
8-1600	2.9	9.4	39	6.3	8.5	1.4	113	39	4.6	<.01	295	8.3	20
15-0930	1.6	9.3	39	6.4	8.5	1.3	112	43	4.6	<.01	-	8.2	-
22-1200	2.3	8.4	38	6.1	8.2	1.2	113	36	4.5	-	282	8.2	-
27-1700	1.7	8.3	38	6.1	8.3	1.3	113	35	4.5	<.01	276	8.1	17
28-1000	2.1	8.2	37	6.1	8.4	1.3	101	35	4.6	.12	-	7.8	14
Nov.-1967													
9-0930	2.5	8.7	36	5.9	8.7	1.3	-	37	4.4	-	259	8.0	13
14-1230	1.6	8.7	22	3.6	6.5	1.0	-	33	3.5	.35	174	7.8	14
15-0800	1.6	10.0	26	4.4	7.2	1.0	-	27	3.9	.27	205	7.8	13
15-1700	1.6	10.0	27	4.6	7.5	1.1	-	32	3.9	.26	218	7.8	14
28-1130	2.2	8.0	34	5.6	8.0	1.0	100	38	4.2	-	245	8.0	9
30-1100	2.2	9.3	20	3.5	6.5	.9	59	25	3.4	-	164	7.5	8
Dec.-1967													
2-0945	18	9.5	21	3.8	6.5	.8	66	25	3.5	-	172	-	8
2-1545	49	9.0	19	3.2	6.4	.9	53	29	3.3	-	157	7.5	9
4-1240	114	9.6	16	2.7	6.0	.8	47	19	3.1	-	131	7.4	-
4-2330	200	8.6	14	2.2	5.0	.8	41	13	3.3	-	111	7.5	-
5-1045	123	10.0	15	2.5	5.4	.8	47	14	3.4	-	121	7.5	-
6-1030	56	11.0	17	3.0	5.9	.9	55	17	3.4	-	137	7.6	-
8-1030	72	11.4	16	2.9	5.7	.9	-	15	-	-	-	-	-
18-1600	-	10.0	19	3.4	6.8	.8	-	20	-	-	-	-	-
Jan.-1968													
5-1500	7.7	10.0	24	4.3	6.9	.8	-	22	-	-	-	-	7
11-1400	91	9.6	12	2.1	4.4	.8	-	9	4.0	-	-	-	8
13-1330	113	12.4	19	3.5	6.3	.8	-	15	4.3	-	-	-	10
15-0900	656	10.2	10	1.7	4.0	.8	-	7	3.1	-	-	-	11
16-1000	230	12.2	14	2.6	5.3	.8	-	10	3.8	-	-	-	10
17-1400	134	12.2	14	2.5	5.0	.9	-	11	3.4	-	-	-	9
18-1030	93	12.1	14	2.6	5.0	.8	-	11	3.4	-	-	-	8
22-1400	37	12.4	17	3.3	5.8	.8	-	14	3.5	-	-	-	10
23-1430	32	12.0	18	3.4	5.8	.8	-	15	3.4	-	-	-	9
Feb.-1968													
4-1400	133	12.9	13	2.5	5.1	.8	-	10	3.4	-	-	-	10
9-1200	41	12.5	17	3.3	5.7	.8	-	12	3.4	-	-	-	12
17-1400	65	11.6	17	3.1	5.8	.8	-	14	3.2	-	-	-	14
25-1330	116	13.1	14	2.6	5.2	.7	-	9	3.1	-	-	-	14
June-1968													
5-0930	4.0	10.3	28	4.7	-	-	-	-	3.6	-	-	-	16
17-1400	2.7	10.6	31	5.0	8.0	1.3	-	23	3.8	-	-	-	25
30-1530	2.1	10.4	33	5.3	8.2	1.4	-	24	4.8	-	-	-	24
Aug.-1968													
10-1530	1.4	8.8	35	5.6	8.7	1.3	-	29	4.8	-	-	-	25
25-1330	3.5	8.4	35	5.5	8.6	1.3	-	34	4.6	-	-	-	20
26-1030	7.5	9.3	33	5.3	9.0	1.3	-	40	5.0	-	-	-	19
27-1230	6.8	9.5	33	5.4	8.7	1.4	-	36	4.7	-	-	-	20
29-1030	3.8	9.3	36	5.7	8.7	1.4	-	36	4.6	-	-	-	21
29-2000	3.4	9.3	36	5.7	8.7	1.4	-	35	4.6	-	-	-	24
30-0930	3.1	9.2	37	5.7	8.6	1.4	-	33	4.6	-	-	-	20
30-1930	2.8	9.5	37	5.7	8.5	1.4	-	36	4.6	-	-	-	22
31-1200	2.7	9.4	37	5.8	-	-	-	36	4.6	-	-	-	22
Sept.-1968													
2-1900	2.2	9.7	38	5.9	9.0	1.4	-	35	4.7	-	-	-	24
17-1730	1.3	9.9	39	6.1	9.0	1.4	-	32	4.8	-	-	-	25
29-1445	1.0	9.5	39	6.1	8.9	1.4	-	31	5.1	-	-	-	21

Table E Discharge data for the Mattole River, 1966-67 water year [1/]

Date	Time	Discharge $m^3\ sec^{-1}$	Date	Time	Discharge $m^3\ sec^{-1}$
10-01-66	2400	0.8	10-30-66	1115	0.9
10-05-66	2400	0.8	10-31-66	2400	0.9
10-06-66	2400	0.8	11-01-66	0030	0.9
10-07-66	2400	0.8		0915	0.9
10-08-66	2400	0.8		1000	1.0
10-17-66	2400	0.8	11-03-66	2400	1.0
10-18-66	2400	0.8	11-04-66	0045	1.0
10-19-66	2400	0.8		0830	1.0
10-21-66	0030	0.8		0915	1.0
	0915	0.8		1400	1.0
	0945	0.8		1430	0.9
10-22-66	0730	0.8		2015	0.9
	0800	0.9		2100	1.0
	0945	0.9		2400	1.0
	1015	0.9	11-05-66	2400	1.0
	1145	0.9	11-06-66	0045	1.0
	1215	0.9		0300	1.0
	1430	0.9		0345	1.0
	1515	1.0		0545	1.1
	1945	1.0		0645	1.1
	2030	1.0		0745	1.1
	2400	1.0		0900	1.1
10-23-66	0045	1.0		1245	1.2
	0430	1.0		1615	1.2
	0515	1.0		2300	1.2
10-24-66	1015	1.0		2400	1.2
	1100	1.0	11-07-66	0230	1.2
10-25-66	2400	1.0		0430	1.3
10-27-66	1445	1.0		0500	1.3
	1515	1.0		0745	1.3
	1630	1.0		0815	1.4
	1715	1.0		1315	1.4
	1745	0.9		1345	1.3
	2400	0.9		2115	1.3
10-28-66	0030	0.9		2145	1.4
	0730	0.9	11-08-66	0900	1.4
	0800	0.9		0930	1.3
	0915	0.9		1445	1.3
	0945	0.9		1515	1.3
	1730	0.9		2215	1.3
	1800	0.9		2400	1.2

[1/] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table E Discharge data for the Mattole River, 1966-67 water year [1/]
(con't)

Date	Time	Discharge $m^3\ sec^{-1}$	Date	Time	Discharge $m^3\ sec^{-1}$
11-09-66	0445	1.3	11-14-66	0415	205.0
	1545	1.2		0430	205.0
	1715	1.2		1315	170.0
	2400	1.2		1930	155.0
11-10-66	1300	1.2		2400	180.0
	2400	1.2	11-15-66	0500	135.0
11-11-66	1700	2.4		0900	155.0
	1745	2.5		1145	185.0
	2145	2.9		1215	300.0
	2300	3.1		1230	210.0
	2400	3.7		1245	255.0
11-12-66	0015	3.9		1345	285.0
	0145	5.4		1600	295.0
	0200	6.5		1945	275.0
	0215	8.2		2200	300.0
	0245	10.0		2315	315.0
	0315	12.0		2330	310.0
	0400	12.0		2400	310.0
	0500	13.0	11-16-66	0015	305.0
	0530	15.0		0645	220.0
	0630	20.0		1100	190.0
	0745	22.0		1645	125.0
	0900	25.0		2400	89.0
	0945	30.0	11-17-66	0830	46.0
	1045	38.0		1815	46.0
	1215	42.0		2400	45.0
	1445	43.0	11-18-66	1315	46.0
	1545	42.0		2130	43.0
	2345	33.0		2330	46.0
	2400	33.0		2400	48.0
11-13-66	0015	30.0	11-19-66	0115	55.0
	0330	30.0		0530	130.0
	0445	31.0		0900	180.0
	0615	39.0		1115	195.0
	0715	49.0		1215	215.0
	0830	63.0		1230	235.0
	1115	85.0		1345	260.0
	1400	95.0		1615	285.0
	1700	120.0		1630	270.0
	1845	135.0		2400	265.0
	2100	165.0	11-20-66	0400	260.0
	2400	185.0		0745	275.0

[1/] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table E Discharge data for the Mattole River, 1966-67 water year [1/]
(con't)

Date	Time	Discharge $m^3 sec^{-1}$	Date	Time	Discharge $m^3 sec^{-1}$
11-20-66	0900	310.0	12-01-66	1130	235.0
	1200	335.0		1315	230.0
	1330	370.0		2000	185.0
	1600	345.0		2400	170.0
	1830	340.0	12-02-66	0015	No Data
	2200	310.0		1230	No Data
	2400	300.0		1245	260.0
11-21-66	0615	240.0		1430	270.0
	0800	240.0		1645	265.0
	0830	230.0		2400	245.0
	1930	230.0	12-03-66	1015	230.0
	2400	235.0		1430	230.0
11-22-66	1415	165.0		1900	250.0
	2400	130.0		2230	265.0
11-23-66	1515	110.0		2245	265.0
	2400	93.0		2400	260.0
11-24-66	1730	72.0	12-04-66	0530	280.0
	2400	67.0		0745	330.0
11-25-66	2145	54.0		1030	395.0
	2400	53.0		1345	450.0
11-27-66	0030	50.0		1515	510.0
	2400	44.0		1630	620.0
11-28-66	1045	43.0		1800	825.0
	1500	46.0		2000	1080.0
	1830	54.0		2100	1180.0
	2230	70.0		2230	1200.0
	2400	73.0		2345	1180.0
11-29-66	0045	76.0		2400	1180.0
	0400	78.0	12-05-66	0015	1170.0
	0530	77.0		0315	910.0
	1800	63.0		0800	640.0
	2400	60.0		1045	520.0
11-30-66	0045	58.0		1345	450.0
	1730	52.0		2215	340.0
	2130	53.0		2230	345.0
	2330	59.0		2400	325.0
	2400	61.0	12-06-66	0600	240.0
12-01-66	0200	73.0		1115	210.0
	0230	82.0		1615	205.0
	0345	120.0	12-07-66	0045	205.0
	0500	155.0		0100	205.0
	0700	215.0		0130	180.0
	0845	235.0		0345	165.0

[1/] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table E Discharge data for the Mattole River, 1966-67 water year [1/]
(con't)

Date	Time	Discharge $m^3 sec^{-1}$	Date	Time	Discharge $m^3 sec^{-1}$
12-07-66	1515	140.0	12-30-66	2400	23.0
	2400	135.0	12-31-66	2400	21.0
12-08-66	0045	135.0	01-01-67	2400	19.0
	2400	100.0	01-02-67	2400	17.0
12-09-66	1930	87.0	01-03-67	2400	16.0
	2400	92.0	01-04-67	2400	16.0
12-10-66	0445	110.0	01-05-67	2400	16.0
	0830	110.0	01-06-67	2400	14.0
	0915	110.0	01-07-67	2400	14.0
	1630	97.0	01-08-67	2400	12.0
	2400	88.0	01-09-67	2400	12.0
12-11-66	1100	81.0	01-10-67	2400	12.0
	1545	88.0	01-11-67	2400	12.0
	1830	100.0	01-12-67	2400	11.0
	2400	110.0	01-13-67	2400	11.0
12-12-66	0430	115.0	01-14-67	2400	11.0
	0530	115.0	01-15-67	2400	10.0
	2400	105.0	01-16-67	2400	10.0
12-13-66	0815	110.0	01-17-67	2400	10.0
	1130	120.0	01-18-67	2400	9.0
	1500	155.0	01-19-67	0715	8.0
	1515	155.0		1745	8.0
	1815	150.0		2015	9.0
	2400	140.0		2245	11.0
12-14-66	2400	110.0		2400	12.0
12-15-66	2400	90.0	01-20-67	0200	20.0
12-16-66	2400	75.0		0245	23.0
12-17-66	2400	64.0		0300	32.0
12-18-66	2400	56.0		0315	39.0
12-19-66	2400	48.0		0530	66.0
12-20-66	2400	44.0		0830	82.0
12-21-66	2400	39.0		1300	98.0
12-22-66	2400	36.0		1530	110.0
12-23-66	1730	41.0		2200	155.0
	2100	42.0		2400	160.0
	2400	42.0	01-21-67	0600	170.0
12-24-66	2400	33.0		1045	200.0
12-25-66	2400	31.0		1130	210.0
12-26-66	2400	28.0		1345	210.0
12-27-66	2400	27.0		1745	205.0
12-28-66	2400	25.0		2400	180.0
12-29-66	2400	24.0	01-22-67	1330	125.0

[1/] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table E Discharge data for the Mattole River, 1966-67 water year[1]
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
01-22-67	2000	115.0	01-30-67	0015	355.0
	2400	110.0		0830	285.0
01-23-67	1400	105.0		1015	290.0
	2400	94.0		1300	335.0
01-24-67	0530	95.0		1530	350.0
	1145	110.0		1915	330.0
	1730	125.0		2230	340.0
	2400	130.0		2400	355.0
01-25-67	0045	130.0	01-31-67	0115	360.0
	2300	115.0		0245	350.0
	2400	115.0		1715	270.0
01-26-67	0515	125.0		2400	240.0
	0730	140.0	02-01-67	0915	205.0
	0915	190.0		2400	160.0
	0930	205.0	02-02-67	1100	140.0
	1230	295.0		2400	120.0
	1430	315.0	02-03-67	2400	95.0
	1600	320.0	02-04-67	2400	78.0
	1830	315.0	02-05-67	1715	67.0
	2345	305.0		1900	65.0
	2400	305.0		2115	68.0
01-27-67	0345	455.0		2400	65.0
	0445	500.0	02-06-67	2400	57.0
	0700	490.0	02-07-67	2400	51.0
	0945	510.0	02-08-67	2400	46.0
	1345	590.0	02-09-67	2400	41.0
	1700	660.0	02-10-67	2400	38.0
	1900	730.0	02-11-67	2400	35.0
	2145	790.0	02-12-67	2400	32.0
	2230	800.0	02-13-67	2400	33.0
	2400	800.0	02-14-67	0600	34.0
01-28-67	0045	790.0		0845	35.0
	0845	720.0		0915	35.0
	1545	550.0		2045	30.0
	2245	490.0		2400	29.0
	2400	510.0	02-15-67	0515	28.0
01-29-67	0215	600.0		1430	32.0
	0430	710.0		2215	34.0
	0545	740.0		2400	33.0
	0645	740.0	02-16-67	1400	29.0
	1030	650.0		2400	28.0
	1545	490.0	02-17-67	0930	26.0
	2145	390.0		2400	25.0
	2400	360.0	02-18-67	2400	24.0

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Table E Discharge data for the Mattole River, 1966-67 water year[1]
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
02-19-67	2400	22.0	03-16-67	0215	220.0
02-20-67	2400	20.0		0300	260.0
02-21-67	2400	19.0		0615	540.0
02-22-67	2400	18.0		0745	570.0
02-23-67	2400	17.0		0930	540.0
02-24-67	2400	17.0		1615	380.0
02-25-67	2400	16.0		2400	275.0
02-26-67	2400	15.0	03-17-67	0530	200.0
02-27-67	2400	14.0		1815	185.0
02-28-67	2400	13.0		2130	180.0
03-01-67	2400	13.0		2400	150.0
03-02-67	2400	12.0	03-18-67	0530	130.0
03-03-67	2400	11.0		2200	97.0
03-04-67	2400	10.0		2400	94.0
03-05-67	2400	9.9	03-19-67	1815	73.0
03-06-67	2400	9.3		2145	76.0
03-07-67	2400	8.8		2400	87.0
03-08-67	2400	8.5	03-20-67	0530	145.0
03-09-67	1845	8.5		0745	150.0
03-10-67	2400	9.7		0830	150.0
03-10-67	0330	14.0		2400	130.0
	0645	17.0	03-21-67	2400	92.0
	1015	22.0	03-22-67	1815	76.0
	1145	26.0		2245	84.0
	1445	37.0		2400	91.0
	2030	58.0	03-23-67	0215	98.0
	2400	72.0		0245	98.0
03-11-67	0345	80.0		1930	75.0
	0630	80.0		1400	71.0
	0815	77.0	03-24-67	2200	60.0
	1945	61.0		2400	59.0
	2400	58.0	03-25-67	2400	46.0
03-12-67	1145	57.o	03-26-67	2400	40.0
	2400	68.0	03-27-67	2400	32.0
03-13-67	1500	76.0	03-28-67	0815	35.0
	2400	88.0		1715	40.0
03-14-67	1515	98.0		2400	39.0
	1815	115.0	03-29-67	2400	33.0
	2400	160.0	03-30-67	0515	37.0
03-15-67	0345	180.0		0730	41.0
	0845	180.0		1000	52.0
	1230	175.0		1215	65.0
	2045	160.0		1500	68.0
	2400	170.0		1900	73.0
				2400	84.0

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[1] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table E Discharge data for the Mattole River, 1966-67 water year [1/] (con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
03-31-67	0800	92.0	04-21-67	0245	77.0
	1945	100.0		1500	72.0
	2400	100.0		2400	67.0
04-01-67	0545	100.0	04-22-67	2400	60.0
	0800	100.0	04-23-67	0745	61.0
	2400	87.0		1245	60.0
04-02-67	2400	71.0		2400	58.0
04-03-67	2400	61.0	04-24-67	2400	51.0
04-04-67	2400	52.0	04-25-67	2400	46.0
04-05-67	1015	54.0	04-26-67	1415	44.0
	2400	62.0		2400	47.0
04-06-67	0630	70.0	04-27-67	1430	51.0
	1330	73.0		2015	51.0
	2400	70.0		2400	50.0
04-07-67	2400	61.0	04-28-67	1745	49.0
04-08-67	2400	53.0		2400	47.0
04-09-67	2400	47.0	04-29-67	2400	43.0
04-10-67	1045	47.0	04-30-67	2400	40.0
	1500	53.0	05-01-67	2400	37.0
	2000	67.0	05-02-67	2400	34.0
	2400	70.0	05-03-67	2400	31.0
04-11-67	0245	71.0	05-04-67	2400	29.0
	0545	69.0	05-05-67	2400	27.0
	2400	58.0	05-06-67	2400	25.0
04-12-67	2400	52.0	05-07-67	2400	23.0
04-13-67	1415	50.0	05-08-67	2400	22.0
	2400	60.0	05-09-67	2400	26.0
04-14-67	1100	59.0	05-10-67	0515	28.0
	2400	54.0		1315	29.0
04-15-67	1245	57.0		1330	29.0
	2400	53.0		2400	28.0
04-16-67	1645	51.0	05-11-67	0715	28.0
	2115	55.0		1545	30.0
	2400	64.0		2000	30.0
04-17-67	0530	87.0		2400	30.0
	1045	97.0	05-12-67	2400	25.0
	2400	105.0	05-13-67	2400	23.0
04-18-67	0515	105.0	05-14-67	2400	22.0
	1130	99.0	05-15-67	2400	21.0
	2400	92.0	05-16-67	2400	20.0
04-19-67	2400	76.0	05-17-67	2400	19.0
04-20-67	0900	75.0	05-18-67	2400	18.0
	2400	77.0	05-19-67	2400	17.0

[1/] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table E Discharge data for the Mattole River, 1966-67 water year [1/] (con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
05-20-67	2400	16.0	07-09-67	2400	2.8
05-21-67	2400	15.0	07-10-67	2400	2.7
05-23-67	2400	15.0	07-11-67	2400	2.7
05-24-67	2400	15.0	07-12-67 [2/]	1200	No Data
05-25-67	2400	13.0	07-13-67	1200	No Data
05-26-67	2400	12.0	07-14-67	1200	No Data
05-27-67	2400	12.0	07-15-67	1200	No Data
05-28-67	2400	12.0	07-16-67	1200	No Data
05-29-67	2400	11.0	07-17-67	1200	No Data
05-30-67	2400	10.0	07-18-67	1200	No Data
05-31-67	2400	9.7	07-19-67	1200	No Data
06-02-67	2400	9.6	07-20-67	1200	No Data
06-03-67	2400	9.1	07-21-67	1200	No Data
06-04-67	2400	8.2	07-22-67	1200	No Data
06-06-67	2400	7.5	07-23-67	1200	No Data
06-08-67	2400	7.1	07-24-67	1200	No Data
06-10-67	2400	6.7	07-25-67	1200	No Data
06-11-67	2400	6.3	07-26-67	1200	No Data
06-12-67	2400	6.2	07-27-67	1200	No Data
06-13-67	2400	5.8	07-28-67	2400	1.9
06-14-67	2400	5.7	07-29-67	2400	1.8
06-15-67	2400	5.5	07-30-67	2400	1.7
06-17-67	2400	5.5	07-31-67	2400	1.7
06-18-67	2400	5.3	08-01-67	2400	1.6
06-19-57	2400	5.2	08-02-67	2400	1.6
06-20-67	2400	4.9	08-03-67	2400	1.5
06-21-67	2400	4.6	08-04-67	2400	1.4
06-22-67	2400	4.6	08-06-67	2400	1.4
06-23-67	2400	4.3	08-07-67	2400	1.4
06-24-67	2400	4.1	08-10-67	2400	1.4
06-25-67	2400	4.1	08-11-67	2400	1.3
06-25-67	2400	4.0	08-17-67	2400	1.3
06-26-67	2400	4.0	08-18-67	2400	1.3
06-27-67	2400	3.8	08-25-67	2400	1.3
06-28-67	2400	3.7	08-27-67	2400	1.2
06-29-67	2400	3.4	08-31-67	2400	1.2
06-30-67	2400	3.5	09-03-67	2400	1.2
07-01-67	2400	3.3	09-04-67	2400	1.2
07-02-67	2400	3.2	09-06-67	2400	1.2
07-03-67	2400	3.0	09-07-67	2400	1.1
07-04-67	2400	2.9	09-10-67	2400	1.1
07-05-67	2400	2.9	09-11-67	2400	1.1
07-06-67	2400	2.8	09-12-67	2400	1.0

[1/] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

[2/] 07-12-67 to 07-27-67 - missing records. No rainfall.

Table E Discharge data for the Mattole River, 1966-67 water year [1]
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
09-16-67	2400	1.0			
09-17-67	0730	1.1			
	1930	1.1			
	2400	1.1			
09-18-67	0230	1.2			
	0645	1.2			
	1130	1.2			
	1945	1.2			
	2400	1.2			
09-19-67	0830	1.2			
	1000	1.2			
	1415	1.2			
	1800	1.2			
	2345	1.1			
	2400	1.1			
09-20-67	0600	1.1			
	1215	1.0			
	2400	1.0			
09-21-67	1130	1.0			
	2400	1.0			
09-23-67	2400	1.1			
09-24-67	0100	1.1			
	0900	1.1			
	2400	1.2			
09-27-67	2400	1.2			
09-28-67	0130	1.2			
	0615	1.2			
	2400	1.2			
09-29-67	2045	1.1			
09-30-67	2400	1.1			

[1] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table F Discharge data for the Mattole River, 1967-68 water year [1]

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
10-01-67	1215	1.1	10-08-67	0630	2.1
	1330	1.2		1115	3.0
	2015	1.2		1700	2.8
	2400	1.2		2400	2.7
10-02-67	0215	1.2	10-09-67	0245	2.6
	0445	1.3		0615	2.5
	0730	1.3		1000	2.5
	0830	1.4		1830	2.4
	1030	1.5		2400	2.3
	1145	1.8	10-10-67	0315	2.2
	1245	2.3		0900	2.1
	1415	3.7		1600	2.0
	1500	4.4		2400	1.9
	1600	5.4	10-11-67	0330	1.9
	1700	7.5		2400	1.8
	1800	11.0	10-12-67	2400	1.7
	2015	20.0	10-13-67	2400	1.7
	2130	23.0	10-14-67	2400	1.6
	2400	23.0	10-17-67	2400	1.5
10-03-67	0230	24.0	10-20-67	2400	1.5
	0400	24.0	10-21-67	0715	1.6
	0445	23.0		1400	1.7
	1200	16.0		1715	1.8
	1815	12.0		2045	1.9
	2400	9.0		2400	1.9
10-04-67	0645	6.7	10-22-67	0130	2.0
	1215	5.5		0500	2.1
	1545	4.9		1000	2.3
	2030	4.8		1800	2.5
	2400	5.3		2100	2.7
10-05-67	0430	6.3	10-23-67	0015	2.7
	0700	7.3		0615	2.8
	1015	9.4		2230	2.8
	1400	9.7	10-24-67	0200	2.5
	2145	9.1		1045	2.3
	2400	8.6		2400	2.1
10-06-67	1015	6.7	10-25-67	0300	1.9
	1645	5.7		2400	1.8
	2400	4.9	10-27-67	2400	1.7
10-07-67	0945	4.2	10-28-67	0100	1.8
	1545	3.8		0515	2.0
	2400	3.4		1400	2.3
10-08-67	0230	3.3		1430	2.2
				2400	2.3

[1] Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonablly detailed hydrograph.

Table F Discharge data for the Mattole River, 1967-68 water year 1/
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
10-29-67	0430	2.3	11-14-67	0045	21.0
	1030	2,2		0100	25.0
	1400	2.3		0115	26.0
	2400	2.3		0130	29.0
10-30-67	1330	2.2		0215	31.0
	2400	2.0		0245	35.0
10-31-67	2400	1.8		0330	46.0
11--1-67	2400	1.7		0400	53.0
11-02-67	2400	1.6		0430	60.0
11-04-67	2400	1.6		0545	63.0
11-05-67	2400	1.7		0700	63.0
11-06-67	2400	1.6		0800	58.0
11-07-67	2400	1.5		0915	61.0
11-08-67	0545	1.7		1100	65.0
	1300	2.0		1345	50.0
	1600	2.2		1545	46.0
	1815	2.8		1730	39.0
	1915	3.0		1900	35.0
	2015	3.3		2015	32.0
	2130	3.9		2400	24.0
	2230	4.3	11-15-67	0100	23.0
11-09-67	0315	4.3		0200	21.0
	0330	4.1		0345	19.0
	0730	3.7		0900	16.0
	0945	3.5		1345	14.0
	2400	3.3		1645	13.0
11-10-67	0745	3.0		2000	11.0
	2400	2.7		2245	11.0
11-11-67	2400	2.3		2400	10.0
11-12-67	2400	2.2	11-16-67	0415	9.4
11-13-67	1615	2.0		1200	8.5
	1630	2.1		1730	7.7
	1715	2.2		2400	7.0
	1830	2.6	11-17-67	0400	6.6
	1930	3.2		1415	6.0
	2000	3.9		2100	5.7
	2030	4.5		2400	5.5
	2115	6.3	11-18-67	0645	5.2
	2130	7.0		2400	4.8
	2230	9.2	11-19-67	1200	4.3
	2300	11.0		2400	4.2
	2315	13.0	11-20-67	0230	4.0
	2400	16.0		1015	3.9
11-14-67	0030	19.0		2400	3.7

1/ Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table F Discharge data for the Mattole River, 1967-68 water year 1/
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
11-21-67	1415	3.5	12-02-67	0915	18.0
	2400	3.3		1145	24.0
11-22-67	2400	3.1		1230	27.0
11-23-67	2400	3.0		1400	37.0
11-24-67	2400	2.9		1530	48.0
11-25-67	2400	2.7		1730	59.0
11-26-67	2400	2.5		2400	64.0
11-27-67	1430	2.5	12-03-67	0215	71.0
	1445	2.7		0615	70.0
	1700	2.9		1500	67.0
	2400	3.0		1515	77.0
11-28-67	1000	3.0		1915	77.0
	1015	3.6		2200	71.0
	2400	3.6		2400	63.0
11-29-67	0430	3.6	12-04-67	1245	115.0
	0530	5.0		1445	165.0
	0600	6.0		1730	225.0
	0630	7.6		1830	260.0
	0715	13.0		1900	265.0
	0815	17.0		1930	260.0
	0930	26.0		2400	195.0
	1000	34.0	12-05-67	0245	170.0
	1100	39.0		0630	145.0
	1215	56.0		1000	125.0
	1315	65.0		1845	90.0
	1415	65.0		2245	80.0
	1530	61.0		2300	75.0
	1630	53.0		2400	75.0
	1800	62.0	12-06-67	0330	70.0
	1900	62.0		1130	55.0
	1945	57.0		1745	50.0
	2115	50.0		1915	50.0
	2400	40.0		2045	60.0
11-30-67	0115	37.0		2400	115.0
	1330	29.0	12-07-67	0100	140.0
	1745	31.0		0315	165.0
12-01-67	0315	28.0		0530	150.0
	0800	26.0		1215	130.0
	1300	23.0		2400	90.0
	1815	20.0	12-08-67	1500	70.0
	2400	18.0		2400	55.0
12-02-67	0815	16.0	12-09-67	0630	50.0
	0830	17.0		2400	40.0

1/ Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

Table F___ Discharge data for the Mattole River, 1967-68 water year 1/
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
12-10-67	2400	32.0	01-11-68	0600	115.0
12-11-67	2400	No Data 2/		1215	96.0
12-12-67	2400	No Data		2400	75.0
12-13-67	2400	No Data	01-12-68	0915	65.0
12-14-67	2400	No Data		2000	78.0
12-15-67	2400	No Data		2400	61.0
12-16-67	2400	No Data	01-13-68	0145	66.0
12-17-67	2400	No Data		0400	83.0
12-18-67	2400	No Data		0900	115.0
12-19-67	2400	No Data		1045	115.0
12-20-67	2400	No Data		2030	120.0
12-21-67	2400	No Data		2215	135.0
12-22-67	2400	No Data		2400	165.0
12-23-67	2400	No Data	01-14-68	0130	200.0
12-24-67	2400	No Data		0415	285.0
12-25-67	2400	No Data		0600	380.0
12-26-67	2400	No Data		0730	490.0
12-27-67	2400	No Data		1015	580.0
12-28-67	2400	No Data		1500	640.0
12-29-67	2400	No Data		1600	630.0
12-30-67	2400	No Data		1700	650.0
12-31-67	2400	No Data		2045	830.0
01-01-68	2400	No Data		2245	910.0
01-02-68	2400	No Data		2400	930.0
01-03-68	2400	7.7	01-15-68	0045	950.0
01-05-68	2400	7.4		0115	950.0
01-08-68	1030	7.4		0345	880.0
	2400	8.0		0700	750.0
01-09-68	0600	9.0		1045	590.0
	1200	15.0		1515	440.0
	1415	45.0		1745	390.0
	1500	34.0		2200	320.0
	1545	55.0		2400	290.0
	1615	76.0	01-16-68	0515	265.0
	2000	275.0		0915	235.0
	2045	315.0		1630	200.0
	2230	350.0		2400	170.0
	2330	355.0	01-17-68	0930	145.0
	2400	350.0		2400	110.0
01-10-68	0230	340.0	01-18-68	0630	100.0
	0730	285.0		1830	85.0
	0930	240.0		2400	80.0
	1445	190.0	01-19-68	0945	68.0
	2045	160.0		2400	60.0
	2400	140.0	01-20-68	1515	53.0

1/ Discharge should be assumed constant or changing at a uniform rate between data points unless otherwise noted. Enough information is presented to permit construction of a reasonably detailed hydrograph.

2/ Data missing. 5.4 cm rain fell.

Table F___ . Discharge data for the Mattole River, 1967-68 water year 1/
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
01-20-68	2400	49.0	02-03-68	0200	230.0
01-21-68	1145	45.0		0300	225.0
	2400	40.0		1445	185.0
01-22-68	2400	35.0		1815	175.0
01-23-68	2400	30.0		2400	165.0
01-24-68	2400	26.0	02-04-68	0845	140.0
01-25-68	2400	24.0		2400	110.0
01-26-68	2400	23.0	02-05-68	2400	84.0
01-27-68	2400	20.0	02-06-68	2400	67.0
01-28-68	1130	20.0	02-07-68	2400	53.0
	1200	20.0	02-08-68	2400	45.0
	1345	22.0	02-09-68	2400	38.0
	1600	22.0	02-10-68	2400	33.0
	1615	28.0	02-11-68	2400	30.0
	1645	29.0	02-12-68	2400	26.0
	1715	33.0	02-13-68	2400	24.0
	1815	42.0	02-14-68	2400	21.0
	1900	58.0	02-15-68	2400	18.0
	2045	87.0	02-16-68	2400	21.0
	2400	87.0	02-17-68	0630	26.0
01-29-68	0400	87.0		0815	29.0
	0830	89.0		0945	39.0
	1445	84.0		1145	54.0
	1545	93.0		1415	65.0
	1700	110.0		1545	61.0
	1930	125.0		2000	60.0
	1945	175.0		2400	50.0
	2230	195.0	02-18-68	0415	43.0
	2400	195.0		2400	35.0
01-30-68	0630	160.0	02-19-68	0815	36.0
	1330	135.0		1315	42.0
	2400	115.0		1530	50.0
01-31-68	0630	100.0		1630	62.0
	2400	95.0		1800	84.0
02-01-68	1500	85.0		1915	120.0
	2400	90.0		2100	160.0
02-02-68	0530	105.0		2400	180.0
	0715	120.0	02-20-68	0430	240.0
	1245	145.0		0530	240.0
	1415	160.0		0900	210.0
	1530	175.0		1545	170.0
	2400	225.0		2400	150.0

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Table F Discharge data for the Mattole River, 1967-68 water year [1]
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
02-21-68	2300	220.0	03-15-68	1145	115.0
	2400	235.0		2215	100.0
02-22-68	0200	245.0		2400	105.0
	1415	220.0	03-16-68	0330	115.0
	2400	195.0		1200	160.0
02-23-68	0400	195.0		2400	140.0
	0800	200.0	03-17-68	2400	120.0
	0930	210.0	03-18-68	2400	93.0
	1445	210.0	03-19-68	2400	73.0
	1715	205.0	03-20-68	2400	58.0
	2400	190.0	03-21-68	2400	48,0
02-24-68	2400	140.0	03-22-68	2400	45.0
02-25-68	1030	120.0	03-24-68	2400	33.0
	2400	105.0	03-25-68	0415	39.0
02-26-68	0600	96.0		0645	47.0
	2400	83.0		0915	57.0
02-27-68	2400	68.0		1100	66.0
02-28-68	2400	56.0		1730	64.0
02-29-68	2400	47.0		2400	52.0
03-01-68	2400	42.0	03-26-68	2400	40.0
03-02-68	2400	37.0	03-27-68	2400	35.0
03-03-68	2400	34.0	03-28-68	2400	31.0
03-04-68	2400	32.0	03-29-68	2400	28.0
03-05-68	1430	36.0	03-30-68	2400	26.0
03-05-68	2400	33.0	03-31-68	2400	23.0
03-06-68	2400	28.0	04-02-68	2400	19.0
03-07-68	2400	28.0	04-04-68	2400	17.0
03-08-68	2400	25.0	04-07-68	2400	14.0
03-09-68	2400	23.0	04-10-68	2400	13.0
03-11-68	2400	19.0	04-12-68	2400	12.0
03-12-68	0130	19.0	04-17-68	2400	9.7
	0515	23.0	04-20-68	2400	8.6
	0915	41.0	04-25-68	2400	7.4
	1030	63.0	04-30-68	2400	6.3
	1545	115.0	05-05-68	2400	5.4
	1815	120.0	05-10-68	2400	4.9
	2015	110.0	05-12-68	2400	4.8
	2400	89.0	05-13-68	0545	4.9
03-13-68	0930	65.0		1345	5.1
	1300	67.0		1800	5.4
	2045	93.0		2400	5.5
	2400	120.0	05-14-68	1400	5.5
03-14-68	1300	140.0		1915	5.3
	1400	130.0		2400	5.0

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Table F Discharge data for the mattole River, 1967-68 water year [1]
(con't)

Date	Time	Discharge m^3 sec^{-1}	Date	Time	Discharge m^3 sec^{-1}
05-15-68	2400	4.6	07-25-68	2400	1.5
05-16-68	2400	4.4	07-30-68	2400	1.5
05-18-68	2400	4.3	08-05-68	2400	1.3
05-19-68	0930	4.0	08-10-68	2400	1.4
	0945	4.3	08-13-68	2400	1.5
	1700	5.7	08-14-68	2400	1.6
	1945	6.5	08-15-68	2400	1.6
	2400	7.3	08-16-68	2400	1.6
05-20-68	1615	7.9	08-19-68	2400	1.7
	1745	7.6	08-20-68	0400	2.0
	2400	7.1		0615	2.4
05-21-68	1045	7.0		0815	2.9
	1145	7.2		1800	4.2
	1645	8.5		2230	6.9
	2145	8.3		2400	8.3
	2400	9.1	08-21-68	0330	9.4
05-22-68	2400	6.5		0830	8.0
05-23-68	2400	5.6		2400	4.8
05-25-68	1530	5.0	08-22-68	0545	4.3
	2400	5.2		1745	3.7
05-25-68	0900	6.1		2400	3.2
	2400	8.1	08-23-68	1130	2.9
05-26-68	0400	8.1		2400	2.5
	2400	6.9	08-24-68	2400	2.1
05-27-68	2400	5.9	08-25-68	0100	2.2
05-28-68	2400	5.4		0830	2.5
05-31-68	2400	4.4		1145	3.1
06-05-68	2400	3.9		1515	4.0
06-10-68	2400	3.3		2400	7.9
06-12-68	2400	3.1	08-26-68	1230	7.8
06-15-68	2400	2.8		2400	7.7
06-20-68	2400	2.4	08-27-68	1000	7.0
06-25-68	2400	2.0		2400	5.8
06-26-68	2400	1.9	08-28-68	1600	4.8
06-27-68	2400	2.1		2400	4.2
06-28-68	1545	2.4	08-29-68	2400	3.3
	2400	2.0	08-30-68	2400	2.7
06-29-68	2400	2.1	09-02-68	2400	2.1
07-01-68	2400	2.1	09-05-68	2400	1.8
07-03-68	2400	1.9	09-10-68	2400	1.6
07-05-68	2400	1.8	09-15-68	2400	1.5
07-10-68	2400	1.6	09-20-68	2400	1.2
07-15-68	2400	1.7	09-25-68	2400	1.1
07-20-68	2400	1.5	09-30-68	2400	1.0

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