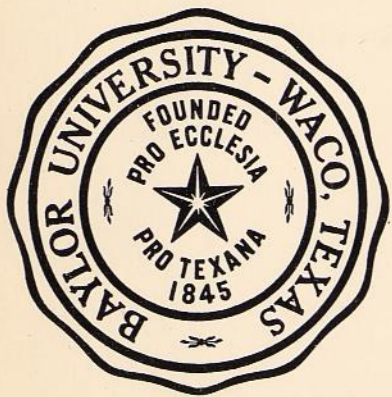


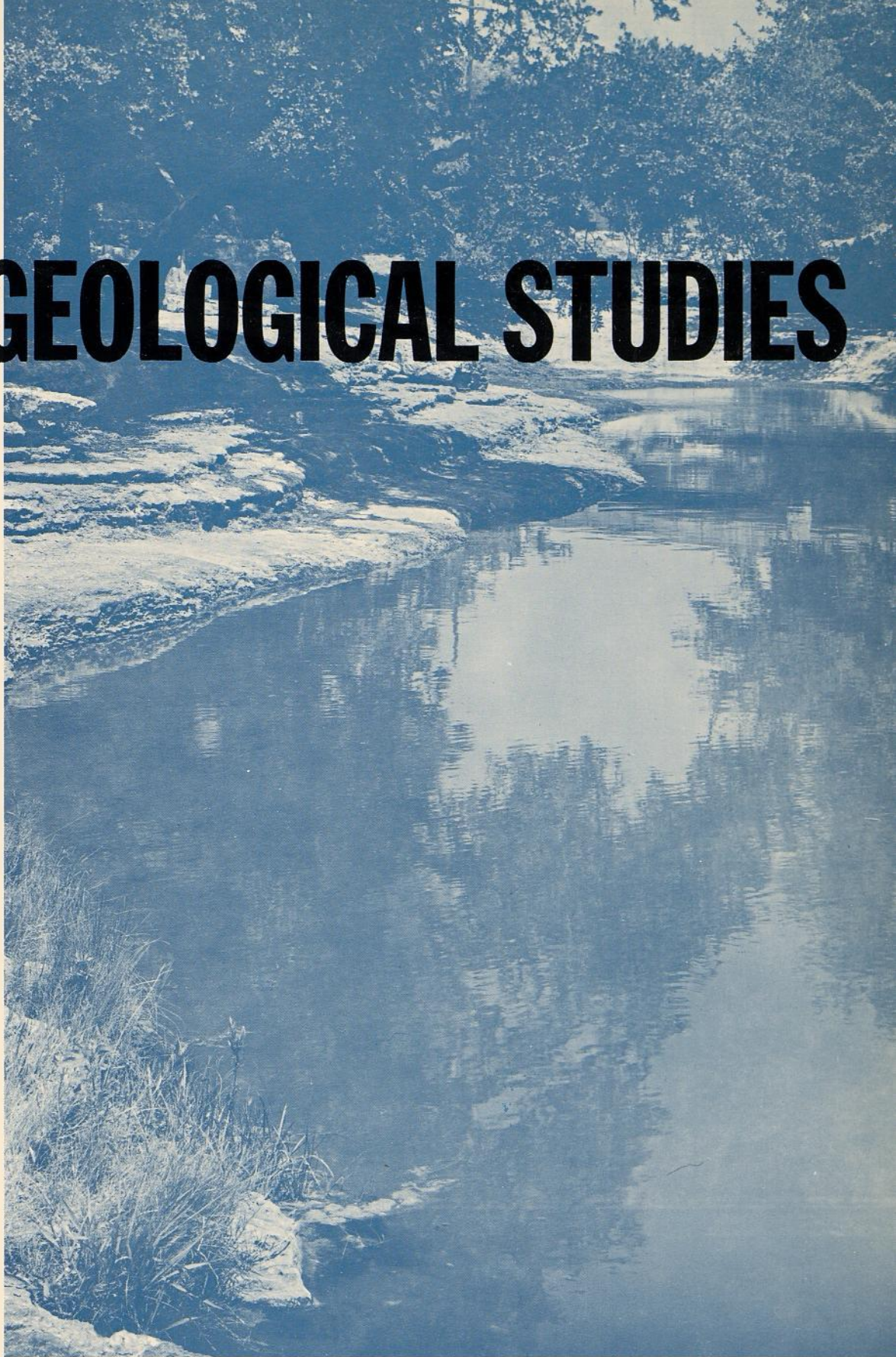
BAYLOR GEOLOGICAL STUDIES

SPRING 1970
Bulletin No. 18



*Water Geochemistry, Hog Creek Basin,
Central Texas*

THOMAS H. MOORE



*"Creative thinking is more important
than elaborate equipment--"*

FRANK CARNEY, PH.D.
PROFESSOR OF GEOLOGY
BAYLOR UNIVERSITY
1929-1934

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BAYLOR GEOLOGICAL STUDIES

BULLETIN NO. 18

**Water Geochemistry, Hog Creek Basin
Central Texas**

THOMAS H. MOORE

**BAYLOR UNIVERSITY
Department of Geology
Waco, Texas
Spring, 1970**

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Photographs by O. T. Hayward, Department of Geology, Baylor University.

Water Geochemistry, Hog Creek Basin

Central Texas

THOMAS H. MOORE

ABSTRACT

The hydrologic system and importance of water in the chemical weathering environment can be better understood if the chemical reactions and geologic environment are studied. The area of this study encompasses parts of Hamilton, Coryell, and Bosque counties, Texas, which are drained by the portion of Hog Creek above the Texas Farm Road 217 bridge. Rocks which crop out in this area are all limestones of the Comanchean Series, Fredericksburg and Washita groups. Qualitative and quantitative chemical tests on Hog Creek water at five sampling stations as well as the geology of Hog Creek basin yield the data for this report. Ions of calcium, bicarbonate, carbonate, chloride, nitrate, phosphate, silica, and sulfate are the principal ions tested in the study.

Highest concentration of dissolved solids in the Hog Creek hydrologic system is found at Hurst Spring. The major differences in salinity at Hurst Spring are the high concentrations of calcium and bicarbonate. The high partial pressure of carbon dioxide in the Edwards Limestone aquifer causes these high concentrations. Calcium carbonate is deposited in Hog Creek as Hurst Spring water flows down the creek and the carbon dioxide partial pressure is reduced.

The Edwards Limestone, a shallow aquifer in Central Texas, is subject to pollution from fertilization of farming areas. Nitrate nitrogen, therefore, can be stored in the aquifer and released at Hurst Spring where it behaves as a cyclic element in Hog Creek.

Solubilities of chloride and sulfate are not controlled by the partial pressure of carbon dioxide. Their concentrations are dependent upon the length of time water is in contact with the rock. During periods of low flow, concentrations of chloride and sulfate increase while ions of calcium and bicarbonate decrease.

Ions of phosphate and silica are cyclic. Their concentrations vary with the life cycles of aquatic plants. Nitrate in Hog Creek originates from fertilizers but is utilized by plants in their life processes.

Highest ion concentration per unit volume is found during periods of normal flow; least is found during periods of runoff. Low flow concentration is intermediate. Since ion concentrations are fairly uniform during each of the three flow regimes, the solution load for practical purposes would be higher during periods of flood in direct proportion to the volume of water in Hog Creek.

INTRODUCTION*

The purpose of this study is to determine the change in water quality from the time it falls as rain near the headwaters of Hog Creek, Bosque County, until it becomes part of surface flow, about 19 miles downstream along the stream course of Hog Creek. Chemical tests were used to determine the quality of rainwater, spring water, and runoff. Special attention was given to waters which drain from farm lands to determine if fertilizers have any effect on the quality of water in Hog Creek. Runoff water from each of

the formations which crops out in the basin area was sampled to determine effect on the stream. The primary aquifer, the Edwards Limestone, was tested to determine chemical composition. A study of the structure of the Edwards Limestone was made to determine how large an area was drained by the aquifer to flow into Hog Creek as spring water. An effort was made to see if the length of time water remained in the aquifer had any effect on the water quality. Contributions of plants and other life on water quality were determined.

*A thesis submitted in partial fulfillment of the requirements for the M.S. degree in Geology, Baylor University, 1968.

Natural waters acquire their chemical characteristics

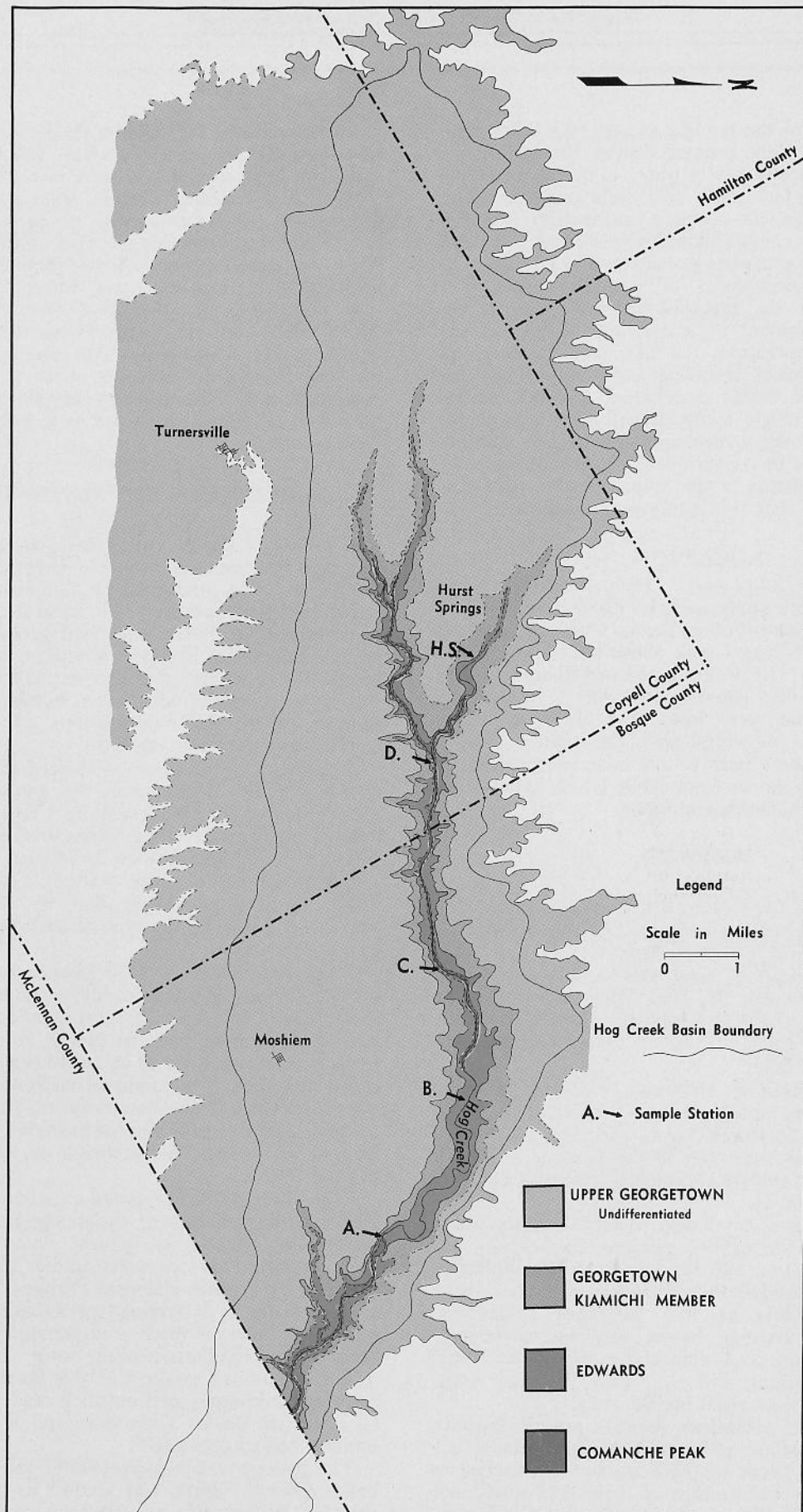


Fig. 2. Geologic map of upper Hog Creek basin, Bosque, Coryell, Hamilton, and McLennan counties, Texas. Letters designate water sampling stations.

are exposed in both Hog Creek and Meridian Creek basins; however, no attempt was made to interpret the significance of ion concentrations in Meridian Creek.

A similar study of the geology and solution load was conducted on the North Bosque River as part of a master's thesis at Baylor University by Cleo V. Proctor in 1967.* No attempt was made to interpret ion concentrations in this study.

GEOGRAPHY

REGIONAL PHYSIOGRAPHY

The Hog Creek basin of Hamilton, Coryell, and Bosque counties lies in two subprovinces of the Grand Prairie: the Lampasas Cut Plain and the Fort Worth Prairie. The Grand Prairie of Central Texas marks the eastward extremity of the Great Plains region of North America. The area is underlain by rocks of the Washita and Fredericksburg groups of the Cretaceous Series. The Grand Prairie is a belt of rolling prairie which trends north and south through North Central Texas (fig. 1).

The Grand Prairie is an area of limestone-derived soils. The surface relief ranges from gently undulating to rolling and hilly with elevations varying from 500 feet in the river valleys near the eastern margin of the Grand Prairie to over 1,200 feet at the Georgetown-capped hills. Cedar is common on the limestone-derived soils of the Edwards, Comanche Peak, and Walnut formations, while pecans and other hardwoods are native in the alluvium-filled stream valleys. The area is largely one of livestock raising; however, cropland may be found on Georgetown soils, particularly Kiamichi soils. The topography is dependent upon the depth to which streams have eroded, as well as the relative resistance of each geologic formation.

The Lampasas Cut Plain is the modified northern extension of the great Edwards Plateau. It is a highly dissected, eastward-dipping plain, which can now be recognized by the general level of its remnant summits. The summits are flat-topped hills which comprise the divides between the drainage valleys. The hills are capped with Edwards Limestone and are bordered by steep slopes formed on the Comanche Peak Limestone. The valley floors in this highly dissected region are formed on the Walnut Clay and Paluxy Sandstone.

The Fort Worth Prairie forms a belt of extensive and open prairie underlain by limestone and clays of the Georgetown Formation. The gently rolling surfaces of the prairie are developed over a large area on the same bed of rock, forming the grass-covered uplands of the Grand Prairie (Hill, 1901, pp. 77-84).

Streams in the area flow eastward down dip, cutting strata of progressively younger age. Gradients are slightly flatter than the dip of the strata (Rich, 1914, p. 470).

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This thesis was prepared under the direction and supervision of O. T. Hayward of Baylor University. Dr. J. L. McAtee, Jr., Department of Chemistry, Baylor University, reviewed the manuscript. Original figures were drafted by John D. Van Camp, and photographs were processed by William Trippet. The author wishes to thank these people for their time and encouragement.

LOCAL PHYSIOGRAPHY

The physiography of the study area is closely related to the stratigraphy and structure of the underlying formations. With the exception of alluvial deposits, all rocks cropping out in this area are of Cretaceous age. Where Hog Creek has cut through the resistant Edwards Limestone, overhanging bluffs form (fig. 3). The Edwards Limestone is by far the most prominent formation. It is preserved as a *cap rock* because of its superior hardness and resistance. Surface relief ranges from gently undulating to rolling with elevations varying from 1,200 feet in the up dip portion of the basin to 850 feet in the down dip portion north of Station A (fig. 2). Hog Creek cuts as deep as 821 feet at Station A. Total relief in the basin is 369 feet.

CLIMATE

The climate of the area lies within the modified Köppen region Caw, subtropical humid climate, characterized by a surplus of precipitation over evaporation with the wettest summer month having 10 times the precipitation of the driest winter month (Moore, 1968). Generally speaking, the climate is a combination of the humid climate of east Texas and the continental climate to the north. Normal annual precipitation is approximately 32 inches; May is the month of highest precipitation with a normal total of nearly 5 inches (U. S. Dept. of Commerce).

Normal monthly temperatures range from 48.0° F. in January to 85.5° F. in August, with a yearly normal of 67.2° F. Summers are warm, with an average of 110 days of maximum temperature above 90° F. (U. S. Dept. of Commerce). Normal annual precipitation and normal annual evaporation are equal in the study area (Visher, p. 195). More water normally enters the Edwards aquifer during the April-May period because this is the period of maximum surplus rainfall over evaporation.

DRAINAGE

The area under study is drained by Hog Creek and two of its tributaries, Hurst Creek and Live Oak Creek (fig. 2). Hurst Spring which feeds Hurst Creek is the major source of water in the Hog Creek

system. Above Station D, where Hurst Creek flows into Hog Creek, Hog Creek does not flow except for brief periods after precipitation. In the study area, Hog Creek drains an area of 48.6 square miles. The basin is linear in shape and fairly narrow—only five miles wide at its greatest width along a line northwest of Lane's Chapel to southwest of Mosheim (fig. 2). The narrowest part of the basin, at the easternmost boundary of the study, is 2.6 miles wide.

The topography in the area is gently rolling farm and grazing land which permits little runoff and promotes high infiltration. Such conditions are desirable in a water diagenesis study, because mixing of runoff with spring water is reduced to a minimum. Runoff only occurs during a brief period after heavy precipitation and can be studied separately from normal creek flow.

East of this area, Hog Creek empties into the north-eastward-flowing South Bosque River which is dammed just below its confluence with the North Bosque River to form Lake Waco. From Lake Waco, the Bosque River flows northeastward and forms an arc as it turns southward to join the Brazos River. The Brazos River flows southeastward and empties into the Gulf of Mexico near Freeport, Texas.

CULTURAL FEATURES

The only community within the upper Hog Creek basin is Mosheim (population 200). It is located 2.8 miles southwest of Station A on Farm Road 217 (fig. 2). Mosheim is a farming and livestock-raising community.

Since Mosheim is a small community, it has no municipal water or sewer system. Wells supply municipal water, and septic tanks dispose of sewage; therefore, there are no direct withdrawals or additions to Hog Creek.

Two paved roads serve the area: Farm Road 217 from Valley Mills through Mosheim and Farm Road 186 which transects the area northward through Turnersville. No railroads pass through the area.

Land in the study area is used for farming and grazing. The Kiamichi Clay member of the Georgetown Formation (fig. 2) forms a black soil of the Denton-San Saba group which supports crops of wheat, grain sorghum, oats, cotton, and corn. The Edwards Limestone and the limestone members of the Georgetown Formation have a rather poor soil cover; therefore, grazing of horses, goats, and cattle is common in the area.

GEOLOGY

The physiography of the study area is closely related to the stratigraphy and structure of the underlying formations. Rocks of the region are all part of the Lower Cretaceous Comanchean Series, Washita and Fredericksburg Groups. Excluding alluvium, Comanche Peak Limestone, Edwards Limestone, and Georgetown Limestone are the only formations that crop out in the study area (fig. 2). In this area, the strata dip slightly south of east about 20 feet per mile.

Comanche Peak Limestone crops out only along a narrow strip at the bottom of Hog Creek valley. Hog Creek flows on Comanche Peak Limestone over most of its length in the study area. Edwards Limestone forms the bluffs along the creek bank and is the most resistant of the formations which crop out in the area. The Georgetown Formation covers a large percentage of the basin and forms the gently rolling farm lands (fig. 2).

STRATIGRAPHY

COMANCHEAN SERIES

The name *Comanchean Series* was applied by R. T. Hill (1887, p. 298) to the Lower Cretaceous series of Texas. He divided it into three divisions which are, in descending order, the Washita, Fredericksburg, and Trinity. These *divisions*, which were later called *groups*, were defined by Hill on their cyclic nature. Only Fredericksburg and lower Washita rocks crop out in the study area.

Fredericksburg Group

The Fredericksburg Group was named and subdivided by R. T. Hill (1891, p. 509) when he defined the Comanchean Series. The Fredericksburg Group in Central Texas is made up of four formations. From bottom to top, these are the Paluxy Sand, the Walnut Clay, the Comanche Peak Limestone, and the Edwards Limestone. The group boundaries are fairly sharp, marked by distinct lithologic changes.

Of the four formations in the Fredericksburg Group, only the Comanche Peak Limestone and Edwards Limestone crop out in the study area.

Comanche Peak Limestone. The Comanche Peak Limestone was named by B. F. Shumard in 1860. The type locality is at Comanche Peak in central Hood County (Sellards *et al.*, 1932, p. 334).

In the study area at Station D, the Comanche Peak Formation consists of massively bedded chalky limestone which weathers to a dull grayish-white color and becomes nodular with irregular, very thin, soft marl partings bounding the nodules. Locally, water softens the limestone which resembles dark clay. The formation is relatively uniform in lithology in the study area.

The Comanche Peak Limestone is transitional with the Walnut Clay below and with the Edwards Limestone above. In the Hog Creek basin, only the upper section of the Comanche Peak Limestone is exposed in the lower elevations in the Hog Creek valley (fig. 2).

Edwards Limestone. The Edwards Limestone was named by Hill and Vaughn in 1898. The name replaced the earlier *Caprina* limestone, which had been assigned by B. F. Shumard in 1860, and *Barton Creek* limestone used by Hill in 1889 (Hill and Vaughn, 1898, p. 227). The type locality of the Edwards Limestone is at Barton Creek near Austin, Texas (Sellards *et al*, 1932, p. 341.).

The Edwards Limestone in the study area is typified by reef and interreef deposits. The reefs are essentially biostromal with local bioherms. Pelecypods belonging to the order Pachydonta are the primary reef inhabitants. Reef lithology is essentially a fossiliferous limestone with either a crystalline or noncrystalline matrix. Chert nodules occur in Edwards Limestone at Hurst Spring (figs. 2, 4).

The Edwards Limestone in the Hog Creek basin crops out along the length of the creek and forms steep banks. In the lower portion of the study area, the creek flows over the Edwards Limestone.

Due to the presence of biostromal reefs, the thickness of the Edwards Limestone in the area varies from 25 to 32 feet. The thickest section is located on Hog Creek southeast of Lane's Chapel (Frost, 1962) where the Edwards Limestone has warped down into the underlying Comanche Peak Formation. Bioherms in the Edwards in many cases control the position of Hog Creek. Numerous *meanders* have been developed where the stream has been diverted by bioherms. Examples can be found between Station B near Lanes Chapel and Station A (fig. 2).

Washita Group

The Washita Group of Central Texas is composed of three formations: Georgetown Limestone, Del Rio Clay, and Buda Limestone. In the study area, only Georgetown Limestone is present.

Georgetown Formation. The Georgetown Limestone was named by Hill (1901, p. 291). The type locality is

on the South San Gabriel River near Georgetown, Texas.

The Georgetown Formation in Central Texas consists of, in ascending order, Kiamichi Clay, Duck Creek Limestone, Fort Worth Limestone, Denton Marl, Weno Limestone, Pawpaw Shale, and Main Street Limestone. Only the Kiamichi, Duck Creek, and Fort Worth members are present in the study area. With the exception of the Kiamichi Clay, the Georgetown Limestone has not been differentiated for mapping purposes in this study.

Georgetown Limestone is composed of nodular to bedded, dense limestones with interbedded soft marls. Near the lower part of the Georgetown Formation, clay is abundant (Fox, 1962, p. 36). The Kiamichi Clay Member consists of soft marl beds and discontinuous shelly nodular limestone in the study area. The Kiamichi develops a rich black soil which produces good crops and supports many farms as compared to the thinner soils of the Duck Creek and Fort Worth members which are suitable for grazing only. Bedding planes of the Duck Creek and Fort Worth members are irregular and appear marly in outcrop. Both members consist of nodular, medium-bedded limestone interbedded with thin soft marl. Separation of the two is not practical for mapping purposes (Fox, 1962, p. 45).

STRUCTURE

Formations of the Comanchean Series dip east-southeastwardly toward the East Texas embayment at about 15 to 20 feet per mile in the study area.

There are no apparent structural anomalies in Hog Creek basin. Structure is in agreement with the regional Cretaceous dip. The Edwards Limestone, however, may have a locally higher dip in reef flanks. Edwards reefs may be overlain by Georgetown Limestone locally.

GEOCHEMISTRY OF WATER

To determine what chemical changes take place in a system, it is necessary to understand the variables in the system and the characteristics of the individual ions to be tested. If these are better understood, the chemical system can be related to such natural influences as geology.

There is a great change in the quality of water from the time it falls as precipitation until it flows past Station A (fig. 2). A series of analytical tests were run to determine exactly what changes occur, and a study was made to determine why each occurred.

Substances commonly determined in water analyses and expressed as ions include the cations calcium, magnesium, sodium, and potassium, and the anions sulfate, chloride, fluoride, nitrate, and those which contribute to alkalinity, which are expressed in this report as equivalent amounts of carbonate and bicarbonate (Hem, 1959, p. 29). Routine tests were run for all these ions except fluoride, since it is reported by

Henningsen to be present only in trace quantities. Other ions tested include phosphate, to measure contribution of plants and fertilizers; silicate, to detect contribution of diatoms; manganese, because of its abundance in some sedimentary rocks; iron, because of its possible presence in fertilizers with sulfates; and copper, because of its solubility as sulfate and chloride. In addition to the above ions, pH and water temperature were recorded regularly.

Tests were run to determine the presence of magnesium, copper, iron, and manganese which were never detected in Hog Creek and therefore will not be discussed further.

CATIONS

CALCIUM

Calcium, because of its presence in limestone (CaCO_3) which crops out in the Hog Creek hydrologic basin, is in solution in Hog Creek waters.

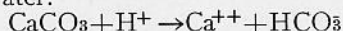


Fig. 3. Hurst Spring and overhanging Edwards Limestone bluffs. Spring flow visible near center of picture. This is the head of perennial flow of Hog Creek and a site of early settlement. Photograph taken in mid-summer at time of lowest flow.

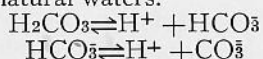


Fig. 4. Chert nodules in Edwards Limestone at Hurst Spring. Chert occurs in gray to white, occasionally vugular masses to 8 inches in diameter at the spring site.

In the presence of H^+ , calcium carbonate is readily soluble in water.



The dissociation of carbonic acid is an important source of H^+ in most natural waters.



In the system $CO_2 + H_2O + CaCO_3$, if there is a sufficient supply of carbon dioxide available, only the first dissociation step takes place, and carbonate ions are not present in solution. Under these conditions calcium carbonate is attacked and calcium and bicarbonate ions are produced. However, the H^+ produced in the second step of dissociation is not available for the reaction with calcium carbonate. If the pH of the solution reaches a high enough level for the production of an appreciable quantity of calcium carbonate, it will precipitate if its solubility product (about 1×10^{-8}) is exceeded (Hem, 1959, pp. 71-73).

Large amounts of calcium and bicarbonate would be expected when much carbon dioxide is available (fig. 5). Such a solution can exist in a stable form if CO_2 is under pressure, as in an underground aquifer. When such water rises to the water table or to the surface as a spring, it may be supersaturated or highly charged with carbon dioxide (CO_2) compared to waters at standard temperature and pressure.

When the carbon dioxide escapes, the equilibrium in the solution is altered, and calcium carbonate may precipitate until a point is reached where the carbon dioxide content at atmospheric pressure is in balance with the dissolved calcium bicarbonate. Carbonate deposition may also be caused by a rise in water temperature (fig. 6), evaporation, removal of carbon dioxide by aquatic plants or algae, and aeration (Goldschmidt, 1954, p. 232).

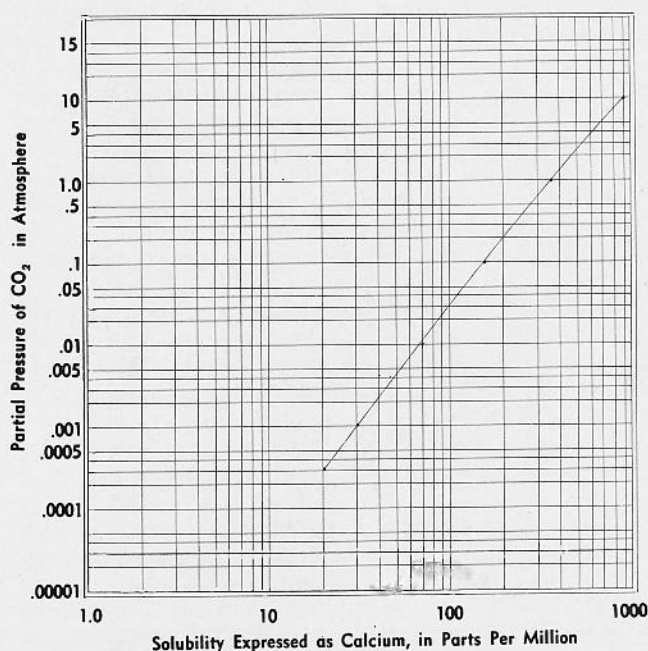


Fig. 5. Solubility of calcium carbonate as a product of the partial pressure of carbon dioxide in the atmosphere. After Hem, 1959, p. 74.

SODIUM

Carbonate rocks, as in the study area, contain relatively minor amounts of sodium. Normally, therefore, waters associated with carbonate rocks are low in sodium unless there is contamination from some other source.

In those waters in which calcium is the predominant cation, limited solubility of calcium carbonate tends to minimize the presence of carbonate ions (CO_3^{--}) in solution and in effect keeps the pH below 8.2 (Hem, p. 86-87).

Sodium can occur as an impurity in the cementing material, or as crystals of soluble sodium salts deposited at the same time or after the sediments were deposited. A low percentage of sodium compounds, mixed with calcium carbonate cementing the mineral grains, would go into solution at a rate comparable to that of calcium carbonate, because the sodium is protected from attack except at surfaces where exposed to water (Hem, p. 85).

ANIONS

ALKALINITY

Alkalinity of water is the capacity of that water to accept protons or it is the quantity and kinds of compounds present which collectively shift the pH to the alkaline side of neutrality.

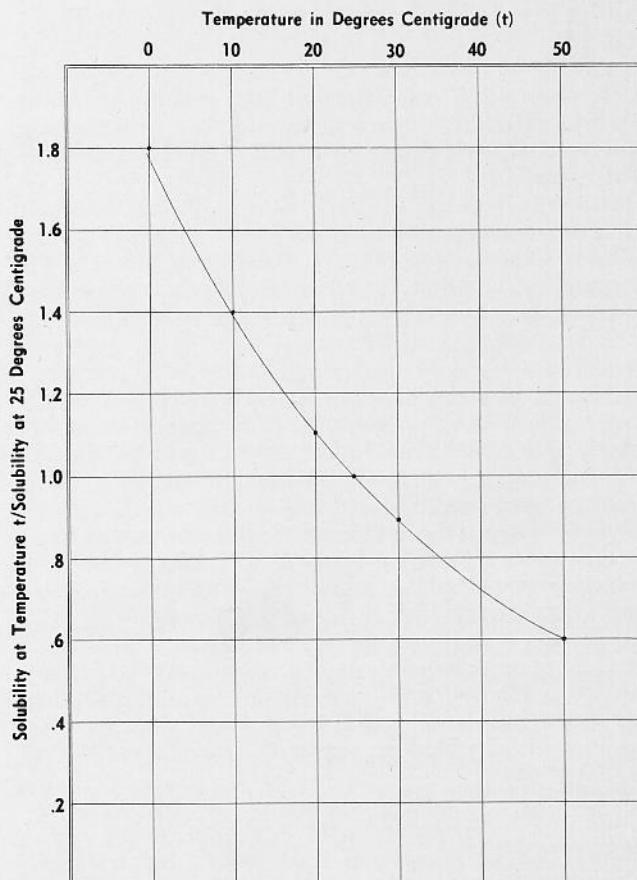


Fig. 6. Effect of temperature on solubility of calcium carbonate. After Hem, 1959, p. 75.

The term *alkalinity* when used by the water chemist does not agree with accepted chemical terminology. The chemist refers to a pH of 7.0 as the neutral point when calculating water alkalinity. Thus, water with a pH of 6 could be acid on the basis of pH but might still have titratable alkalinity (Hem, p. 92).

Alkalinity as used in this study is the bicarbonate ion unless otherwise stated. The pH of Hog Creek normally remains between 4.5 and 8.2, where titratable alkalinity is in the form of HCO_3^- .

Other compounds can also affect the water alkalinity. Silicate and orthophosphate both titrate stoichiometrically by lowering the pH to 4.5 and may be reported as alkalinity. Both occur in Hog Creek.

Silicate (SiO_3^-) should not be present in waters in measurable amounts unless the pH is above 11. The HSiO_3^- form, however, might represent about half the silica present at pH 9 and about a tenth of it at pH 8. These data are based on dissociation constants for silicic acid (Huckel, 1950, p. 223). It is, therefore, very unlikely that dissociated silica will interfere with standard alkalinity titrations in Hog Creek, since the pH is between 4.8-8.2, and silica concentrations in the study area are relatively low.

Orthophosphate may occur in water in three forms: PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- . The trivalent form is present in appreciable amounts only above pH 10. The HPO_4^{2-} ion predominates from pH 7 to pH 2. Phosphate ions are not completely converted to orthophosphoric acid even at pH 1; however, practically all the HPO_4^{2-} ion would be converted to H_2PO_4^- ions in an alkalinity titration stopped at pH 4.5 (Hem, p. 99). Phosphate rarely occurs in a concentration high enough in nature to affect alkalinity to any great degree. If phosphate were present, only about a third of it would be titrated as alkalinity.

Alkalinity reported as carbonate is present in small amounts generally less than 10 ppm, if the pH of the water is above 8.2. In alkaline waters, pH 4.5 or over, the range of alkalinity reported as bicarbonate is from zero to more than 1,000 ppm in many cases (*idem*, p. 97).

CHLORIDE

Chloride is present in nearly all natural waters. In most surface streams, chloride is present in amounts considerably lower than sulfate or bicarbonate. This is also true in the Hog Creek hydrologic system.

Chloride may reach Hog Creek in two ways: in rainfall and through the inclusion of connate water from the limestone. Chloride is present in rainwater in concentrations reported by investigators as averaging 3.0 ppm (Riffenburg, 1925). Chloride is present in central Texas precipitation in concentrations which average 1.8 ppm. Chloride in the atmosphere, through which precipitation falls, comes from air contamination near cities and from ocean mists. High chloride content in rainfall would be expected near the coast and near large cities.

Much more important sources of chloride are associated with sedimentary rocks in the study area. Chloride can be present in resistates as the result of inclusion of connate water; this condition would be expected in any incompletely leached deposit that was deposited under the sea or in any closed basin where chloride was present. "Concentrations of chloride in

saturated sodium chloride brines are near 155,000 ppm" (Hem, p. 111). The highest concentration of chloride in Hog Creek was 0.02 percent of this saturation point.

NITRATE

Nitrogen, as it is found in the natural hydrologic environment, is in the highly oxidized form of nitrate (NO_3^- , N^{+5}). All nitrate compounds are readily soluble in water, and all the nitrogen weathered from the rocks or added to the soils will be in solution at one time or another. That all the nitrogen will reach the aquifer is doubtful, because nitrogen is a cyclical element and is utilized by organisms. However, once in the aquifer, nitrate is stable below the water table.

Lightning discharges can combine atmospheric nitrogen with oxygen, and these oxides dissolve in rainwater to produce nitrous and nitric acids. Riffenburg (1925) reported the average nitrate content of rainwater to be 0.2 ppm. This investigator, however, detected an average concentration of 0.44 ppm of nitrate in Central Texas rainwater during the study period. This may be a source of nitrate in surface waters, although much of the nitrate in rainwater is left in the soil where it is used by plants. Certain nitrogen-fixing plants which utilize nitrogen with the aid of bacteria add to the nitrate content of the subsoil. Water then percolates through the soil and carries nitrate to the aquifer. In addition to nitrogen-fixing plants, decaying plant debris, animal excrement, and inorganic nitrate or liquid ammonia fertilizers, are other major sources of nitrogen which can reach the aquifer. Discharge of untreated sewage is a major source which can account for high nitrate concentrations downstream from towns or farm houses. Water which percolates through or flows over caliche deposits can carry small amounts of nitrate and add it to the hydrologic system. The closer these deposits are to the sample location the higher the concentration will be since nitrate is quickly used by terrestrial and aquatic plants.

Control tests were conducted on water from Comanche Peak Limestone, Edwards Limestone, and Kiamichi Clay. Average concentrations are as follows: Comanche Peak Limestone, 0.57 ppm; Edwards Limestone, 2.59 ppm; and Kiamichi Clay, 0.35 ppm. The actual amounts determined by these tests are not valid; however, the relative amount of each formation is. The Edwards Limestone, therefore, appears to contain more nitrate.

Nitrate content in surface waters not subject to extensive pollution is seldom higher than 5 ppm, and often less than 1 ppm. In ground water, the concentration may have a wide range from practically zero to nearly 1,000 ppm (Hem, p. 118). The concentration of nitrate in water does not have any consistent relation to concentrations of other cations.

PHOSPHATE

Due to biotic activity, phosphorus is a cyclic element, its concentration in the water fluctuates with decomposition and synthesis of plants; lower levels are expected at times of high synthetic activity. Phosphorus is derived either directly or indirectly (through organisms) from weathering of phosphatic rocks (*i.e.*, apatite) and from the soil and is (in inorganic form) present as dissolved phosphate. Phosphate is firmly held by the soil and is not easily leached by rainwater as is

nitrate. For this reason, spring waters contain much less phosphate than nitrate (Ruttner, 1966, p. 90). Since phosphorus is essential in plant nutrition, considerable amounts are probably withheld from the water by vegetation. When aquatic vegetation dies, small amounts of phosphorus are released. A phosphorus decline is noted as common in the late summer as plants store it.

The HPO_4^- ion is probably the normal form for phosphate in the pH range of natural waters. The monocalcium salt CaHPO_4 is soluble in carbon dioxide-free water to the extent of 96 ppm phosphate at 25° C and about four times as soluble in CO_2 saturated water at 25° C. This solubility is high; however, phosphate concentrations are largely controlled by aquatic vegetation and the nonabundance of phosphate minerals (Hem, p. 119).

SILICA

Silica is common in nature as a constituent of igneous rocks, quartz, quartz sand, and diatoms. Natural waters often contain 5 to 10 ppm of silica and rarely exceed 60 ppm.

Silicon in solution has a coordination number of 6 and forms ions of the same type as the fluosilicate ion (SiF_6^-) (Iller, 1955, p. 19). This would be equivalent to the metasilicate (SiO_2) ion plus three molecules of water. Dissociation constants ($k \times 10^{-10}$) for metasilicic acid indicate that at pH 9 probably less than a tenth of the silica would be dissociated. Only a few natural waters have a pH as high as 9. Dissociated silicate ions must theoretically be rare in natural water.

Krauskopf (1956) concluded that "amorphous" silica is taken up by water in both colloidal form and in solution as H_4SiO_4 . The process of solution is slow and the portion of silica in the colloidal form is gradually converted to hydrated dissolved molecules until the saturation point, 160 mg/l (ppm) of SiO_2 at 25° C, is reached.

Silica cycles in stream water can be closely related to the diatom cycle. One of the major sources of silica in stream water is aluminosilicates which dissolve from dying diatoms by the action of CO_2 . Concentrations of 10 mg/l are common. Diatom blooms normally result in low silica concentrations, and diatom kills result in the highest concentrations in the stream (Ruttner, F., 1966, p. 93).

Silica which enters the stream system through springs must come from a different source, since diatoms do not exist within the aquifer. Water percolates through the soil and into the aquifer then into the stream. Controlled experiments by this observer indicate that when demineralized water is passed over soil samples, silica concentrations average 13 ppm.

Another possible source of silica in Hog Creek may be from the Edwards Limestone aquifer which contains beds and nodules of chert (fig. 4). Nodules of chert are exposed in the Edwards outcrop at Hurst Spring. The cryptocrystalline and amorphous forms of silica, such as chert, are probably considerably more soluble in water than quartz (Hem, p. 52).

SULFATE

Sulfates of most common metallic elements are highly soluble and are stable in solution in natural waters. Sulfate can enter the Hog Creek system in three ways: precipitation, leaching of rocks and soils, and fertilizers.

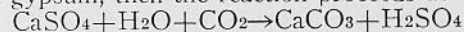
Riffenburg (1925) reported that rainwater collected at Washington, D. C. contained 1 to 17 ppm of sulfate. This investigator did not detect measurable amounts of sulfate in Central Texas rainfall; however, the turbidmetric analytic method was employed which is not accurate in the 1-10 ppm range. The sulfate in precipitation in rural areas is largely dissolved from dust which acts as nuclei on which rain drops form. The dust is derived from the rocks below. In the Hog Creek area, however, precipitation is a very minor source of sulfate.

Controlled tests indicate that the Comanche Peak Formation contains the highest average concentration of SO_4^- of the three formations that crop out in the basin. The high concentration of sulfate in the Comanche Peak Formation would significantly contribute to the sulfate in Hog Creek; however, it would not contribute to sulfate in Hurst Spring. Sulfates of the Comanche Peak Limestone are believed to be derived from chemical breakdown of gypsum within the formation.

In the upper oxidized layers of soil and rock, sulfides have been converted to sulfates depending on the degree of oxidation. They are then gradually leached away by water. The rate at which the soluble sulfates are removed is dependent on the amount of precipitation. In humid regions, the upper layers of soil and rock are kept thoroughly leached by precipitation as fast as soluble products are formed. Low sulfate concentrations in ground water and streams would, therefore, be exposed in humid regions (Hem, pp. 100-103).

In semiarid regions, soils are not fully leached, and when rains do fall, sulfate concentrations are expected to be high. Sulfates used in fertilizers can also be a source of sulfate in natural waters (Henningson, 1960, p. 41); however, in fertilizers it is commonly in combination with iron, and no iron was detected in Hog Creek.

Calcium sulfate at room temperature is soluble to the degree of 1,500 mg/l at 25° C (Hodgman, p. 554). Assuming the sulfate present in Hog Creek is in the form of gypsum, then the reaction proceeds as follows:



Highest concentration of SO_4^- recorded in Hog Creek, about 150 mg/l at Station D on September 7, 1967, is only 10 percent of saturation. Therefore, fertilizers may be discounted as a source of sulfate in Hog Creek. pH (HYDROGEN ION CONCENTRATION)

The pH of a liquid is a measure of its acidity or hydrogen ion concentration. Free carbon dioxide, mineral acids, or salts can all contribute to the pH of a liquid. In pure water at 20° C, the hydrogen ion concentration is 10^{-7} moles/liter. From measurements of the electrical conductivity of very pure water, it is possible to determine the concentrations of hydronium and hydroxyl ions. The pH is the negative logarithm of the concentration of the hydronium ion. In pure water the concentration of hydronium and hydroxyl ions are equal. If the pH of a water sample is below 7.0, it is said to be acid; if it is above 7.0, it is said to be alkaline. The pH of natural unpolluted water usually does not vary more than 2 pH units. Waters in the Hog Creek system vary between pH 6.9 and 8.5.

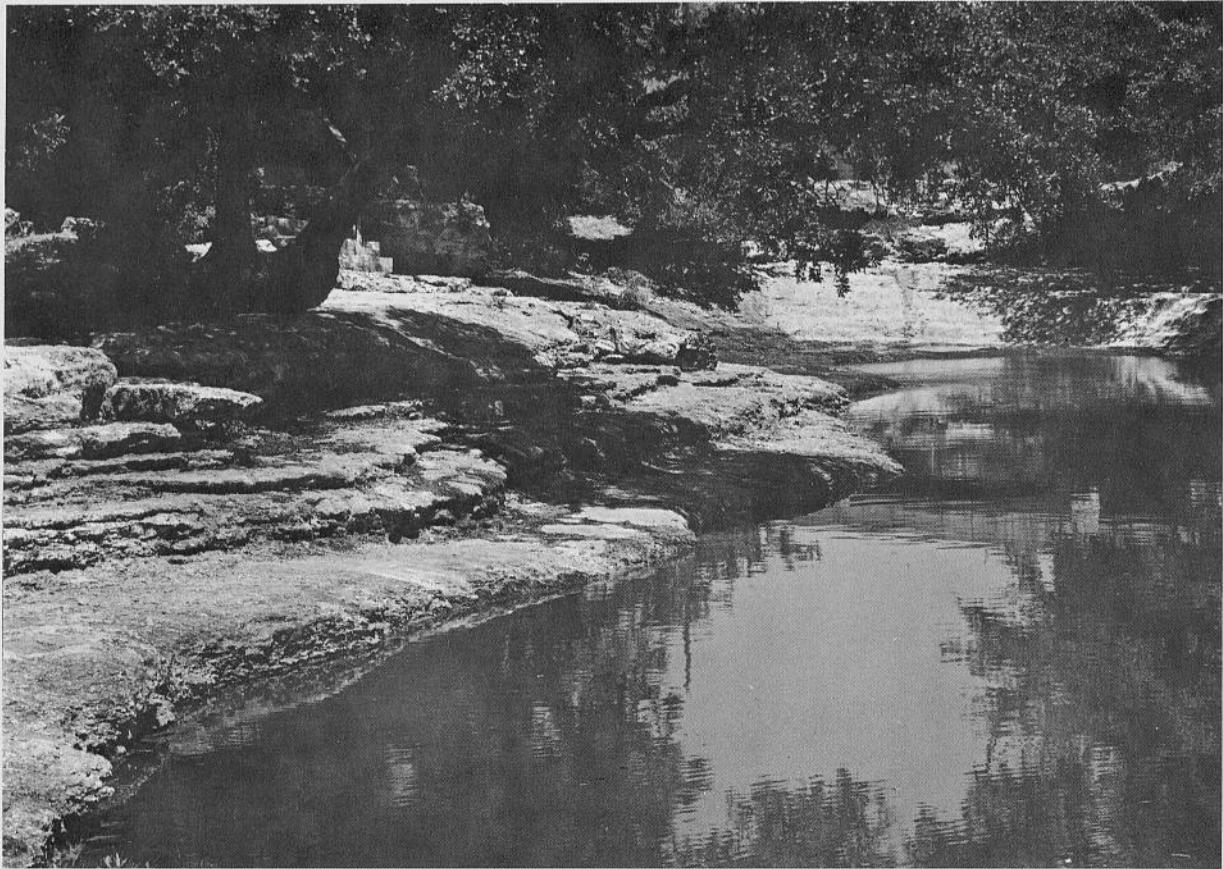


Fig. 7. Hurst Spring locality (H.S. on map). Spring enters at left side of pool, near head, at center of picture. Samples were collected as near the spring mouth as possible. Photograph taken in mid-summer during period of lowest flow.

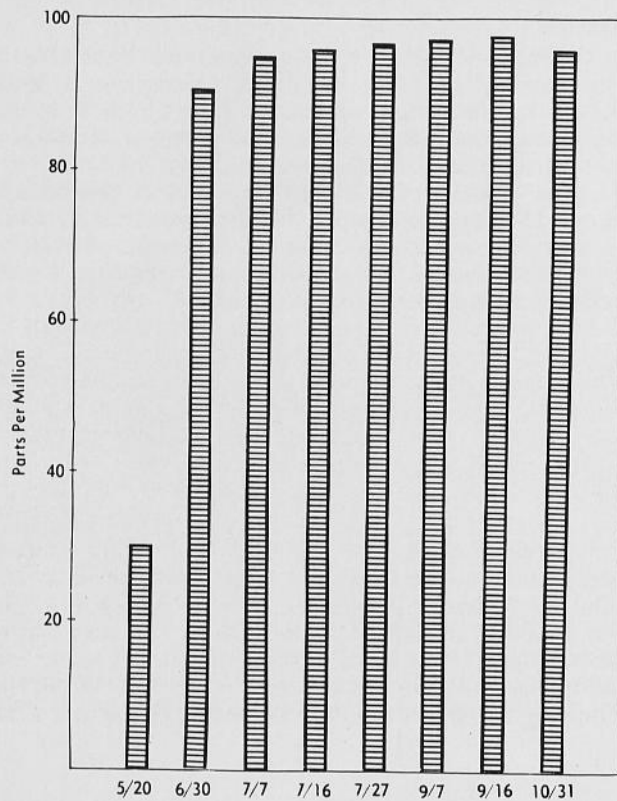


Fig. 8. Calcium—Hurst Spring.

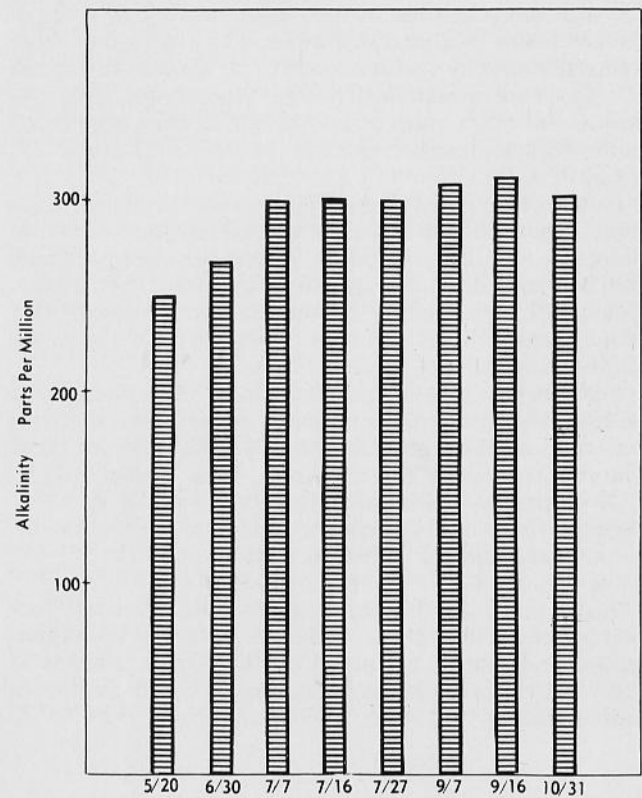
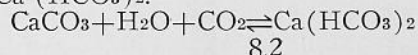


Fig. 9. Alkalinity—Hurst Spring.

In a natural system, the pH is largely controlled by the amount of CO₂ in solution. The higher the CO₂ concentration, the more H₂CO₃ is formed. H₂CO₃ is then ionized to produce more H⁺ ions, therefore, a lower pH. Carbon dioxide (CO₂) is added to natural waters in two ways: through contact with the atmosphere during precipitation and by percolation of water through the soil. Water in the aquifer near the recharge area would, therefore, have a lower pH. This explains why Hurst Spring has the lowest pH of all the stations along Hog Creek. The pH of Hog Creek is controlled by the CaCO₃—CO₂—H₂O buffer system. A saturated solution of CO₂ in water at the normal CO₂ partial pressure in the atmosphere has a pH of 5.2. A solution of calcite in air-saturated water has a pH near 8 (Mason, 1958, p. 159). If the pH rises above 8.2 due to loss of CO₂, deposition of CaCO₃ may occur. On the other hand, the more CO₂

present the more CaCO₃ is dissolved and added to the water as Ca (HCO₃)₂.



8.2

Hurst Spring, therefore, has a higher concentration of calcium bicarbonate [Ca(HCO₃)₂] than the other stations since it has the lowest pH (highest CO₂ concentration).

TEMPERATURE

Temperature also influences the amount of material which can be held in solution. Calcium carbonate (fig. 6), for example, is more soluble in cold water (1390 mg/l) than in hot water (773 mg/l) (Hodgman, p. 551). If calcium concentrations are near saturation, a rise in water temperature can initiate deposition of calcium salt. The solubility of sodium salts is increased by a rise in temperature; therefore, higher temperature waters usually have a high sodium content.

GEOCHEMISTRY OF HOG CREEK

The geochemistry of Hog Creek can best be discussed by describing the behavior of the individual ions studied at each station. All stations are compared with Hurst Spring, and changes are noted and discussed.

HURST SPRING

Hurst Spring is located 4.8 miles northeast of Turnersville on Hurst Creek just below the bridge on Farm Road 182 (fig. 2). The spring flows from the Edwards Limestone. The floor of the creek and the bluffs along the creek are also Edwards Limestone (fig. 7).

Water from Hurst Spring is remarkably constant in chemical composition except for nitrate, phosphate, chloride, and sulfate. In the section which follows, composition and variation of each tested ion over the test period are described beginning with calcium, and including sodium, alkalinity, chloride, nitrate, phosphate, silica and sulfate.

Calcium, like alkalinity, varied from the norm only once (fig. 8). On May 20, 1967, calcium concentration was 30 ppm, compared to a normal of approximately 96 ppm. This low concentration was caused by dilution from rapid runoff following a heavy general rain. Calcium, because of its occurrence in the limestones which crop out in Hog Creek basin, is the predominant cation in the system.

Sodium was tested for only once during the period because of the special equipment required for the test. The concentration of sodium was found to be 22 ppm. The ratio of calcium to sodium is approximately 4.5 to 1. No firm conclusions can be drawn as to the behavior of sodium ions in Hurst Spring.

Hardness from which magnesium can be calculated remained constant throughout the study period, near 100 ppm (fig. 9). The 5/20/67 sample was diluted to 87 ppm. Laboratory analyses indicate that the normal ratio of calcium to hardness in Hurst Spring is about 1:1. Therefore, the total hardness in Hurst Spring is equivalent to the concentration of calcium. On 5/20/67,

the calcium-hardness ratio was approximately 1:3, which indicates that magnesium was washed into the aquifer from some outside source. Magnesium was not detected again in later analyses and must have been washed into the system as runoff from one of the upper Georgetown members.

The *alkalinity* figures for Hurst Spring are nearly constant, about 300 ppm throughout the study period with one exception on 5/20/67 (fig. 9). Alkalinity at this sampling was 254 ppm. This figure is roughly 50 ppm lower than the normal alkalinity figures over the study period. This low figure can be attributed to dilution by overland flow. Central Texas received a heavy general rain in the week preceeding 5/20/67, which charged the porous Edwards aquifer with fresh water.

Chlorides present no consistently occurring concentration through the study period as do alkalinity and calcium. Generally speaking, chlorides rise in concentration from 5.6 ppm on 5/20/67 to 19.6 ppm on 7/16/67 (fig. 10). During the summer months of June, July, and August there was little rain in the study area. The water that flowed from the spring during the summer period had been stored in the aquifer over a longer period, thus the water had been in contact with the rocks for a long period of time, and chloride concentrations rose. As showers increased in August and general rains came in September and October, the concentration of chloride dropped due to dilution by the fresh water. Concentrations of chloride in saturated sodium chloride brines are near 155,000 ppm (Hem, p. 111). The highest concentration of chloride in Hurst Spring is 0.02 percent of the saturation point.

In Hurst Spring, the periodic high *nitrate* concentration might be explained by the widespread use of soluble nitrates and aqueous ammonia as fertilizers in the farming area of the Hog Creek drainage basin. Because the Edwards aquifer is shallow, pollution from barnyards and animal excreta also contributes nitrate. The highest concentration of nitrate 13.2 ppm occurred

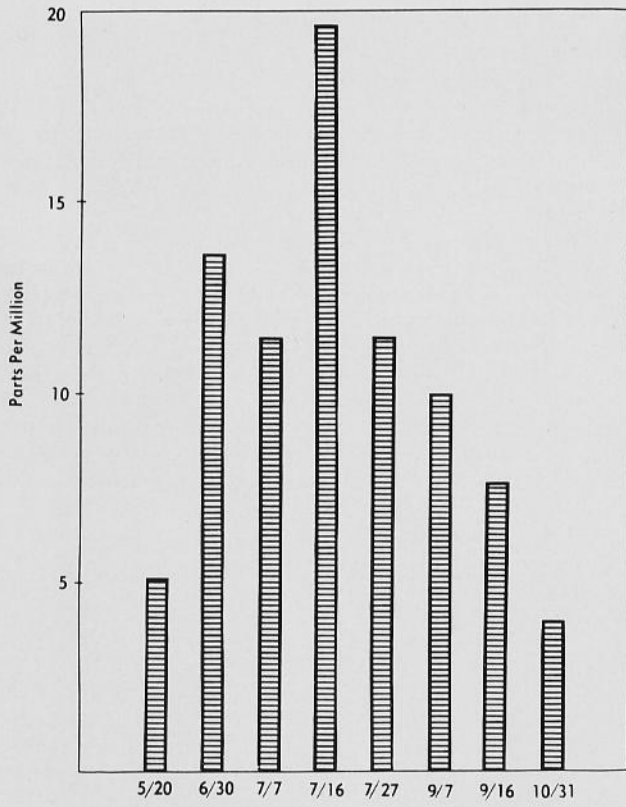


Fig. 10. Chloride—Hurst Spring.

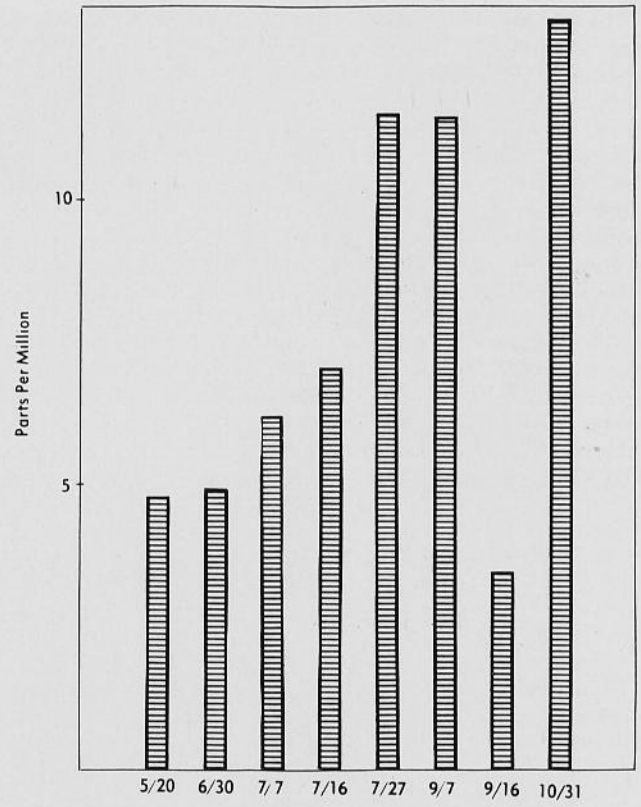


Fig. 11. Nitrate—Hurst Spring.

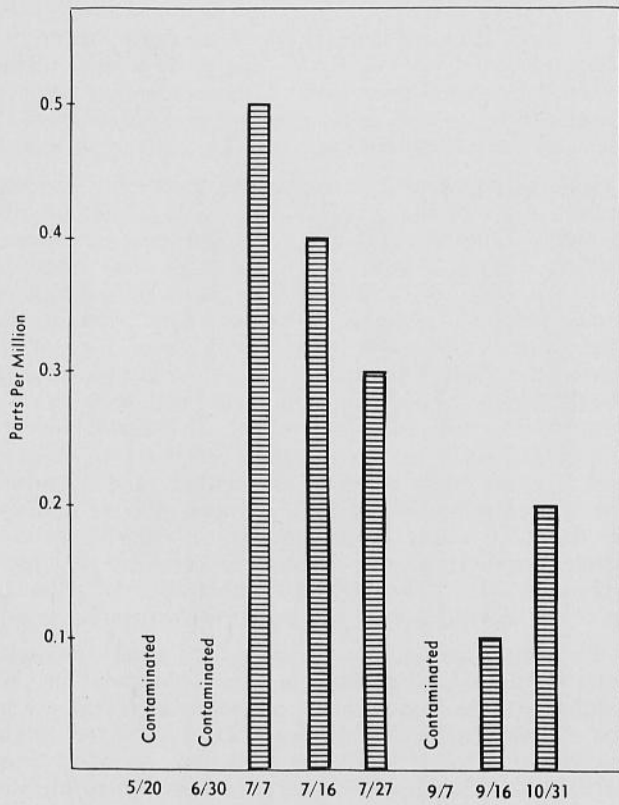


Fig. 12. Phosphate—Hurst Spring.

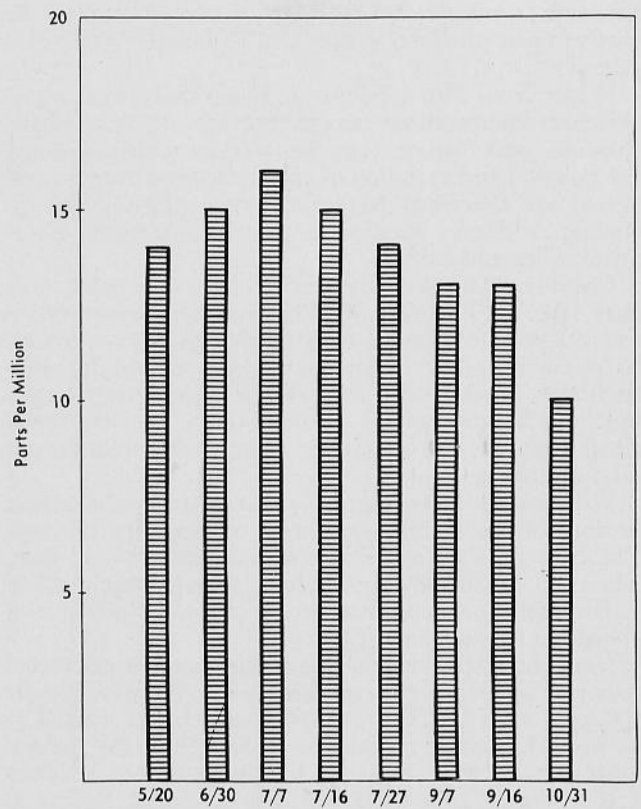


Fig. 13. Silica—Hurst Spring.

during the wet period on 10/31/67 during maximum aquifer recharge. The lowest concentration of 3.5 ppm occurred also during a wet period, 9/16/67, after a heavy rain. The amount of rain received on 10/31/67 was much more than was received on 9/16/67; therefore, more nitrate entered the aquifer on the earlier date. There is no general trend of nitrate concentration in Hurst Spring during the study period (fig. 11).

A steady decrease in *phosphate* concentration in Hurst Spring is noted after a peak of 0.5 ppm was reached on 7/7/67. The 5/20/67 and 6/30/67 determinations were contaminated in the laboratory (fig. 12). Peak concentration on 7/7/67 occurred when many of the plants in the area were dying from lack of water. Phosphate from plant remains could reach the aquifer.

Silica concentration in Hurst Spring reached a peak in the summer as the dry period began. Lowest figures were recorded in the more moist periods (fig. 13). The changes in silica concentration were very subtle; only 3 ppm separates the highest concentration from the lowest. It might, therefore, be assumed that the source of silica in Hurst Spring is associated with the soil and rocks rather than a cyclic source such as diatoms. The lower readings in the moist periods were probably due to dilution.

The concentration of *sulfate* presents no general pattern during the study period (fig. 14). If the 6/30/67 analysis is considered anomalous, the general trend shows peak concentrations during the dry period and lower concentrations during the more moist period. This

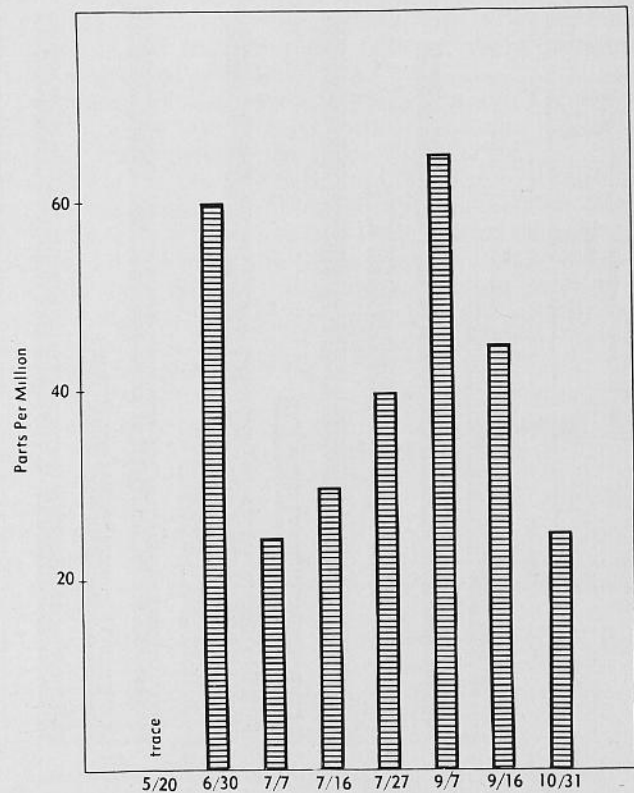


Fig. 14. Sulfate—Hurst Spring.

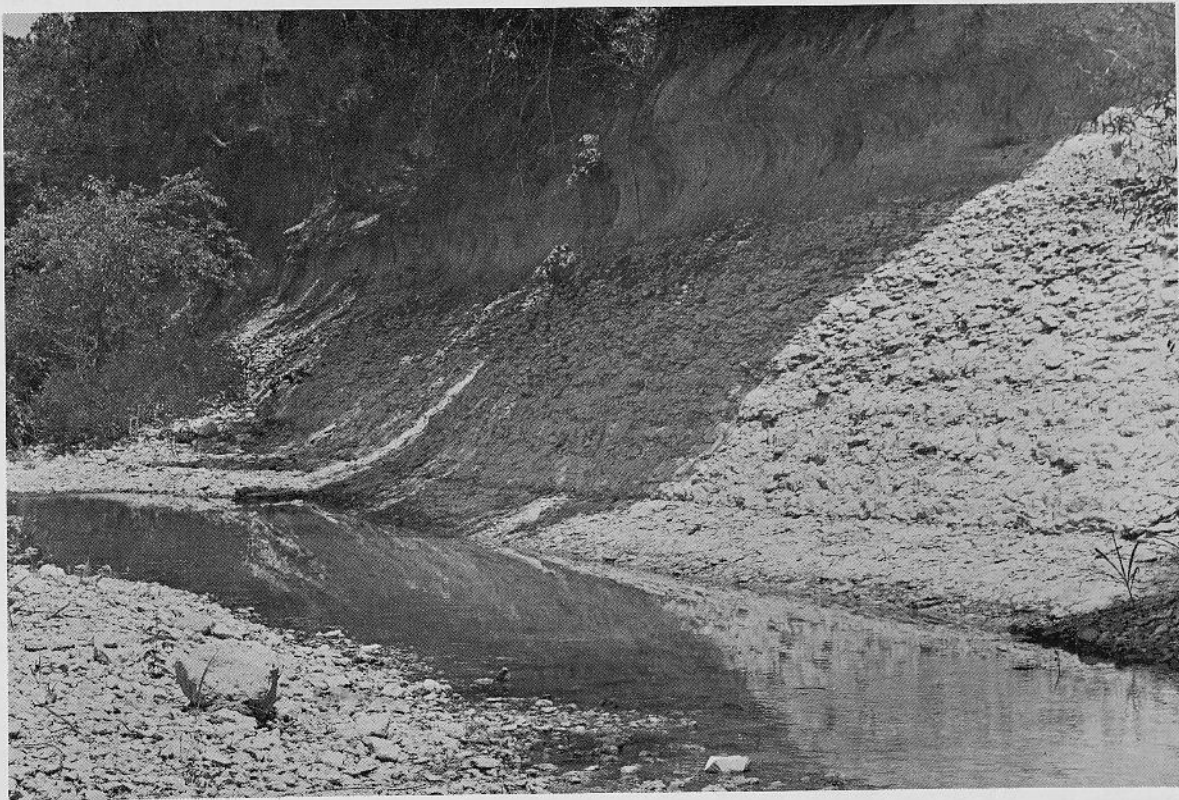


Fig. 15. Station D: Confluence of Hog Creek with Hurst Creek. Sampling station is in the pool at right of photo. County road crosses stream immediately below this point. Photograph taken in mid-summer when stream has ceased to flow.

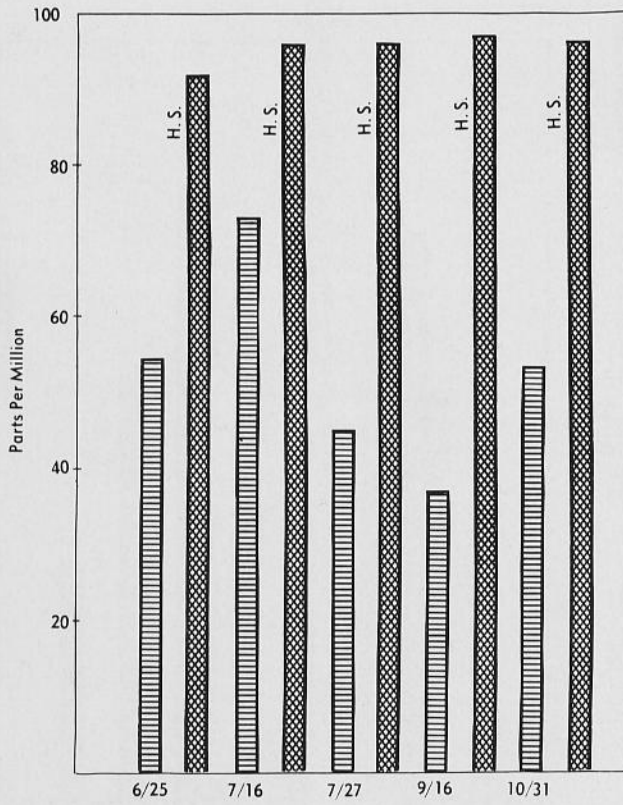


Fig. 16. Calcium—Station D and Hurst Spring.

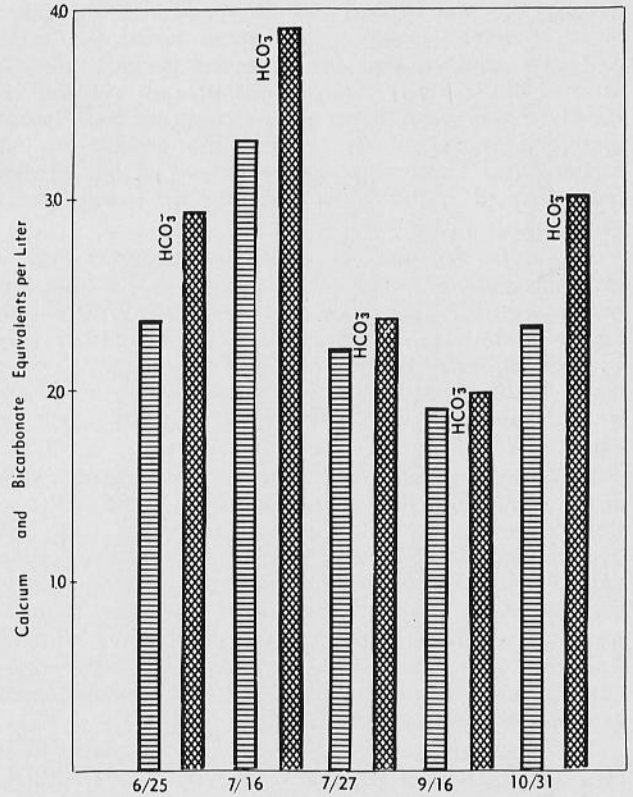


Fig. 17. Calcium and bicarbonate.

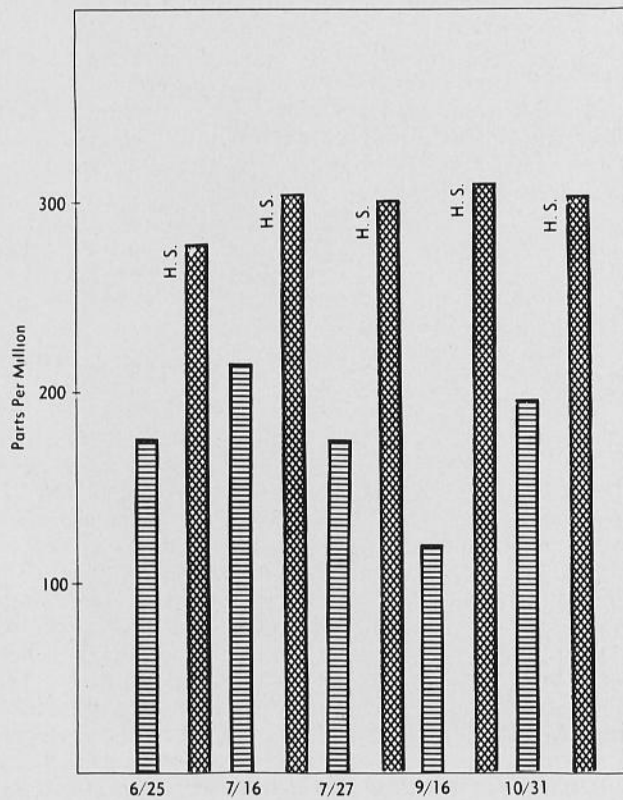


Fig. 18. Alkalinity—Station D and Hurst Spring.

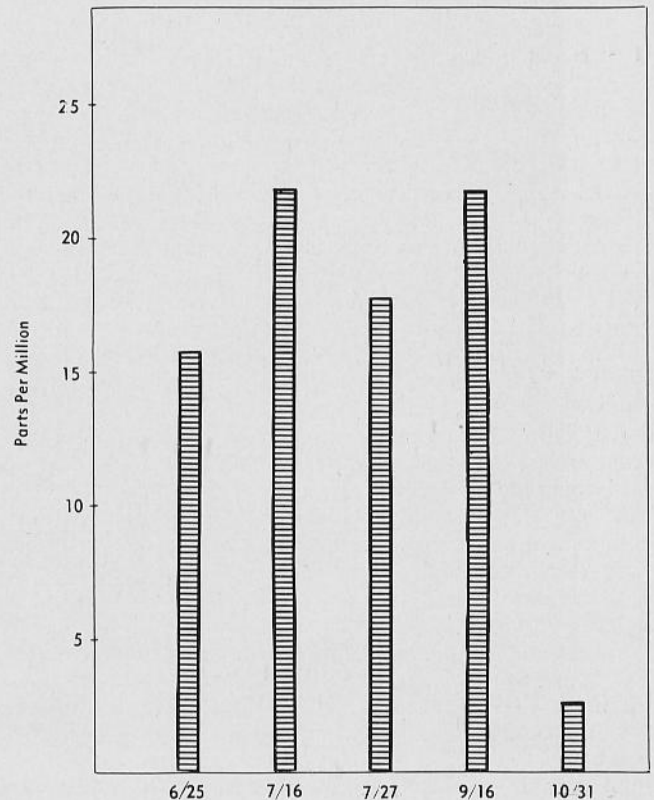


Fig. 19. Chloride—Station D.

pattern, as with chloride, suggests that the source of the sulfate is associated with the weathering of the rock material in the basin. The longer the water stays in the aquifer, the more time it has to leach sulfate from the rock.

The pH at Hurst Spring remains near 7.0 during the summer period when no fresh water enters the aquifer. During the wet periods in May, September, and October the pH rose as high as 7.6. A possible explanation for this phenomenon would be that material in suspension was washed into the aquifer which absorbed or reacted with CO_2 to lower its concentration. The pH should normally be lowered when a fresh supply of CO_2 enters the aquifer with rainfall.

The temperature of Hurst Spring water remained at a constant 21°C . After water enters the aquifer, which has uniform permeability, there is essentially nothing to change the temperature.

In the section which follows, the analyses of each succeeding lower station will be explained and compared with Hurst Spring and with all upstream stations.

STATION D

Station D is located on Hog Creek 2.1 miles downstream from Hurst Spring and about 50 yards below the junction of Hurst Creek and Hog Creek (figs. 2, 15). At Station D, the creek flows on the Comanche Peak Limestone. The Edwards Limestone holds up the steep bluffs on either side of Hog Creek. Hog Creek at Station D dried up during the month of August and did not flow again until the September 16, 1967 sampling. Samples taken during the no flow period were from pools.

The calcium ion concentration on 6/25/67 was 54 ppm, compared with 91.6 ppm at Hurst Spring (fig. 16). This is a difference of 41 percent. Temperature of the water which entered the creek system at Hurst Spring had risen nearly 9 degrees, probably causing some loss of CO_2 to the atmosphere; and in addition partial pressure of carbon dioxide in the water was lowered by the activity of plants. The water was, therefore, not able to hold as much calcium as before. Deposition of calcium in the form of calcium carbonate probably takes place between Hurst Spring and Station D.

On 7/16/67, the calcium ion concentration at Station D was 72.6 ppm, compared with 95 ppm at Hurst Spring, a difference of 24 percent.

Calcium ion concentration on 7/27/67 was 49 ppm, compared with 96.2 ppm at Hurst Spring, a change of 49 percent. Flow in Hog Creek at this time was very low with much pooling. Some calcium was probably complexed by organic tannic and humic acids which form as a result of decaying leaves in pools.

Concentration of calcium ions on 9/16/67 was 37.6 ppm, compared with 96.2 ppm at Hurst Spring, a difference of 61 percent. There was very little flow at this time; most of the water in the creek bed was runoff from a recent rain and had a low concentration of calcium, typical of runoff in this area.

The 10/31/67 concentration of calcium was 52.5 ppm compared with a concentration of 97.1 ppm at Hurst Spring, a difference of 46 percent. Much of the

water in the creek at this time was runoff; however, normal flow was occurring between Hurst Spring and Station D, so the difference between these stations is not as great as on 9/16/67.

Alkalinity is a measure of HCO_3^- and CO_3^{2-} ions. The pH of the water ranged between 7.5 and 8.0 during the study period; therefore, the alkalinity was in the form of HCO_3^- . Equivalents of alkalinity outnumber equivalents of calcium throughout the study period (fig. 17). Since calcium was the only cation tested at Station D and alkalinity alone combines with all the calcium, there must be other cations present that were not investigated; one of which is probably sodium. A decrease or increase in alkalinity brought a corresponding change in calcium.

On 6/25/67, the alkalinity at Station D was 179 ppm, compared with 254 ppm at Hurst Spring on the same date, a difference of 23.5 percent. The 7/15/67 alkalinity concentrations were higher than the 6/25/67 concentrations because the dilution effect on 6/25/67 was ended. The rise of alkalinity to the 300 ppm level at Hurst Spring also affected a rise of alkalinity at Station D on the same date. The difference in alkalinity concentrations between Hurst Spring and Station D was caused by the rise in water temperature and the release in partial pressure of the carbon dioxide as it left the aquifer. A rise in temperature and loss of carbon dioxide decreased the solubility of CaCO_3 (fig. 18).

On 7/27/67, the alkalinity at Station D was 164.4 ppm, compared with 301 ppm at Hurst Spring, a difference of 45 percent. While Hurst Spring remained nearly constant from 7/16/67, Station D dropped nearly 22 percent. The loss can be accounted for by either deposition or organic complexing between Hurst Spring and Station D.

On 9/16/67, the alkalinity was 121 ppm, compared with 314 ppm at Hurst Spring, a difference of 61.5 percent. After 7/27/67, Station D dried up and did not flow until 9/16/67 when precipitation fell. At that later date, water in the creek was runoff and not related chemically to Hurst Spring water.

On 10/31/67, the alkalinity at Station D was 185 ppm, compared with 303 ppm at Hurst Spring, a difference of 39 percent. A heavy rain occurred on this date; however, the water at Station D was clear and did not appear to contain runoff. The alkalinity concentration, therefore, is more closely related to Hurst Spring.

Generally, during the study period, concentration of the chloride ions at Station D was higher than that at Hurst Spring (fig. 10, 19). The chloride concentration at Hurst Spring reached its peak on 7/16/67 at perhaps its lowest flow period. The same situation exists at Station D. Highest concentrations were recorded at a time when there was no flow (fig. 19). The lowest concentrations were recorded at peak flow periods when there was no pooling along the stream. During flow periods, concentrations at all stations are very close (fig. 20). There seems to be a relationship of chloride concentrations between Hurst Spring, Station D, and Station C (fig. 21). Chloride concentrations are lowest at Hurst Spring, intermediate at D, and highest at Station C. Downstream migration of the water seems to bring about an increase in chloride.

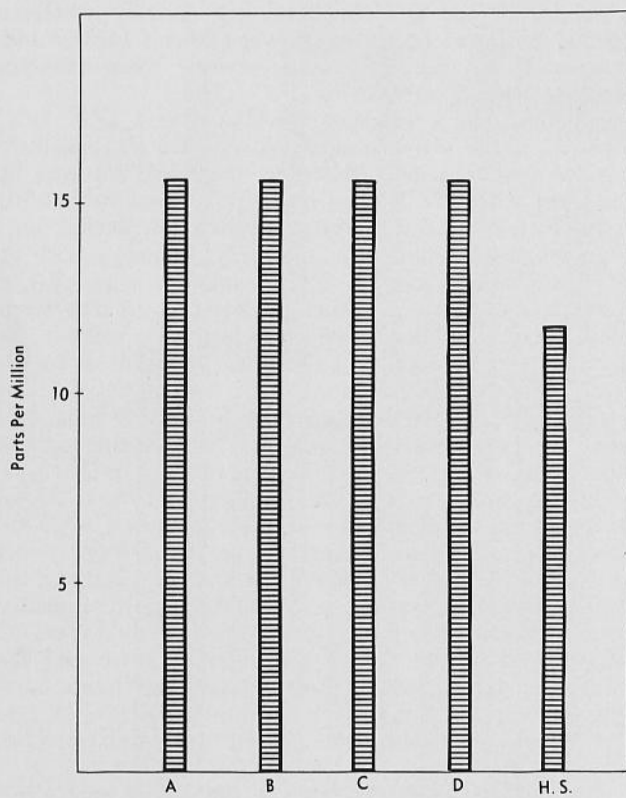


Fig. 20. Chloride 6/25/67.

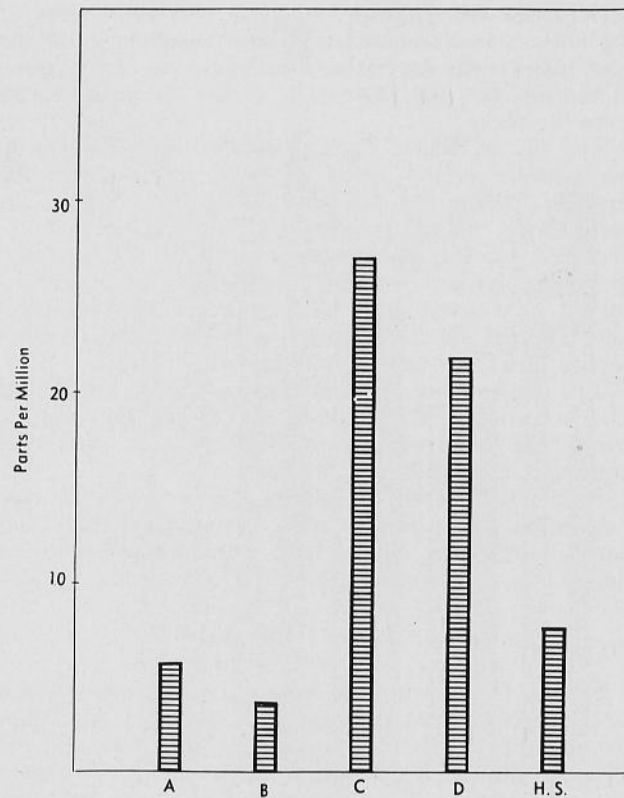


Fig. 21. Chloride 9/17/67.

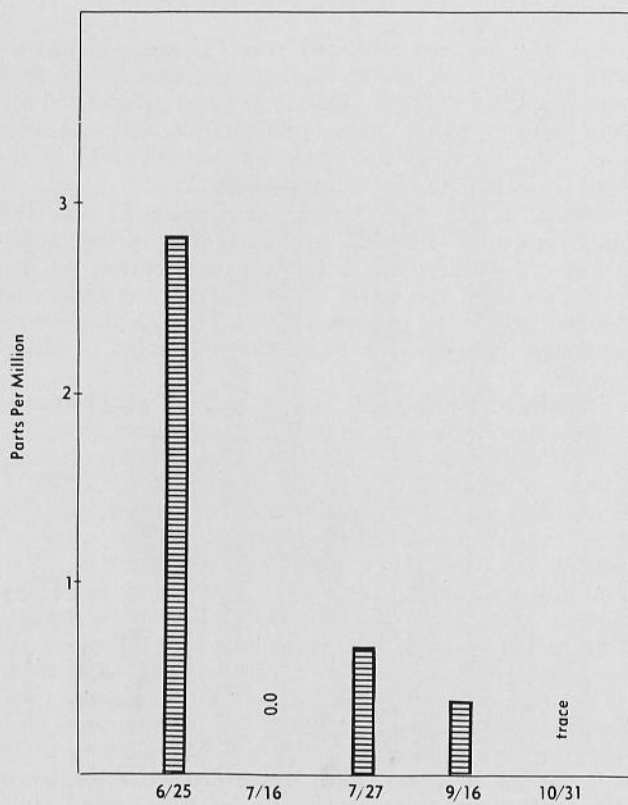


Fig. 22. Nitrate—Station D.

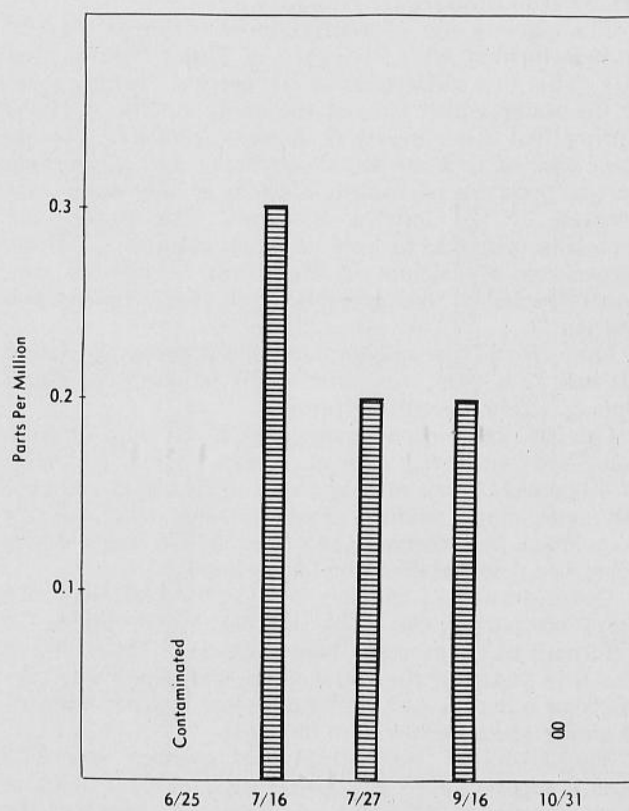


Fig. 23. Phosphate—Station D.

Evaporation of Hurst Spring water and contact with the rocks as it flows downstream could account for the increase. Stations A and B do not fit this pattern and will be discussed later.

Nitrate concentration during the study period was in a steady decline at Station D; however, this relationship does not hold true at any of the other localities. Concentrations of nitrate at Station D and Hurst Spring have no apparent relationship. Pooling during the dry period does not seem to have any effect on the amount of nitrate in solution (fig. 22).

Phosphate at Station D remained fairly constant during the test period (fig. 23). The concentration seemed to decrease with increased flow. If the source of phosphate is considered to be organic wastes, decay of vegetation, or leaching of soils, it is possible that phosphate from any of these sources could accumulate in pools during the dry season.

Phosphate concentration at Station D roughly corresponded to the concentration at Hurst Spring, in that they both rose and fell at the same time (fig. 12). Stations C, B, and A have no predictable pattern so it must be assumed that the source of phosphate is local to each station. Plants use phosphate in the growth process, taking it from solution.

Silica concentration at Station D seemed to have no relationship to the amount of silica at Hurst Spring. Generally, the concentration increased as the creek dried up (fig. 24). The lowest concentration of silica occurred during the flow periods. The low readings can be correlated with the diatom blooms in the flowing creek. The high concentrations correlate with the diatom kills in the dry creek.

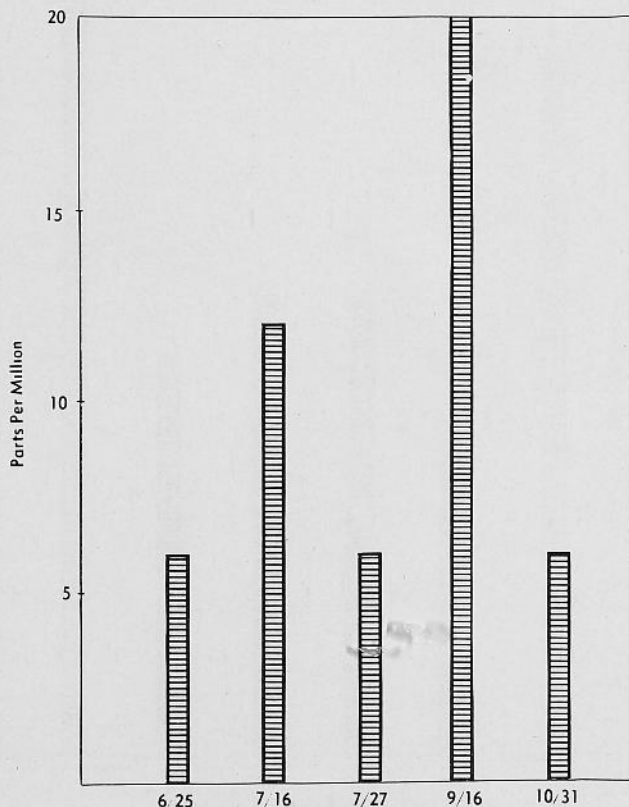


Fig. 24. Silica—Station D.

When comparing concentrations of *sulfate* ions at Hurst Spring and Station D, it is difficult to find any relationship. Concentrations at both stations through the study period were erratic and did not correlate with wet or dry periods (fig. 25).

STATION C

Station C is located on Hog Creek 3.2 miles downstream from Station D (fig. 2). Hog Creek at this point flows over its own gravel which covers the Comanche Peak Limestone (fig. 26). Samples were taken on the upstream side of the low water crossing. Hog Creek dried up at Station C on 7/15/67 and did not flow again until 10/31/67. Samples taken during this period were from pools.

Calcium concentration rose during the study period (fig. 27). The rate of flow seemed to have little effect on the calcium concentration at this station. The peak concentration on 10/31/67 and the low concentration on 6/25/67 were both periods of flow. Calcium concentration at Station C is roughly intermediate to the concentrations at the other stations in the system indicating that calcium is still being lost from solution progressing downstream from Hurst Spring (fig. 28).

A test for *sodium* was made only once during the period at Station C. A concentration of 15 ppm was detected. This level was intermediate between the concentration at Hurst Spring (22 ppm) and Station A (8 ppm). This fact suggests that Hurst Spring is the source of sodium in Hog Creek and that dilution from runoff increased on this date.

At Station D it was noted that equivalents of alkalinity (HCO_3^-) outnumbered equivalents of calcium. This relationship is not found at Station C. Equiva-

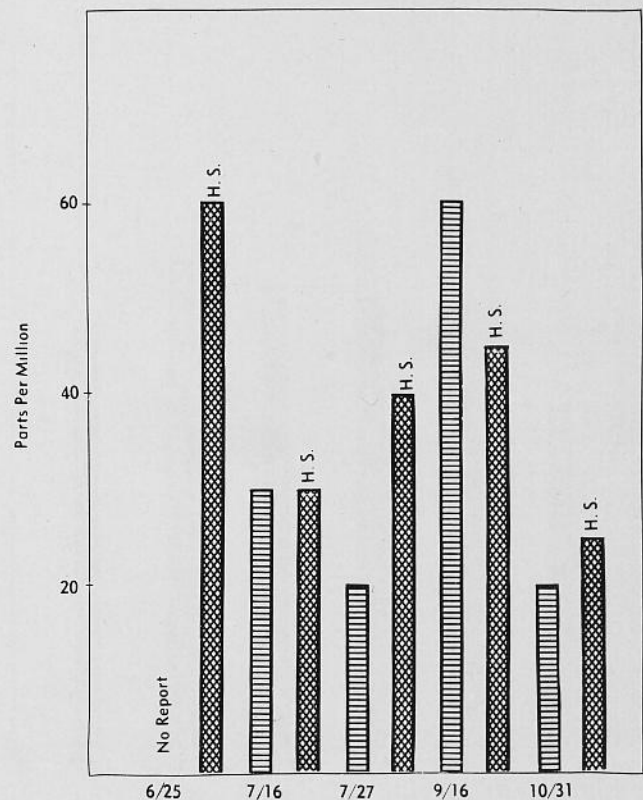


Fig. 25. Sulfate—Station D and Hurst Spring.



Fig. 26. Station C: At low-water crossing on farm road, about 3 miles north of Mosheim. Photograph taken in mid-summer during period of no surface flow.

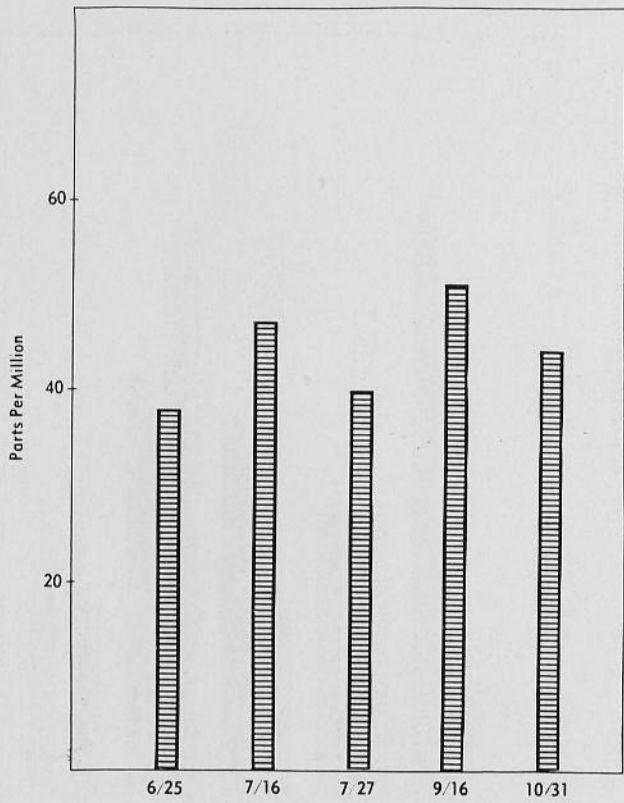


Fig. 27. Calcium—Station C.

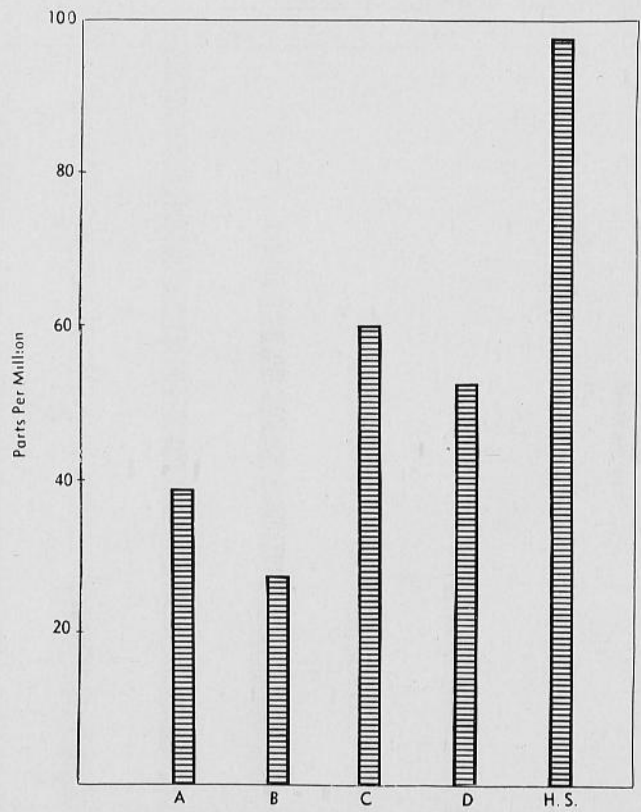


Fig. 28. Calcium 10/31/67.

lent weights of cations and anions are now in balance.

A steady rise in *alkalinity* concentration may be noted through the study period with the exception of 7/16/67 (fig. 29). The alkalinity at Station C is always less than that at Hurst Spring and more than that at Station A with one exception (fig. 30).

The concentration of *chloride* at Station C seems to have a relationship with concentrations at Station D and Hurst Spring (fig. 31). Of the three locations, Station C has the highest concentrations of chloride. This trend was observed at each sampling. The rise in concentration from Hurst Spring to Station C, since it is slight, could be caused by evaporation or added contact time with the rocks.

Chemical analyses of rocks in this area show that they contain chloride; therefore, chlorides are readily available to the stream system at all points along Hog Creek.

Stations A and B do not reflect the upward trend of chloride concentrations expressed between Hurst Spring and Station C. This indicates either the influence of a new water source or the influence of the Edwards Limestone over which Hog Creek flows at Stations A and B. The more resistant Edwards Limestone may not contribute as much chloride as the less resistant Comanche Peak Limestone.

Highest concentration of chloride occurs during periods of no flow and low flow (fig. 32). On 10/31/67, a period of flow after a hard rain, highest chloride concentration in Hog Creek was at Station C, and it was only 0.3 ppm.

Nitrate concentration at Station C rose steadily dur-

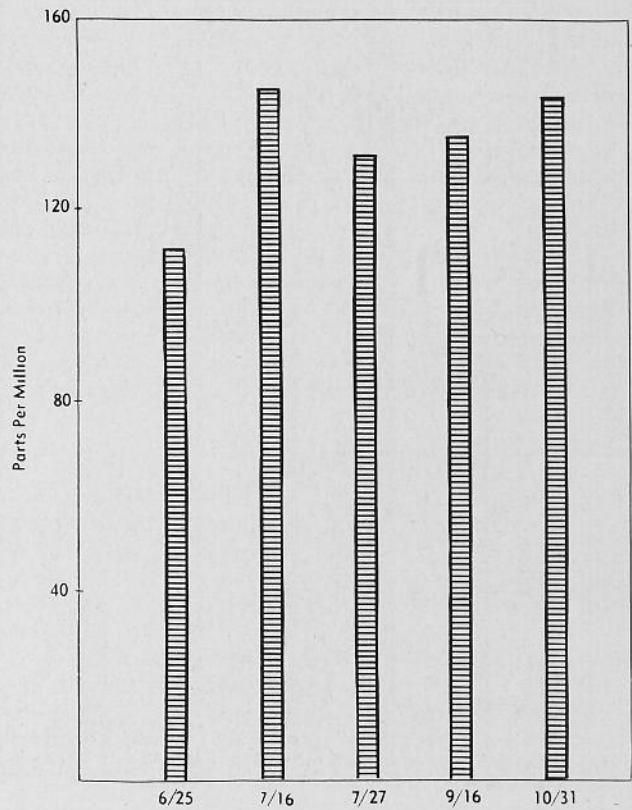


Fig. 29. Alkalinity—Station C.

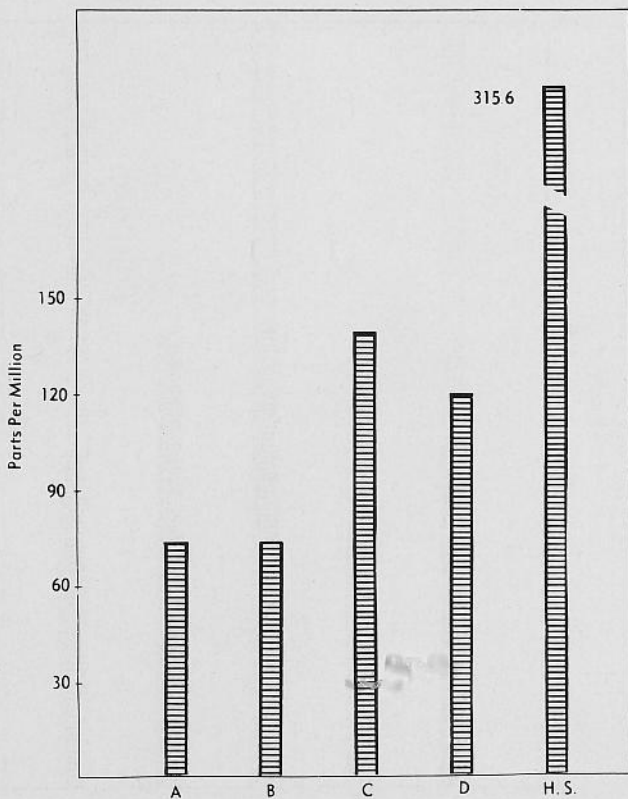


Fig. 30. Alkalinity 9/16/67.

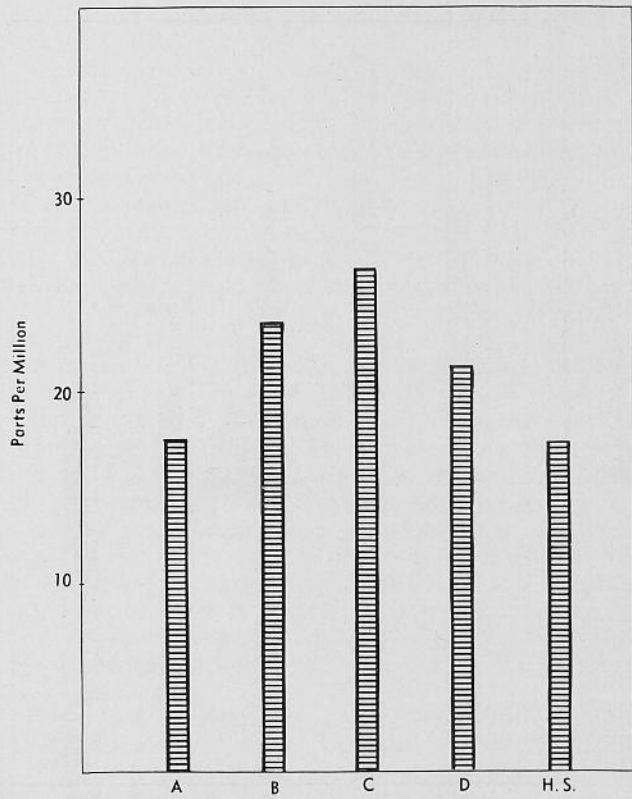


Fig. 31. Chloride 7/16/67.

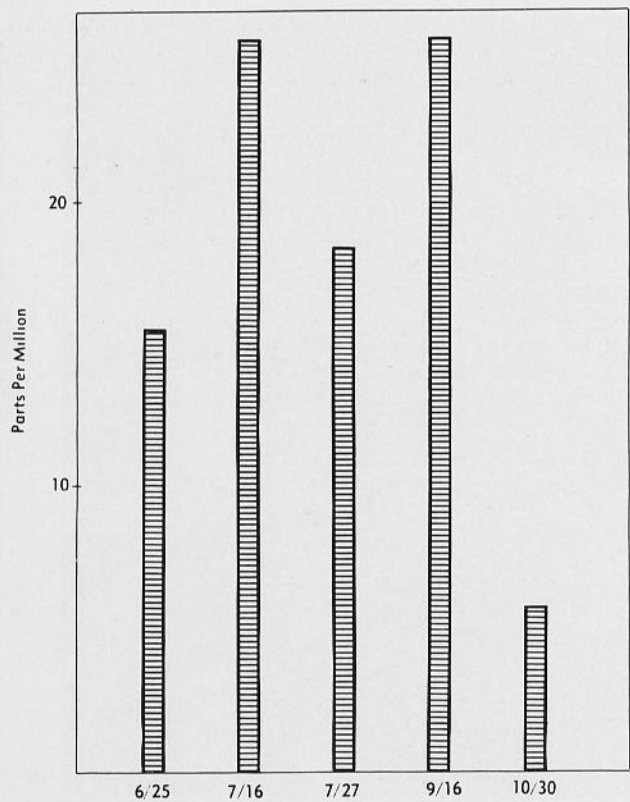


Fig. 32. Chloride—Station C.

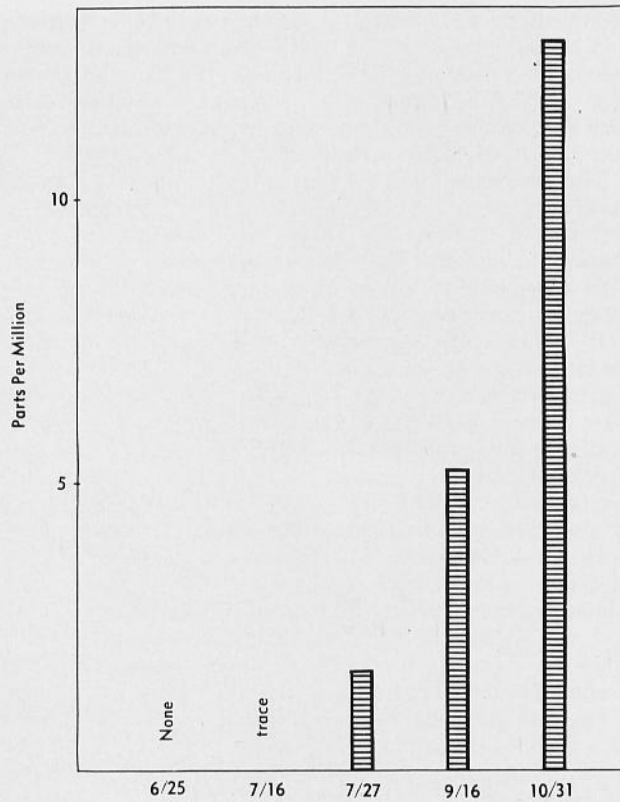


Fig. 33. Nitrate—Station C.

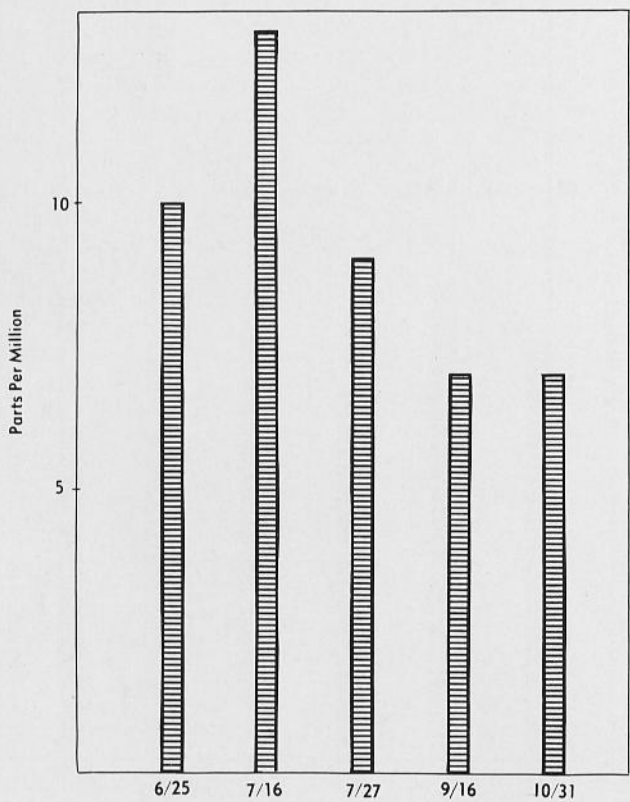


Fig. 34. Silica—Station C.

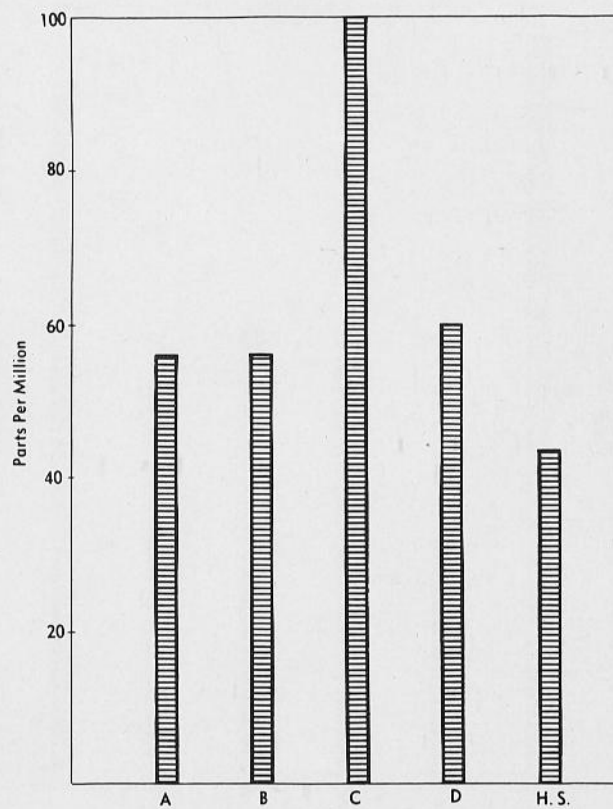


Fig. 35. Sulfate 9/16/67.

ing the study period (fig. 33). On 6/25/67, no nitrate was detected. On 10/31/67, the highest concentration (12.3 ppm) was detected. The rate of flow seems to have no effect on the concentration. If Station C is compared with the other stations, it is obvious that no trend is visible from station to station.

Since there is no trend in nitrate concentration in Hog Creek, it is probable that nitrate is derived locally in the vicinity of each station. The use of liquid ammonia as fertilizer is probably the source of much of the nitrogen which is converted to nitrate by organic processes. Liquid ammonia tanks are seen occasionally in the fields of Hog Creek basin, especially in early September.

Station C showed a measurable *phosphate* concentration only once during the study period; 0.7 ppm was recorded on 7/27/67. There is no correlation between the concentration of nitrate and phosphate at this locality. On 7/27/67, the only water found at Station C was in pools. Phosphate could be accumulated in these pools when plants decay and phosphate is released to the stream system.

Silica concentration at Station C seems to correspond with the diatom cycle (fig. 34). Low concentrations of silica are expected during diatom blooms and higher concentrations when diatoms die. Diatom blooms do not occur simultaneously at all points in the creek; therefore, silica concentrations appear to be somewhat erratic. Generally, however, silica is highest during the summer months as the creek dries up and only shallow pools of water remain. Silica may also enter the system as runoff leaches the soil. Runoff in the vicinity of Station D contained 13 ppm of silica.

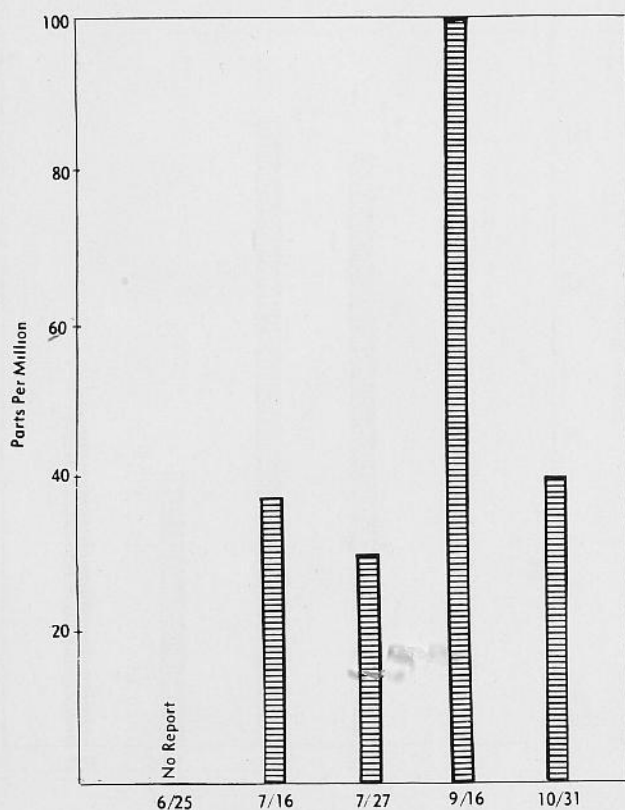


Fig. 36. Sulfate—Station C.

Sulfate concentrations at Station C were constantly higher than the other stations throughout the study period (fig. 35). Peak concentration occurred on 9/16/67 after a rain brought fresh water into the dry creek basin (fig. 36). Water flowed only through the gravels at this station. Station C had the highest sulfate concentrations because at this point water flowed over the sulfate-rich Comanche Peak Limestone for the longest time period. Downstream from Station C water flows over the Edwards Limestone.

Peak concentration of sulfate on 9/16/67 was probably the result of leaching of gypsum. In the upper oxidized layers of rock and soil, particularly in the dry summer, sulfides are converted to sulfates and rapidly leached away by the first fall rains.

STATION B

Station B is located on Hog Creek, 2.2 miles downstream from Station C (fig. 2). The creek flows over the Edwards Limestone at this locality (fig. 37). Hog Creek did not flow at Station B from 7/15/67 until 10/31/67. Samples during this period were taken from pools.

Calcium concentration remained fairly constant with only a small increase through the 6/25/67 to 9/16/67 period (fig. 38). This small increase was due to evaporation from pools during the summer. Low readings on 9/16/67 and 10/31/67 were the result of rainfall dilution.

Alkalinity (HCO_3^-) seemed to be stable with only a slight rise in concentration during the dry period from 6/25/67 until just before 9/16/67. Concentration during the period from 9/16/67 to 10/31/67 was much lower because rainfall introduced fresh water into the creek (fig. 39).

As was observed at Hurst Spring and Station D, equivalents of anions, namely HCO_3^- , outnumbered equivalents of calcium. This is significant because it means that some unknown cation(s), possibly sodium, is present at Stations B, D, and Hurst Spring.

Peak concentration of *chloride* was recorded on 7/15/67 during a period of no flow (fig. 40). July 15, 1967, was also the peak chloride concentration at the other stations. Evaporation and contact with the base rock is believed to cause the high chloride concentration during the summer. Periods of high flow on 9/16/67 and 10/31/67 contained lower concentrations as a result dilution by rainfall.

Stations A and B showed nearly identical concentration patterns during the study period (fig. 30). Stations C, D, and Hurst Spring are related and have different patterns. The different patterns could be caused by the influence of a different water source, a lessening of Hurst Spring influence, or influence of the Edwards Limestone. Hog Creek flows over Edwards Limestone at both A and B. Edwards Limestone is more resistant than Comanche Peak Limestone and probably does not contribute as much to the solution load of the stream.

There was no detectable amount of *nitrate* at Station B until 7/27/67 when 2.65 ppm was detected (fig. 41). There was no flow in the stream and water was found only in pools. On 9/16/67, after a rain, nitrate concentration rose to 14.9 ppm, the highest concentration during the study period. The high concentra-



Fig. 37. Station B: Immediately below bridge on paved road across Hog Creek at Lane's Chapel, Bosque County. Photograph taken in mid-summer during period of no flow.

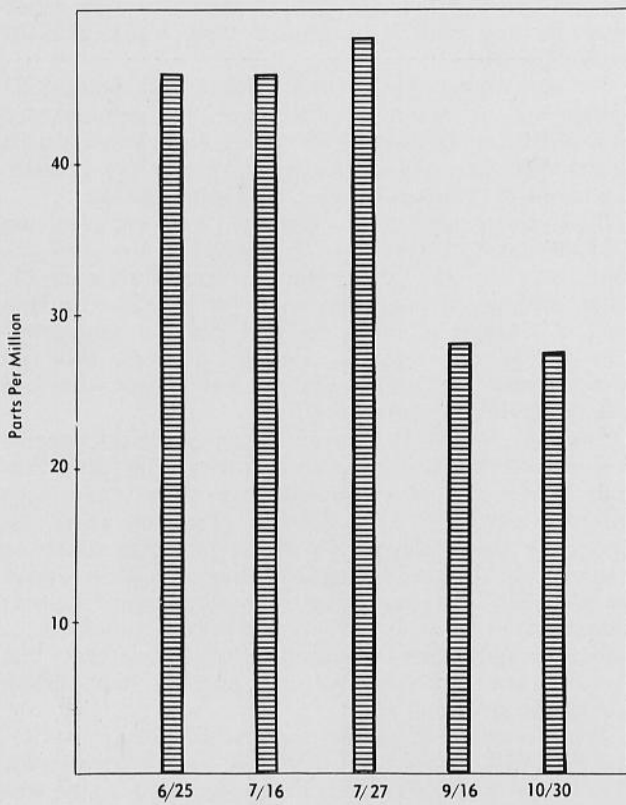


Fig. 38. Calcium—Station B.

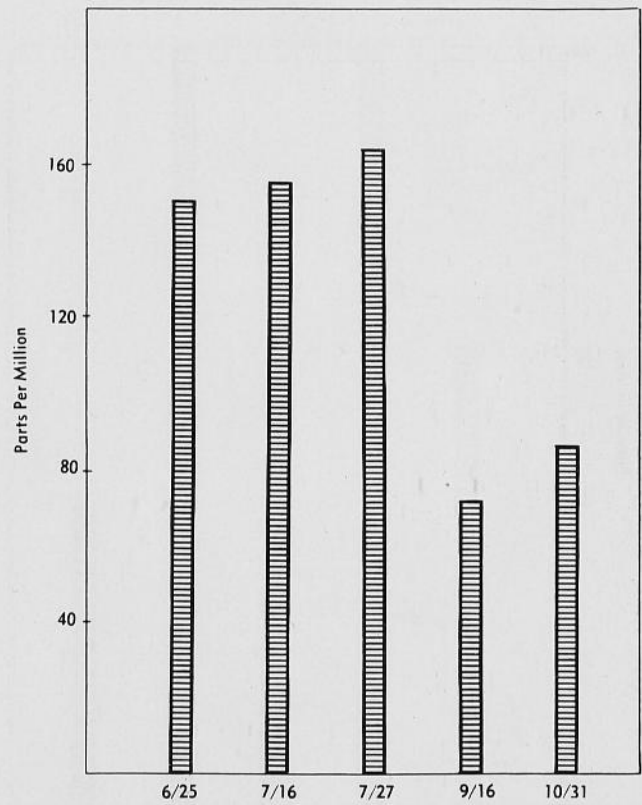


Fig. 39. Alkalinity—Station B.

tion is probably the result of nitrogen-rich plant decay products and nitrate fertilizers washed into the stream by runoff. Fields are usually fertilized just prior to the advent of the fall rainy season. Liquid ammonia tanks were observed at this time. The 9/15/67 rain washed much of the nitrogen-rich organic materials into Hog Creek, and the presence of a caliche pit at Station B probably also contributes to the high nitrate concentrations after heavy runoff. All stations reported higher concentrations at this time (fig. 42). On 10/31/67, after another rain, the level of nitrate was only 1.65 ppm, indicating that fields were not fertilized in this area after September.

Station B contained a measurable concentration of phosphate only once during the study period; 0.4 ppm was detected on 7/27/67. There seems to be no relationship between the concentrations of nitrate and phosphate. Source of the phosphate is probably from the decay of organics in and around the pools in the nonflowing creek.

Silica concentration showed steady decrease from 13 ppm on 7/16/67 to 4 ppm on 10/31/67 (fig. 43). As with the other stations, this corresponds roughly with the diatom cycle. There seems to be no clear relationship with the rate of flow at this location.

Peak concentration of sulfate occurred on 9/16/67 (fig. 44). The other stations also contained high concentrations at this date due to leaching.

Lowest concentration on 10/31/67 occurred during a flood period when dilution was a major factor.

Stations A, B, and D, all of which flow over base rock, have sulfate concentrations in the same range (fig. 35). Station C is the only anomalous situation.

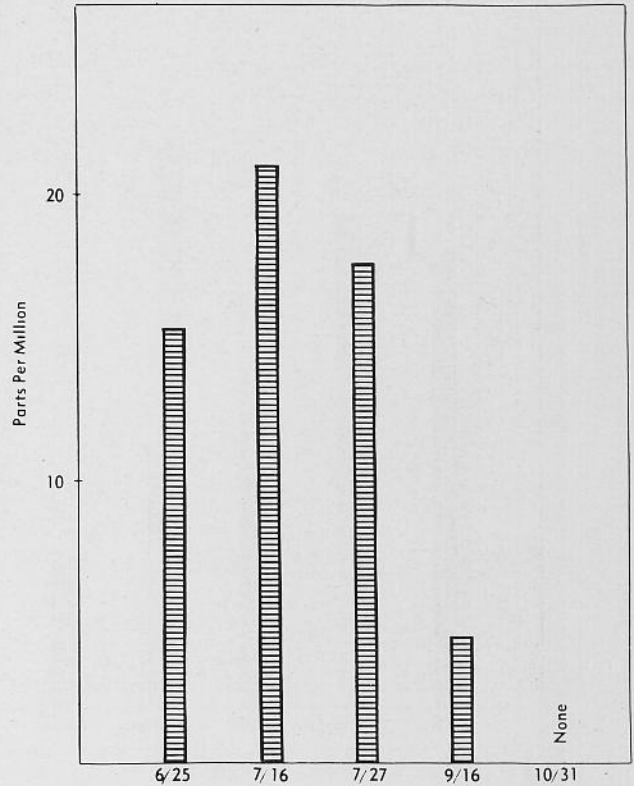


Fig. 40. Chloride—Station B.

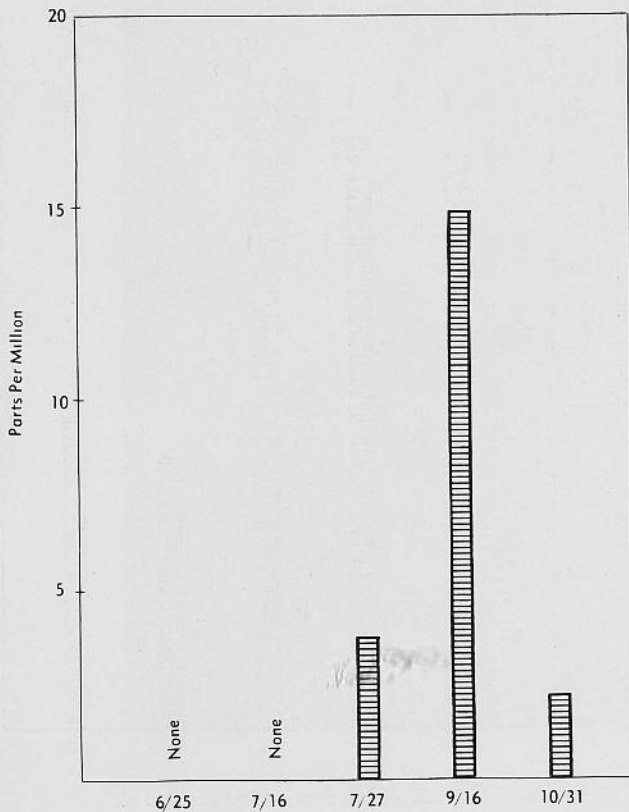


Fig. 41. Nitrate—Station B.

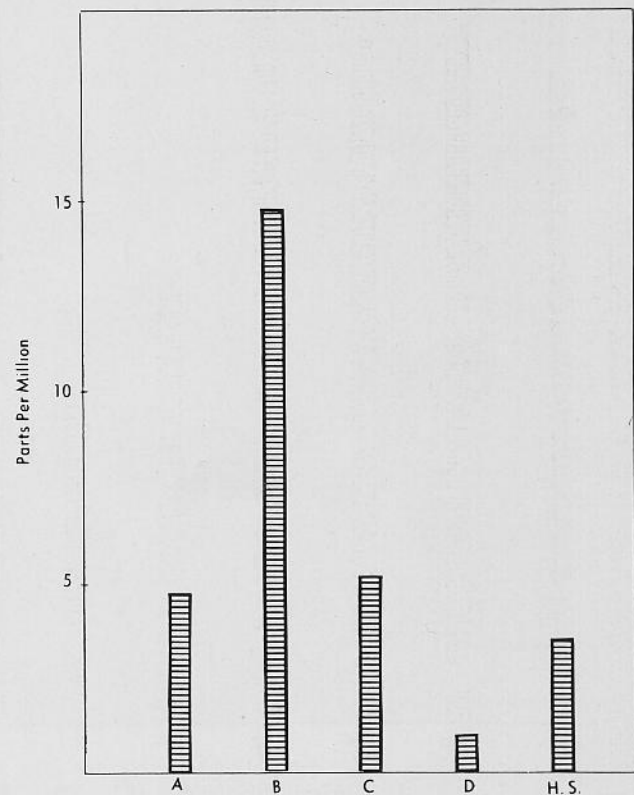


Fig. 42. Nitrate 9/16/67.

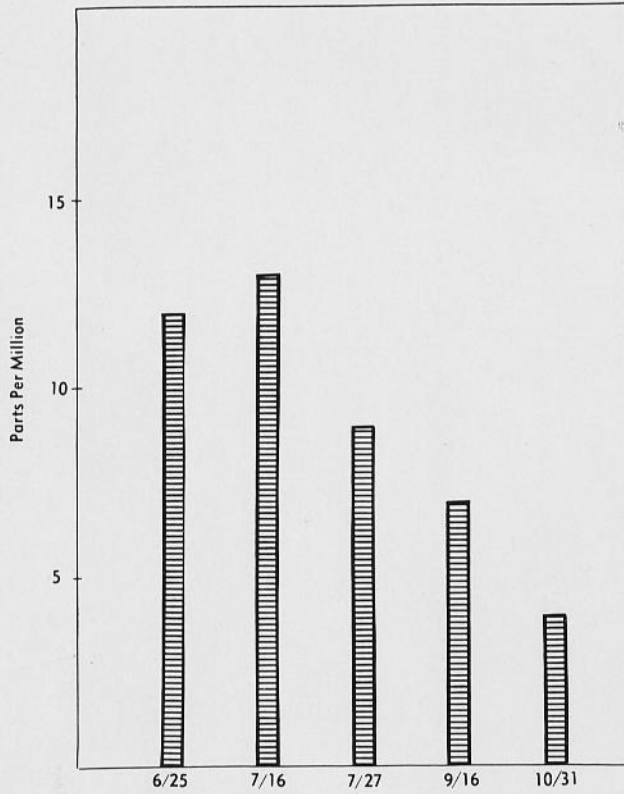


Fig. 43. Silica—Station B.

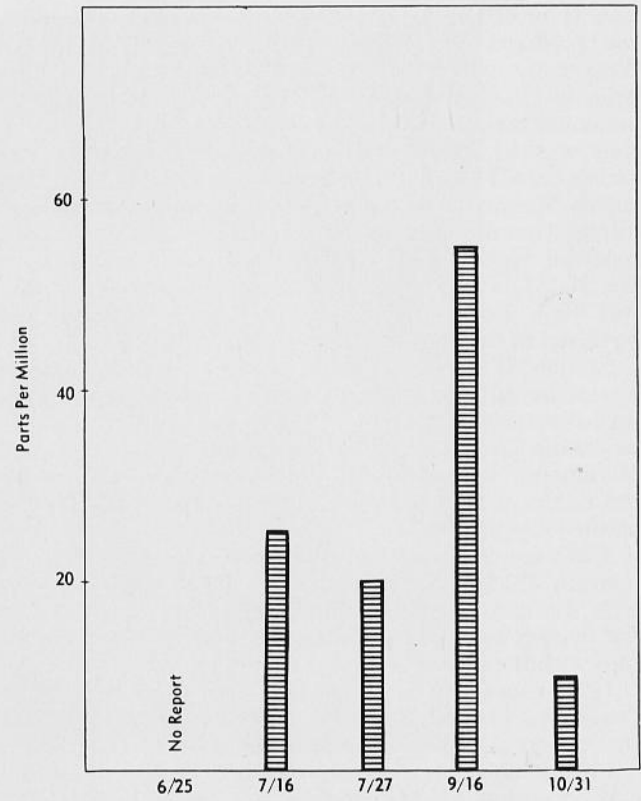


Fig. 44. Sulfate—Station B.



Fig. 45. Station A: At bridge over Hog Creek on Farm Road 217, about 6 miles west of Valley Mills, Bosque County. Photograph taken in mid-summer during period of no flow.

Hog Creek flows over limestone gravels and has higher sulfate concentrations at C.

STATION A

Station A, located on Hog Creek, is 3.3 miles downstream from Station B (fig. 2). At Station A, Hog Creek flows over the Edwards Limestone which also forms steep bluffs on either side of the creek (fig. 45). Hog Creek, at Station A, did not flow after 7/16/67 or before 10/31/67. Samples were taken from pools during this period.

Calcium concentration reached a peak on 6/25/67 during a period of normal flow. Lowest concentration was observed on 7/16/67 when the pH was 8.5 and precipitation of CaCO_3 occurred (fig. 46). Since there was no fresh supply of carbon dioxide to dissolve more calcium, the concentration remained low until rains came. Algae and other biota kept the concentration of carbon dioxide down; therefore, the water in pools was not capable of dissolving more calcium from the limestone creek bottom. Fresh water from rains contained carbon dioxide and dissolved more calcium.

A test for sodium was made only once; its concentration was found to be 8 ppm. The sample was predominantly runoff. During periods of normal flow the sodium concentration should be higher and closer to the concentration at Hurst Spring (22 ppm). During periods of flow, equivalent weights of anions outnumber equivalent of cations by 0.25 indicating the presence of some untested cations.

Highest concentrations of alkalinity (HCO_3^-) were found on 6/25/67 and 10/31/67 during periods of flow. Low concentrations were found when water was pooled (fig. 47).

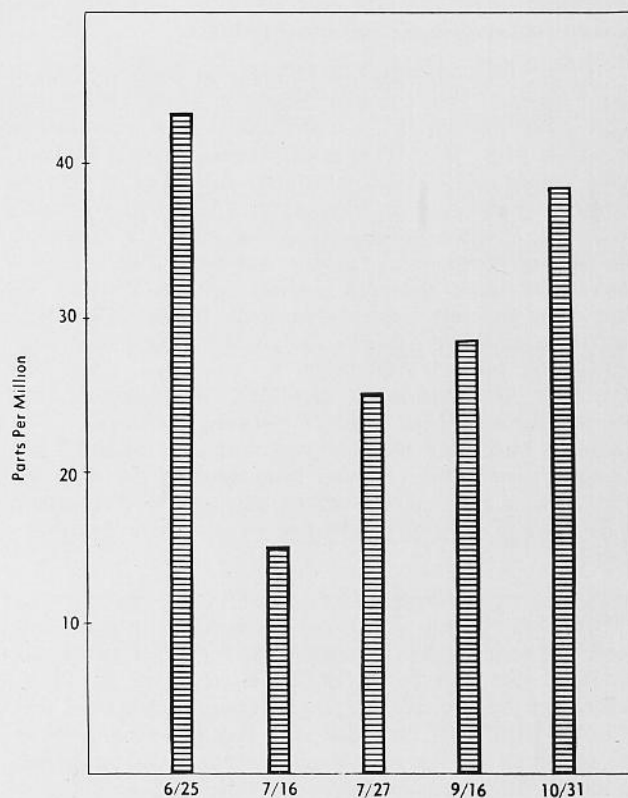


Fig. 46. Calcium—Station A.

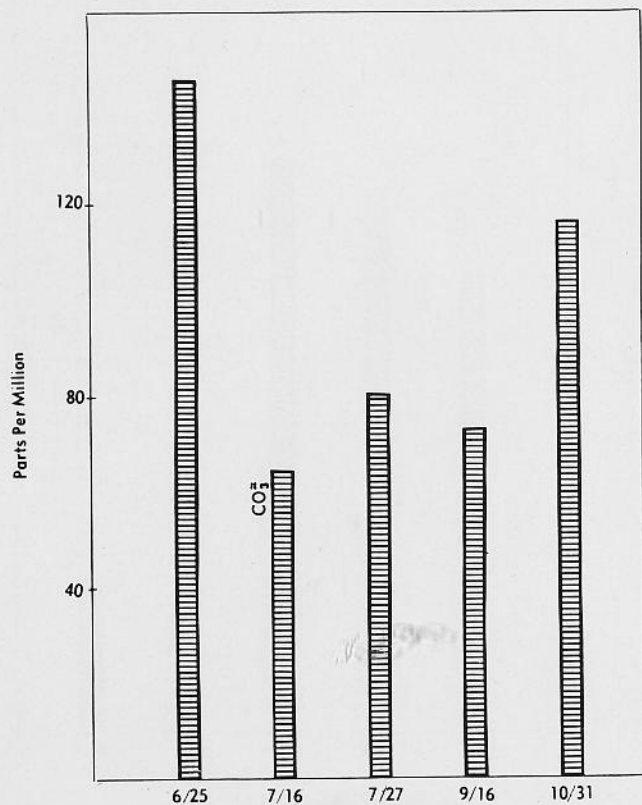


Fig. 47. Alkalinity—Station A.

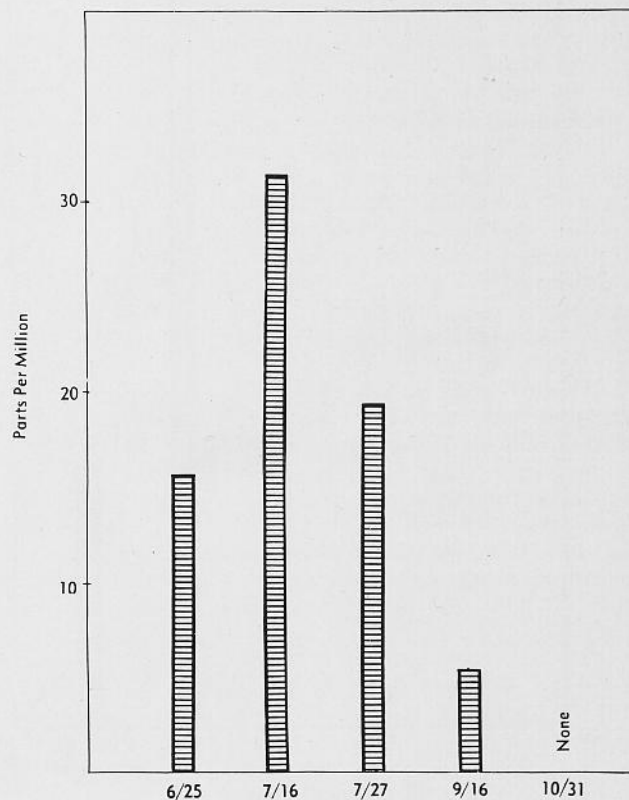


Fig. 48. Chloride—Station A.

On 7/16/67, when water was pooled, the pH rose to 8.5; therefore, alkalinity was in the form of CO_3^{2-} and HCO_3^- . Deposition of CaCO_3 was possible. The lowest concentration of calcium was found at this site indicating that precipitation was taking place.

Highest concentrations of *chloride* at Station A were found during the summer months when there was little water movement and pools were the only source of water (fig. 48). The pools found at this location make conditions ideal for evaporation and continued addition of chloride to the water from the limestone base rock. Either process could account for the high chloride concentrations in the summer. Lowest concentrations were detected during periods of flow or after rains had left fresh water in the basin. Tests were run on rainfall for chloride and it was found that concentrations ranged from zero to 1.8 ppm. This concentration of chloride is negligible; therefore, rainfall can be discounted as a major source of chloride. The limestone base rock must be the source of most of the chloride. Controlled tests on limestone in the area indicate that demineralized water may dissolve as much as 21 ppm of chloride from the rock (Edwards Limestone).

Highest concentrations of *nitrate* were detected on 9/16/67 after a rain which put fresh water into the dry creek bottom (fig. 49). Runoff from farmlands probably contained nitrogen from fertilizers. Stations A, B, C, and Hurst Spring all had high concentrations on this date. On 10/31/67, another rain brought more nitrate into the system. Stations A and B contained moderate amounts (1.67 ppm); however Stations C and Hurst Spring had concentrations near 13 ppm (fig. 42).

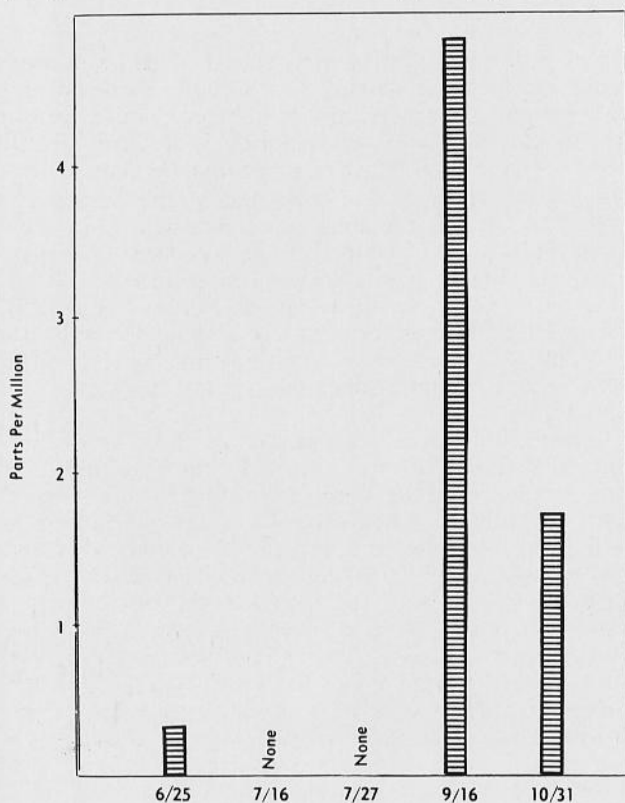


Fig. 49. Nitrate—Station A.

Since there is no trend in nitrate concentrations from station to station, it is probable that the nitrate is derived locally. The use of liquid ammonia as a fertilizer is probably the source of the nitrate.

Phosphate was detected only twice at Station A. On 7/16/67 and 7/27/67, concentrations of 0.3 and 0.4 ppm, respectively, were found. It was during this period of the summer that the last pools of water were drying up. Decay of algae and other plants was probably responsible for the phosphate concentration. There is no relationship between nitrate and phosphate at this location.

Silica concentration at Station A showed a steady rise from 6/25/67 until 7/27/67, moving from 12 ppm to 15 ppm. On 9/16/67, the concentration was down to 7 ppm after a heavy rain. Again, on 10/31/67 after a rain, the concentration was down to 4 ppm (fig. 50). Diatoms probably were at least partly responsible for variations in concentrations.

Sulfate concentrations at Station A were nearly identical with those at Station B (fig. 51). Both stations are located on the Edwards Limestone.

CONTROL TESTS

Controlled tests were run on water-soluble ion concentrations from each of the rock formations over which Hog Creek flows. Equal weights of crushed rock from each of the formations were placed in a 250 ml. flask; 200 ml. of distilled and demineralized water was added to each sample. Temperature and pH were held constant during the period. Water quality tests for each ion investigated in Hog Creek during the study were run to determine what ions were possibly derived from the rock.

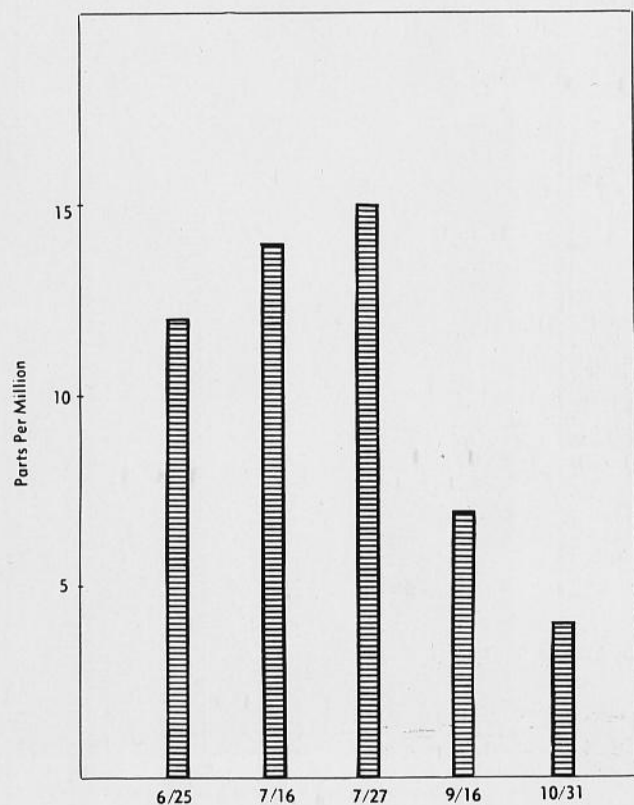


Fig. 50. Silica—Station A.

Measureable amounts of calcium, alkalinity, chloride, nitrate, and sulfate were found in each of the formations under test conditions. The high concentration of sulfate ion in Comanche Peak rocks may explain the high sulfate concentration found regularly at Station C.

Other ions detected on occasion in Hog Creek must come from sources other than the rocks which crop out along Hog Creek.

The ions of calcium, chloride, nitrate, sulfate, and alkalinity can all enter solution directly from the rock. The other ions investigated, silica and phosphate, must reach solution from some other source.

SUMMARY OF RESULTS

Each station has been discussed and it is now possible to examine each ion as it behaves in the whole stream system.

CALCIUM

With few exceptions, through the test period, the concentration of calcium decreased downstream from Hurst Spring. When relatively high carbon dioxide concentrations occur, as at Hurst Spring, high calcium concentrations are expected in a limestone region. Downstream from Hurst Spring toward Station A, carbon dioxide partial pressures are lowered by reduced pressure outside the aquifer, higher temperatures, and/or plant activity. Through the study period, the average difference in calcium concentration between Hurst Spring and Station D was as high as 61 percent. The difference in concentration is the result of carbon dioxide seeking equilibrium after it leaves the Edwards Limestone aquifer. The concentration of

calcium in Hog Creek is controlled solely by the partial pressure of carbon dioxide in the water since calcium is available in abundance at all points along the stream course.

SODIUM

Analysis for sodium was made only once; therefore, only tentative conclusions can be drawn. Sodium is present in Hurst Spring, and its concentration decreases downstream toward Station A. However, the downstream stations were strongly influenced by runoff and did not reflect the influence of Hurst Spring. It is probable that the concentration of sodium remains nearly constant at Hurst Spring since the other cation, calcium, behaves in such a manner.

ALKALINITY

The trend of alkalinity in Hog Creek during the test period shows a decrease in concentration downstream from Hurst Spring.

The presence of large amounts of bicarbonate in solution is possible when a large amount of carbon dioxide is available. When under a pressure sufficient to prevent the escape of carbon dioxide, such a solution can exist in a stable form. Gas bubbles have been known to escape from Hurst Spring samples upon slight heating. If carbon dioxide is released as the water leaves the aquifer, both calcium and bicarbonate should decrease in concentration downstream from the spring, if the spring is the chief source of bicarbonate. Such must be the case in Hog Creek. Hurst Spring water pools about 15 feet from where it emerges (fig. 4). Water in this pool is cloudy at all times even though the only source of water is the spring. Cloudiness of the water may be the result of the precipitation of CaCO_3 .

CHLORIDE

The concentration of chloride in the Hog Creek system is highest during dry periods when the creek is not flowing or is flowing slowly. Unlike calcium, the concentration is not related to the partial pressure of carbon dioxide; therefore, chloride is leached directly from the limestone. This is supported by control tests run on the rocks which crop out in the basin. The longer the water remains in contact with the rock, while the volume of water is being reduced by evaporation, the higher the chloride concentration will be. This pattern is best illustrated at Stations A and B. When Hog Creek flows normally without the influence of runoff, concentrations of chloride are fairly uniform from station to station including Hurst Spring.

NITRATE

Concentration levels of nitrate in Hog Creek present no definite pattern. This indicates that nitrate at each station must be derived locally. Fertilization of fields at different times can cause various stations to be high at one time or another. All stations were relatively high on 9/16/67 as a result of rains which washed nitrate into the creek from farmlands. Concentrations of nitrate at Hurst Spring are generally higher than the other stations throughout the study period, because water which enters the aquifer must first filter through farmland soils in the hydrologic basin. There is nothing in the aquifer to remove nitrate from solution, and it enters Hog Creek at Hurst Spring.

PHOSPHATE

Phosphorus is a cyclic element due to biotic activity;

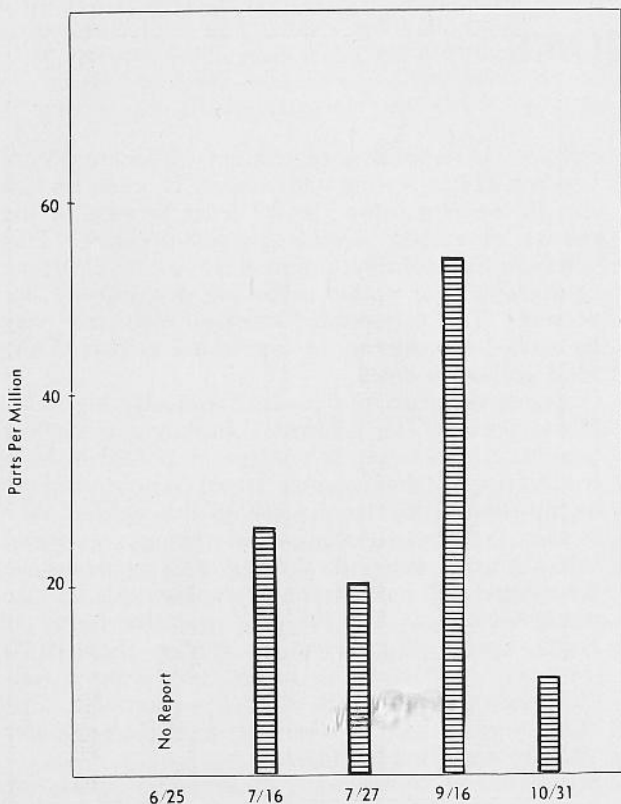


Fig. 51. Sulfate—Station A.

its concentration in the water fluctuates with decomposition and synthesis. High levels are expected during decomposition and low levels during high synthesis periods. Since phosphorus is essential in plant nutrition, it is probable that considerable amounts are withheld by vegetation and will never reach Hog Creek directly. Phosphorus is also firmly held by the soil; therefore, little will reach the stream in runoff. When aquatic vegetation dies, small amounts of phosphorus are released and added to Hog Creek waters.

During the study period, concentrations increased at each sampling until the creek dried up. This observation supports the theory that the phosphorus found in Hog Creek is there as a result of plant decomposition during the dry period. There seems to be no relationship between phosphates and nitrate concentrations in Hog Creek. Nitrate and phosphate appear to come from two different sources: nitrate from fertilizers and phosphates from plant decomposition.

SILICA

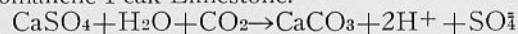
One of the sources of silica in limestone-drained areas is aluminosilicates which dissolve from dying diatoms through the action of carbon dioxide. While silicic acid is not a constituent of protoplasm, it forms the basis of the skeletal structure of the most important group of algae in the water, the diatoms. It resembles carbon dioxide in its chemical properties. However, because it is much more weakly dissociated than the latter, it is removed from its strongly hydrolyzed compounds, the silicates, in the presence of carbon dioxide or bicarbonate and is then held in the water as free silicic acid in a dissolved form (Ruttner, p. 93).

Another possible source of silicate in Hog Creek is the soil in the drainage basin. Control tests on soil samples indicate that runoff from soils may contain approximately 13 ppm silica. Silica probably reaches the aquifer by percolation of water through the soils since there is no algae or diatoms in the aquifer.

At Stations A and B, for example, the concentration of silica increased and reached a peak on 7/27/67. This gradual increase may be interpreted as a diatom kill as Hog Creek dried up. A sharp decrease in silica occurred on later dates when rains brought fresh water into the creek basin. Either dilution by rainwater or diatom blooms could produce the low silica concentrations. The relative importance of diatoms and silicic acid in soils toward silica concentrations in Hog Creek was not determined by this study.

SULFATE

Sulfate can enter the Hog Creek system from decomposition of gypsum and/or from fertilizers. Since most sulfates in fertilizers are in chemical combination with iron, nitrogen, and phosphorus, and no iron is detected in Hog Creek, fertilizers may be discounted as a potential sulfate source although it can not be ruled out. Most sulfate in Hog Creek probably is derived from gypsum in various formations, chiefly the Comanche Peak Limestone.



Water flows over leached rocks and soil and carries the sulfate into the creek and aquifer. The first rain after a dry period should bring with it higher sulfate concentrations due to leaching. The 9/16/67 analysis confirmed this idea.

CONCLUSIONS

1. Hog Creek of Hamilton, Coryell, and Bosque counties has a very narrow, straight drainage basin which drains approximately 48.6 square miles in the study area. Water in Hog Creek except for brief periods of runoff comes from springs, principally Hurst Spring. The rocks which crop out in the basin are formations of the Fredericksburg and lower Washita groups, Comanchean Series.
2. In the Hog Creek hydrologic system, the highest concentration of dissolved solids is found at Hurst Spring with an average ion concentration of approximately 480 ppm. Station D, located 2.1 miles downstream from Hurst Spring, had an average salinity of approximately 260 ppm over the study period. Stations C, B, and A vary in relation to Station D but not as greatly as with Hurst Spring. The major difference in salinity is the high concentrations of calcium and bicarbonate in Hurst Spring water. The higher concentration of calcium and bicarbonate is caused by the higher partial pressure of carbon dioxide in the Edwards Limestone aquifer. As water is expelled from the aquifer at Hurst Spring and the partial pressure of carbon dioxide is reduced, concentrations of calcium and bicarbonate drop to lower levels, as expressed at

- Station D. Deposition of calcium carbonate occurs between Hurst Spring and Station D, even though the pH remains below the 8.2 fence because of the release of carbon dioxide partial pressure. This situation is probably common to most limestone aquifers even if visible carbonate deposits are not present. The precipitated calcium carbonate may be carried downstream in suspension as part of the solid load of the creek.
3. Nitrogen concentration is also frequently higher at Hurst Spring. The Edwards Limestone, a shallow aquifer in this area, is subject to pollution from fertilization of the farming areas. When once the highly soluble nitrates are within the aquifer, they remain there until expelled in springs or seeps. When nitrates enter the flowing stream, plants use the nitrate and concentrations are lowered. Nitrate concentrations as high as 13.2 ppm are found at Hurst Spring. Concentrations higher than 10-20 ppm may be harmful to babies, producing a condition known as cyanosis or oxygen starvation. The situation may occur anywhere a shallow aquifer underlies fertilized farmlands.
4. Solubilities of certain ions, chloride and sulfate for example, are not controlled by the partial pressure

of carbon dioxide. Their concentrations are dependent upon the length of time water is in contact with the source of the chloride or sulfate, the relative resistance of the rock, the temperature of the water, and the concentration of the ion in the rock. Since all concentrations of these ions are far below saturation levels, the relative resistance of the rock and the concentration of the ion in the rock determine the concentration of chloride and/or sulfate in the stream. On a single formation, length of time of water contact with the rock is the most important factor. As was noted by Hutchinson, during the summer low-flow period the concentration of chloride is the highest because of the longer time of contact with the rock. Concentrations of calcium and bicarbonate decrease, while chloride concentrations increase during the low flow period.

5. Other ions such as phosphate, silica, and to a partial degree nitrate are cyclic. Concentrations vary irregularly from station to station; however, their concentrations can be correlated with the life cycles of aquatic plants. Nitrate in Hog Creek originates from fertilizers but is utilized by plants in their life processes. Plants can contribute only small amounts to the salinity of a stream. If concentrations of phosphate and nitrate are above a few parts per million, pollution may be the cause. In the Hog Creek basin pollution sources include farmlands.
6. If the average concentration of ions of all the stations is observed during a period of normal flow (6/25/67), during a period of no flow (7/27/67), and during a period of runoff-influenced flow (10/31/67), it is observed that the difference among the three is small (fig. 52). Highest ion concentration per unit volume is found during periods of normal flow; least is found during periods of runoff. Since ion concentrations are fairly uniform during each of the three periods, the solution load

would, therefore, be much higher during periods of flood in direct proportion to the volume of water in the creek.

7. As Hog Creek flows over different lithologies, the chemical character of the water also changes in relation to the chemistry of the rock it flows over.

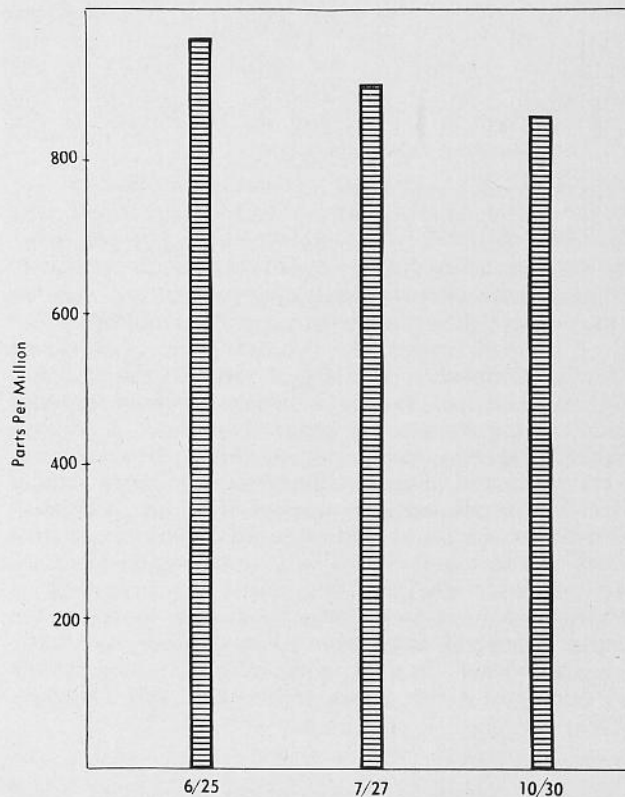


Fig. 52. Total ion concentration of all stations.

APPENDIX I

GLOSSARY

Quality of water. All properties of water that can affect water's use. Quality of water in this report refers to dissolved chemical constituents and physical properties. Problems related to sediment and to organic or bacterial pollution are not considered.

Parts per million (ppm). Unit weights of dissolved mineral contained in one million unit weights of water.

Equivalent per million (epm). An equivalent weight of an ion or salt in grams per one million grams of water. Computed by dividing concentration of chemical constituent, in parts per million, by equivalent weight of the ion or salt.

Dissolved solids. Concentration of dissolved minerals in water. In this report the dissolved solids were obtained by adding individual constituents shown in analysis.

Salinity. General term used in this report to denote any of the numerous chemical compounds dissolved in water.

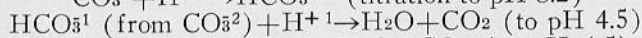
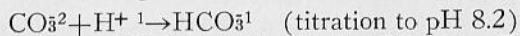
Pollution. As used in this report, pollution defines conditions in which dissolved-mineral concentration of water exceeds acceptable limits for a particular use. Artificial pollution refers to conditions which are made by man; natural pollution refers to conditions that man did not create.

APPENDIX II

SAMPLING AND ANALYTICAL PROCEDURES

ALKALINTY

In the potentiometric method, alkalinity is determined by titrating the water sample with a standard solution of strong acid. The equivalency, or end points, are selected as the inflection points in the titration of Na_2CO_3 with H_2SO_4 . The carbonate end point is taken as pH 8.2 and the bicarbonate as pH 4.5. The following reactions occur:



HCO_3^- (natural) + $\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$ (to pH 4.5)
The presence of hydroxide is indicated if the carbonate titrant volume exceeds the bicarbonate titrant volume.

For waters that contain only small quantities of dissolved mineral matter, the determination of alkalinity is likely to introduce the largest error in the analysis. Reproducibility of results between duplicate samples cannot be expected to be better than about 2 percent. Alkalinity is very susceptible to change between time of collection and analysis. Changes occur more rapidly after the sample bottle is opened. The total-alkalinity value is probably somewhat more stable than the relative values of the common alkalinity components. Unless a gross error is made in the initial determination of alkalinity, it is seldom advisable to try to check the results if several days have elapsed since the bottle was first opened. In some water alkalinity may change appreciably in a few hours (Rainwater and Thatcher, 1960).

Apparatus:

Titration assembly, consisting of a medium speed mechanical stirrer, and a 50 ml. buret.

Phenolphthalein indicator solution.

Standard sulfuric acid, (0.01639N).

Brom cresol green-methyl red indicator.

Procedure:

Water samples for the determination of alkalinity should not be filtered, diluted, concentrated, or altered in any way.

1. Measure 50 ml. or more of fresh water sample into a titration dish.
2. Add 2 or 3 drops of phenolphthalein indicator solution. If a pink color develops, titrate with sulfuric acid until the pink color disappears, and record ml. of acid used. If no pink color appears, no carbonate or hydroxyl is present. Proceed to next step.
3. Add 3 or 4 drops of brom cresol green-methyl red indicator solution. A greenish color will develop.
4. Titrate with sulfuric acid until each end point is reached, recording the amount of acid used to reach each end point. Calculate the epm of total alkalinity for each point as given below.

SURFACE-WATER SAMPLING

The proper sampling of a flowing stream must take into account first the need for each sample, or set of samples, taken simultaneously to represent the whole flow of the stream at the sampling point at that instant. Second, the need for enough samples distributed in time to define the changes which occur in water passing the

sampling point must be taken into account (Hem, 1959).

In a complete study of surface-water quality, samples should be collected at intervals such that no important cycle of change in concentration could pass unnoticed between sampling times. A determination of temperature and pH should be run in the field because they will obviously change before the sample can be taken to the laboratory. Solubility of most ions is dependent upon these two factors.

Calculations:

$$\text{ppm Alkalinity as CaCO}_3 = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times 0.82 \times \text{ml. titrant}$$

$$\text{ppm OH}^- = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times (\text{ml. to pH 8.2}) - (\text{ml. to pH 4.5}) \times 0.2788$$

$$\text{ppm CO}_3^{2-} = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times (\text{ml. to pH 8.2}) \times 0.9835 - (\text{ppm OH}^- \times 3.527)$$

$$\text{ppm HCO}_3^- = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times (\text{ml. to pH 8.2 to 4.5}) - (\text{ml. to pH 8.2})$$

It is important to note that most naturally occurring brines and fresh waters exhibit no carbonate or hydroxide alkalinity; therefore, bicarbonate and total alkalinity are equal.

Total alkalinity of a sample should be a reproducible figure, provided that similar conditions of sample treatment are followed. Agreement much closer than 2 to 5 percent, however, cannot be expected on duplicate samples, and differences this size should not be considered significant in making interpretations.

CALCIUM

The complexometric method of calcium ion determination is applicable to most natural waters but may fail in the analysis of brines or some acid or polluted waters that contain excessive amounts of heavy metals (Rainwater and Thatcher, 1960).

Principle of determination:

Disodium dihydrogen ethylenediamine tetraacetate (Na_2EDTA) forms a slightly ionized, colorless, stable complex with calcium ions. Murexide is dark purple in the absence of calcium, but with calcium forms a light-salmon-colored complex which has an ionization constant higher than the Na_2EDTA complex. Hence, by using murexide as an indicator, a solution containing calcium ions may be titrated with Na_2EDTA . The optimum pH of the titration is 10.4 or above (*idem*).

The salt, Na_2EDTA , reacts with iron, manganese, copper, zinc, lead, cobalt, nickel, barium, strontium, calcium, magnesium, and several other metals. Murexide reacts with strontium but not with magnesium or barium; however, the end point in the presence of strontium is sluggish, and the titration is not strictly stoichiometric. Barium does not titrate as calcium but affects the indicator in some unknown way so that no end point, or at best a poor end point is obtained. Barium can be removed by prior precipitation with sulfuric acid. The interference of heavy metals is minimized by the addition of hydroxylamine and cyanide. Concentrations of 5 ppm iron and 10 ppm of manganese can be tolerated (*idem*).

According to Rainwater and Thatcher, the interference of heavy metals is relatively easily detected because of the typical end point. Conventional methods of hydroxide and sulfide treatment can be used, if necessary, to remove these metals from solution before titration. Magnesium in high concentrations may precipitate as magnesium hydroxide, but the precipitation is not significant unless the photometric-titration assembly is used to determine the end point. The results are generally accurate and reproducible to ± 0.025 mg. in the 1 mg. range and to ± 0.05 mg in the higher concentrations.

Apparatus and reagents:

Visual titration apparatus consists of a motor-driven stirrer, 125 ml. buret, white porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain-base and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from the side and at about 90° from the line of vision.

Buret, 25 ml.

Hydroxylamine hydrochloride, 3 percent

Sodium hydroxide, 2 N

Sodium cyanide, 2.5 percent

Murexide, dry mixture

Na_2EDTA , 1.00 ml.=0.50 mg. Ca^{+2}

Procedure:

1. Pipet a volume of sample containing less than 10 mg. Ca^{+2} (50.0 ml. max.) into a 150 ml. beaker and adjust the volume to approximately 50 ml.
2. Insert beaker in titration assembly and start stirrer.
3. A. 1 ml. 3 percent $\text{HN}_2\text{OH} \cdot \text{HCl}$.
4. Add 1 ml. 2N NaOH.
5. Add 1 ml. 2.5 percent NaCN (poison).
6. Add 0.2g murexide indicator and proceed immediately with the titration.
7. Titrate with Na_2EDTA (1.00 ml.=0.50 mg. Ca^{+2}) until purple swirls begin to show. The end point is reached when the sample color changes from salmon to orchid purple. At the end point, the addition of a small increment of titrant will not cause a deepening of the purple color.
8. Determine a blank correction by similarly treating 50 ml. metal-free water. The normal blank correction is 0.05 or 0.10 ml.

Calculations:

$$\text{ppm } \text{Ca}^{+2} = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times (\text{ml. titrant} - \text{ml. blank}) \times 0.5$$

Calcium is highly soluble in water and is present in high concentrations in limestone and alkaline soils in the Central Texas area.

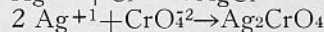
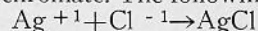
CHLORIDE

The volumetric method for the determination of chloride ion is recommended for waters whose chloride concentration is less than 2,000 ppm and can be used satisfactorily for measuring chloride concentrations up to 5,000 ppm.

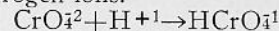
Principle of determination:

In the well-known Mohr method for determination of chloride, use is made of the fact that in the titration of sodium chloride with silver nitrate, the solution is saturated with silver chloride at the equivalence point and contains equal concentrations of silver and chloride ions. Addition of an excess of silver precipitates silver

chloride, whose solubility decreases with an excess of either silver or chloride ions. When potassium chromate is used as an indicator, the chromate ion combines with the excess silver to form very slightly soluble red silver chromate. The following reactions occur:



The pH for the titration should be between 7.0 and 10.5. In an acid medium, the sensitivity of the method is decreased; the second ionization constant of chromic acid is small, and therefore the chromate ion reacts with hydrogen ions.



The solution should not be too alkaline because silver hydroxide might then precipitate before the silver chromate. Calcium carbonate can be used to adjust the pH of acid waters without danger of making the solution too alkaline. Detection of the end point is facilitated by viewing the titration through yellow goggles or a filter.

Iodine and bromide titrate stoichiometrically as chloride. Phosphate, sulfite, and cyanide interfere. Sulfide and cyanide can be removed by acidifying and boiling the sample, then adjusting the pH with calcium carbonate. Hydrogen sulfide can often be removed simply by passing pure air through the sample. Sulfite interferes but can be oxidized readily to sulfate with hydrogen peroxide.

Two strengths of silver nitrate are provided. The dilute titrant is recommended if the chloride concentration is less than 5 mg. in a 50- or 25-ml. sample. The end point with the dilute silver nitrate is not as sharp as when the concentration is greater than 200 ppm. In high-chloride waters, the voluminous precipitate masks the end point, and the maximum chloride concentration that can be titrated satisfactorily is about 50 mg. Sample dilution can be carried only so far before the dilution factor decreases the precision and accuracy considerably. If a 10-ml. sample were taken, 0.1 ml. silver nitrate (1.00 ml.=5.00 mg. Cl^{-1}) is equivalent to 50 ppm of chloride. Sample volumes less than 10 ml. are not recommended.

Results are usually accurate and reproducible to ± 0.05 mg. when the dilute silver nitrate (1.00 ml.=0.50 mg. Cl^{-1}) is used. When the concentrated silver nitrate (1.00 ml.=5.00 mg. Cl^{-1}) is used, accuracy and reproducibility of $\pm 2-3$ percent can be expected (Rainwater and Thatcher).

Apparatus and reagents:

Yellow light (not necessary if not available)

Buret, 25 ml.

Potassium chromate indicator solution

Silver nitrate, 1.00 ml.=5.00 mg. Cl^{-1}

Silver nitrate, 1.00 ml.=0.50 mg. Cl^{-1}

Procedure: (Rainwater and Thatcher)

1. Pipet a volume of sample containing less than 50 mg. Cl^{-1} (50.0 ml. max.) into a porcelain evaporating dish and adjust the volume to approximately 50 ml.
2. Add 10 drops K_2CrO_4 indicator.
3. With constant stirring, titrate with AgNO_3 until the pink-red Ag_2CrO_4 persists for 10-15 seconds.
4. Determine a blank correction by similarly treating 50 ml. dilution water. The normal blank correction with AgNO_3 (1.00 ml.—0.50 mg. Cl^{-1}) is 0.05

or 0.10 ml. No blank correction is required with the stronger titrant.

Calculations:

$$\text{ppm Cl}^{-1} = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times (\text{ml. titrant} - \text{ml. blank}) \times (\text{mg. Cl}^{-1} \text{ per ml. titrant})$$

Report chloride concentrations of > 10 ppm to 1 decimal place of between 10 and 999 ppm to whole numbers and of > 999 ppm to 3 significant figures only.

Chloride may be present in resistates as the result of inclusion of connate water, and is to be expected in an incompletely leached deposit laid down under the sea.

COPPER

Most copper minerals are relatively insoluble, and little copper found in water is of natural origin. The presence of copper in more than trace amounts can usually be attributed to corrosive action of water on copper pipes, to industrial wastes, or to the use of copper salts for the control of algae and other aquatic growths.

Copper imparts a disagreeable metallic taste to water. As little as 1.5 ppm can usually be detected, and 5 ppm can render the water unpalatable. Copper is not considered to be a cumulative systemic poison like lead and mercury; most copper ingested is excreted by the body and very little is retained. The pathological effects of copper are controversial, but it is generally believed very unlikely that humans could unknowingly ingest toxic quantities from palatable drinking water (Rainwater and Thatcher).

Principle:

Cupric ions form a yellow-colored chelate with the reagent bis (2—hydroxyethyl) dithiocarbamate, whose popular name is "cuprethol." The colored compound is soluble and is formed quantitatively.

Interference:

Bismuth, cobalt, mercurous, nickel, and silver ions interfere seriously and must be absent. It is believed that excessive concentrations of interfering ions will seldom be encountered in unpolluted waters.

The Cuprethol Method (Hach Chemical Company) used in the copper test uses a single, dry powder reagent called Cuprethol Powder. This is a stable formulation and is packaged in powder pillows for convenient field use.

The test is carried out by adding the contents of one Cuprethol powder pillow (Hach) to the water sample and mixing. If copper is present, a yellow color develops and is compared with a Hach color comparator disc. The results obtained are expressed in parts per million copper. The copper color disc (Hach) has a range of 0-5 ppm copper.

Procedure: (Hach Chemical Company)

1. Fill the two glass sample tubes to the mark with the water sample.
2. Add the contents of one Cuprethol powder pillow to one of the test tubes.
3. Stopper and invert several times to mix. If copper is present a yellow color will develop.
4. Insert the prepared color comparison tube in the opening nearest the middle of the color comparator.
5. Insert the sample tube with the original water sample in the outside opening of the color comparator.

6. Hold the color comparator up to a light and view through the two openings in the front. Rotate the Copper color disc until a color match is obtained. Read the parts per million copper from the scale on the color disc through the scale reading opening.

HARDNESS

The complexometric method of hardness is applicable to most natural and treated waters, but the method fails conspicuously at times with acid or polluted waters that contain excessive amounts of heavy metals.

Principle of determination:

Disodium dihydrogen ethylenediamine tetraacetate (Na₂EDTA) forms a slightly ionized colorless stable complex with alkaline earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths, but with them forms a deep red complex which has a higher ionization constant than the Na₂EDTA complex. Hence, by using Eriochrome Black T as an indicator, the alkaline earths can be titrated with Na₂EDTA.

All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, as the color of the solution will fade upon standing. The optimum pH of the titration is 10.4 or above.

The salt Na₂EDTA also reacts with iron, manganese, copper, lead, cobalt, zinc, and nickel. Heavy-metal interferences can usually be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure can be used with undiluted samples for analysis of water having metal concentration as high as 10 ppm iron, 10 ppm copper, 10 ppm zinc, and 10 ppm lead.

The higher oxidation states of manganese above Mn⁺² react rapidly with the indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent-manganese interference can be removed by addition of 1 or 2 small crystals of potassium ferrocyanide.

In the presence of high aluminum concentrations, a characteristic effect will be observed as the end point is approached. The blue color that indicates that the end point has been reached will appear and then on short standing will revert to red. This reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed. Although it has been stated that the titration cannot be used in the presence of excessive amounts of heavy metals, it should be pointed out that most heavy metal interference can be alleviated by applying conventional separations. Results are accurate and reproducible to ±0.1 mg.

Apparatus and reagents:

Titration assembly: Conventional lighting with a variable speed stirring device

Buret, 50 ml.

Hydroxylamine hydrochloride, 3 percent

Ammonium hydroxide, conc. (ap. gr. 0.900)

Sodium cyanide, 2.5 percent

Potassium ferrocyanide, crystals

Eriochrome Black T indicator solution

Na₂EDTA, 1.00 ml.=1.00 mg. CaCO₃

Procedure:

1. Pipet a volume of sample containing less than 25

- mg. hardness (50.00 ml. max.) into a 150 ml. beaker and adjust the volume to approximately 50 ml.
2. Insert the beaker in the titration assembly and start the stirrer.
 3. Add 1 ml. 3 percent $\text{NH}_2\text{OH} \cdot \text{HCl}$.
 4. Add 1 ml. conc. NH_4OH (if NH_2OH is not tightly stoppered it tends to lose strength) and 1 ml. of weak NH_4OH will not buffer the solution to the desired pH.
 5. Add 2 ml. 2.5 percent NaCN (poison), NaCN may be eliminated if copper, zinc, lead, cobalt and nickel are entirely absent and if the sample contains less than 0.25 mg. Fe and 0.025 mg. Mn.
 6. If manganese is present, add 1 or 2 small crystals $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. Stir and wait at least 5 minutes until the $\text{Mn}_2\text{Fe}(\text{CN})_6$ precipitates.
 7. Add 2.0 ml. Eriochrome Black T indicator.
 8. Titrate with Na_2EDTA (1.00 ml.=1.00 mg. CaCO_3) until blue or purple swirls begin to show. The end point is reached when all traces of red and purple have disappeared and the solution is clear blue in color. The detection of the end point may be facilitated by comparison of the titration solution with a color-free blank prepared of metal-free water and the reagent.

Calculations:

$$\text{ppm Hardness as CaCO}_3 = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. sample}} \times \text{ml. titrant.}$$

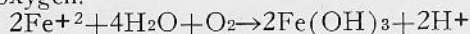
Report hardness of 1,000 ppm to whole number and of 1,000 ppm to 3 significant figures only (Rainwater and Thatcher).

A determination of hardness and determination of calcium will provide information sufficient for a computation of magnesium.

IRON

Iron is one of the most abundant minerals in the earth's crust. It occurs in the dark-colored silicate minerals of igneous rocks and as sulfides and oxides. In sandstone, iron oxide and iron hydroxide are often present as cementing materials. Iron is also present as oxides and sulfides in shale. Some of the common humic complexes causing color in water may also be iron bearing.

Because iron is readily precipitated as the hydroxide, it seldom is one of the major constituents of water. The metal occurs in water in both the ferrous and ferric state. Ferrous iron is unstable in solution in the presence of oxygen.



If the sample is subjected to a strong reducing environment the reaction is reversed, and the solution may contain large quantities of ferrous iron. In the 6 to 8 pH range the amount of ferric iron in true solution is theoretically limited to the solubility of ferric hydroxide, about 4×10^{-10} to 5×10^{-6} ppm.

Concentrations greater than 1 ppm of iron are rare in alkaline surface water. However, higher concentrations are common in ground water and acid surface water.

For the determination of iron the phenanthroline method is excellent. If iron is present an orange color develops (Rainwater and Thatcher).

The test is sensitive to small amounts of iron and is free from nearly all interferences. The phenanthroline

reagent is formulated into a single powder: commercially called FerroVer (Hach Chemicals) which performs all of the required functions to give an accurate test for iron irrespective of the sample. Thus, the sample will give an accurate test even if the iron is present as rust. Color comparison is made using a color disc (Hach) for the range of 0-5 ppm.

Procedure: (Hach Chemical Company)

1. Fill a sample tube to the mark with water sample.
2. Add the contents of one pillow of FerroVer for 5 ml. sample and shake to mix. An orange color will develop if iron is present. Place the tube of prepared sample in the comparator in the opening nearest the middle.
3. Fill the other sample tube with clear water and place it in the other opening in the comparator.
4. Hold the comparator up to the light and view through the openings in the color comparator. Rotate the disc until a color match is obtained. Read parts per million iron from the scale in the comparator.

MAGNESIUM

The calculation method for magnesium determination is applicable to all waters with which complexometric calcium and hardness determinations can be made satisfactorily.

Principle of determination:

Equivalents per million of hardness is calculated from the hardness determination. The equivalents per million of calcium is subtracted and the remainder multiplied by the equivalent weight of magnesium. Strontium does not interfere because strontium is included almost quantitatively in either the complexometric or permanganometric calcium determination. Barium interferes with both the complexometric and single-precipitation permanganometric calcium determination but in different ways. In the presence of barium, magnesium should be determined by other methods. Nonrounded values of hardness and calcium should be used in the calculation.

With the listed apparatus and reagents, results are accurate and reproducible to about ± 0.002 mg.

Calculations:

1. $\text{epm Hardness} = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. hardness sample}} \times \text{ml. titrant} \times 0.01998$
2. $\text{epm Ca}^{+2} = \frac{1}{\text{density}} \times \frac{1,000}{\text{ml. Ca}^{+2} \text{ sample}} \times (\text{ml. titrant} - \text{ml. blank}) \times 0.5 \times 0.0499$
3. $\text{ppm Mg}^{+2} = 12.16 \times (\text{epm hardness} - \text{epm Ca}^{+2})$

The presence of dolomite, a magnesium-rich carbonate, in Central Texas necessitates a calculation of the magnesium ion.

Sampling and storage:

Manganese may exist in a soluble form in a neutral water when first collected but oxidizes readily to a higher state and precipitates from solution or becomes absorbed on the walls of the container. Manganese should be determined very soon after sample collection. When delay is unavoidable, a total manganese can be determined if the sample is acidified at the time of collection (American Public Health Association, 1966).

MAGNESIUM, PERIODATE METHOD

Principle of determination:

Periodate as the oxidizing agent acts upon soluble

manganous compounds to form permanganate. The intensity of color is not affected by variation in acid or periodate concentration, and the color is stable for many months. In this test the manganese present in the water sample is oxidized to permanganate which is purple. The test is carried out by the addition of two powders to the water sample, after which the purple color develops without boiling.

Procedure: (Hach Chemical Company)

1. Fill a sample mixing bottle to the shoulder with water sample.
2. Add the contents of one pillow of Citrate buffer powder and swirl to mix and dissolve the powder.
3. Add the contents of one pillow of Sodium Periodate and swirl to mix. A pink color will develop if manganese is present. Allow the prepared sample to stand for one minute before measuring the color.
4. Pour the prepared sample into one of the sample viewing tubes to within 1/16" of the top. Stopper the tube so as to expel all air bubbles.
5. Insert the tube of prepared water sample into the back side of the comparator in the opening nearest the middle.
6. Fill the other sample tube with clear water and stopper in a manner to expel air bubbles. Insert this tube in the comparator in the opening in the back.
7. Hold the comparator up to a light and view through the opening of the comparator. Rotate the disc in the comparator until the color match is obtained. Read the parts per million manganese from the scale reading opening. Range 0-3 ppm.

Manganese found in water is probably most often the result of solution of manganese from soils and sediments aided by bacteria or complexing with organic materials. Manganese occurs in sediment carried by streams in some areas (Hem, 1959).

NITRATE

Nitrate is usually the most prevalent form of nitrogen in water because it is the end product of the aerobic decomposition of organic nitrogen. Nitrate from natural sources is attributed to the oxidation of nitrogen from the air by bacteria and to the decomposition of organic materials in the soil. Fertilizers may add nitrate directly to water resources. Nitrate concentrations range from a few tenths to several hundred parts per million, but in unpolluted water seldom exceed 10 ppm. Nitrate and chloride are major components of human and animal wastes, and the occurrence of abnormally high concentrations of both constituents suggest possible pollution of the water resources (Rainwater and Thatcher).

The following test for nitrate uses a new procedure (Hach Chemicals) which is most desirable because it avoids the use of concentrated sulfuric acid, requires only one powdered reagent, and is easy to perform in the field. It is also possible to determine nitrate with the same equipment and reagents by the omission of the cadmium wire.

Procedure: (Hach Chemical Company)

1. Rinse a color comparison tube twice with demineralized water. To do this, fill the empty tube about 1/2" deep with demineralized water. Stopper and shake vigorously, then pour out the rinse water.

2. With a medicine dropper, add one drop of water sample to the rinsed sample tube.
3. Fill the tube to the mark with demineralized water.
4. Add the contents of one NitraVer III Powder Pillow. (Hach reagent)
5. Place the cadmium wire in the test tube of the sample and stopper the tube. Shake vigorously for two minutes. A pink color will develop if nitrate is present. Allow an additional three minutes for complete color development.
6. Pour the prepared sample into an empty sample tube and place the tube in the color comparator in the opening nearest the middle of the comparator.
7. Place a test tube of demineralized water in the outside opening of the color comparator.
8. Hold the color comparator up to the light and view through the openings in the front. Rotate the color disc until a color match is obtained. Read the ppm 0-100 nitrogen from the scale on the color disc through the scale reading opening.

SILICA

Silicon is the most abundant element in igneous rocks and some other types of deposits. Most silica in water is probably derived from the decomposition or metamorphism of silicate minerals rather than from solution of quartz, as quartz is one of the rock minerals most resistant to attack by water. Many waters contain less than 10 ppm of silica; those that drain deposits high in silicate minerals, particularly feldspars, often contain up to 60 ppm; concentrations exceeding 100 ppm are not commonly found. The chemistry of silica in solution is not known with certainty. It is believed that most silica is present in a nonionized form, but ionized silicate(s) is undoubtedly present in some waters.

Silica is not physiologically significant to humans, livestock, or fishes, nor is it of importance in irrigation waters.

SILICA, MOLYBDATE BLUE METHOD

The molybdate blue method is not recommended for normal waters whose silica content is more than 100 ppm.

Principle of determination:

Silica in solution as silicic acid or silicate has the property of reacting with ammonium molybdate in an acid medium to form the yellow-colored silicomolybdate complex. The silicomolybdate complex is then reduced by sodium sulfite to form the molybdate blue color.

Phosphate gives a similar molybdate complex under certain pH conditions. In the following determination, the conditions are such that the phosphate complex is not formed. There is also evidence that ferric and ferrous iron interfere with the determination. The addition of EDTA eliminates the effect of high concentrations of iron and also complexes calcium and prevents precipitation of calcium sulfite. This test gives silica in the 0-40 ppm range.

Apparatus and reagents:

- Color comparator (Hach)
- Ammonium molybdate solution (Hach)
- Oxalic acid (Hach)
- Na₂EDTA 1 percent.
- Sodium sulfite powder (Hach)
- Silica color wheel (Hach)

Procedure: (Hach Chemical Company)

1. Fill both sample tubes to the mark with water sample.
2. To one of the tubes add 4 drops of ammonium molybdate solution. Shake to mix and allow the sample to stand for 10 minutes. If silica or phosphate are present, a yellow color will develop.
3. Add 4 drops of EDTA solution.
4. Add 4 drops of oxalic acid solution. Shake to mix and allow the solution to stand for 2 minutes. The acid will cause the yellow color due to phosphate to fade or disappear.
5. Add 2 shots of sodium sulfite powder from the dispenser bottle. Shake to dissolve and mix. If silica is present, a blue-green color will develop. Allow 5 minutes for color development.
6. Place the sample tube of prepared sample in the right opening of the comparator. Place the sample tube of untreated sample in the left opening of the comparator.
7. Hold the comparator up to a light and view through the two openings in the front. Rotate the disc until a color match is obtained. Read parts per million silica from the scale.

The presence of chert, silicate, in the Edwards Formation would make the silicon a probable member of the dissolved solvents in this area.

SULFATE

Sulfate is dissolved from most sedimentary rocks. Large quantities may be derived from beds of gypsum, sodium sulfate deposits, and some types of shale. Water from mines may be high in sulfate from the oxidation of pyrite. In natural waters, concentrations range from a few parts per million to several parts per million.

Salts of sulfate are saline cathartics and a quantity equal to that of 1 liter of water containing 1,000 to 2,000 ppm sulfate constitutes an average dose. The U.S. Public Health Service recommends that the sulfate concentration not exceed 250 ppm in drinking and culinary waters.

SULFATE, TURBIDIMETRIC METHOD

The turbidimetric test is limited to rough approximations of sulfate. Its maximum utility is as a laboratory aid in the field when the accuracy requirements are low.

Principle of determination:

Sulfate is precipitated as barium sulfate, and the resultant turbidity is compared with that produced in standards of known concentration.

Apparatus and reagents:

Test tubes

Sodium sulfate, 1.0 ml.=0.10 mg. SO_4^{2-}

Barium chloride, acidified, 10 percent

Procedure:

1. Pipet a volume of sample containing less than 0.25 mg. SO_4^{2-} (10.0 ml. max) into a test tube and adjust volume to 10.0 ml.
2. Prepare sufficient standards in the 0.00 to 0.25 mg. range and adjust the volume to 10.0 ml.
3. Add 1.0 ml. to 10 percent BaCl_2 .
4. Shake vigorously and allow suspension to stand 10 minutes.
5. Compare the turbidity of the sample with that of the standards. Comparison is best made by looking down through the tubes against a black background.

Calculations:

$$\text{ppm } \text{SO}_4^{2-} = \frac{1,000}{\text{ml. sample}} \times \text{mg. } \text{SO}_4^{2-} \text{ in standard.}$$

(Rainwater and Thatcher).

SODIUM

Sodium salts are very soluble; therefore, much of the sodium leached from the soils or rocks tends to remain in solution.

The exact procedure used in the flame-photometric method is governed principally by the design and performance of the particular flame photometer used; hence, no specific instructions can be given. Many suggestions are provided by the manufacturers of the individual instruments.

Report sodium concentrations of < 10 ppm to 1 decimal place, of between 10 and 999 ppm to whole numbers, and of > 999 ppm to significant figures only.

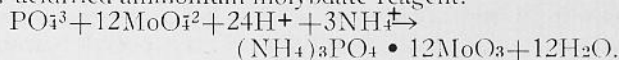
All tests for sodium in this study were run by O. D. Baldwin of Rice University, Houston, Texas.

PHOSPHATE

Phosphate is prevalent in nature both in the organic and inorganic form. Because of its role in animal and vegetable metabolism, phosphorus is a cyclic element, similar to nitrogen, in that the combined form is continually changing by decomposition and synthesis. Both organic and inorganic phosphorus in water may result from leaching of soil and rock, and from fertilizer, normal decomposition of plants and animals, sewage, and industrial effluents. In concentrations normally found in water, phosphorus is not reported to be toxic to man, animals, or fish (Rainwater and Thatcher, p. 245).

As far as is known, the phosphomolybdate method is specific for the orthophosphate form of phosphorus. Weak tests are reported with pyrophosphate and polyphosphates, but these positive tests may well result from orthophosphate contamination of the material.

Orthophosphate is converted to phosphomolybdate by acidified ammonium molybdate reagent.



The phosphate disc used in the test has a range of 0-5 ppm.

Procedure: (Hach Chemical Company)

1. Fill both glass sample tubes to the mark with the clear water sample.
2. Pour one of the samples from the sample tube into the 1x4 inch glass test tube.
3. To this, add 3 drops of ammonium molybdate and heat the sample to boiling over the burner. Maintain the sample at the boiling point for 10 minutes. Boil gently. Then allow the sample to cool and pour it back into the original sample tube. If necessary add demineralized water to bring the sample level to the mark on the tube.
4. When the sample is cooled to room temperature, add the contents of one Phosphate 2 powder pillow. Insert the rubber stopper and shake to mix. If phosphate is present, a blue color will develop. Allow 5 minutes for color development.
5. Insert the prepared color comparison tube in the opening nearest the middle of the color comparator.
6. Insert the test tube with the untreated, clear water sample in the outside opening of the color comparator. Rotate the Phosphate color disc until a color match is obtained. Read parts per million phosphate from the scale on the color disc.

APPENDIX III

Flow Record of Hog Creek
(Discharge in CFS, October 1966-September 1967)

Day	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Day	Apr.	May	June	July	Aug.	Sept.
1	12	3.5	2.2	1.5	1.0	.80	1	.67	47	11	2.9	.27	.09
2	11	3.5	2.1	1.5	.9	.78	2	.57	19	7.9	4.7	.26	.09
3	11	3.4	1.9	1.3	.9	.76	3	.47	16	6.3	6.1	.25	.11
4	10	3.6	2.0	1.3	.8	.73	4	.41	13	5.3	4.3	.25	.21
5	10	3.7	2.2	1.3	.8	.70	5	.33	11	4.7	2.3	.23	.44
6	9.5	3.8	2.2	1.3	.8	.67	6	.31	9.9	4.2	2.2	.22	.23
7	9.2	4.0	2.4	1.2	.8	.64	7	.28	8.2	3.8	2.1	.21	.21
8	8.4	4.0	2.4	1.1	.8	.59	8	.26	7.1	3.4	1.7	.21	.20
9	8.0	3.9	2.2	1.1	.7	.59	9	.26	6.1	3.1	1.4	.20	.17
10	7.4	3.6	1.9	1.1	.7	.62	10	.25	5.3	2.8	1.1	.18	.16
11	6.7	3.2	1.9	1.1	.7	.59	11	7.8	4.7	420	.98	.15	.16
12	6.8	3.0	1.8	1.1	.8	.57	12	7.0	4.0	835	.94	.13	.14
13	6.7	3.0	1.7	1.1	.7	.50	13	17	3.7	42	.79	.12	.13
14	6.4	2.9	1.7	1.2	.7	.49	14	3.7	4.3	26	.70	.12	.12
15	5.7	2.7	1.8	1.1	.7	.46	15	2.3	4.6	20	.65	.12	13.0
16	6.3	3.1	1.7	1.1	.7	.40	16	1.7	3.8	17	.59	.12	9.6
17	7.0	3.0	1.7	1.0	.7	.42	17	64	3.4	14	.57	.13	.89
18	7.3	2.8	1.7	1.0	.7	.40	18	26	3.1	12	.59	.13	.57
19	6.7	2.7	1.7	1.0	.8	.44	19	11	2.9	11	.90	.12	.46
20	6.1	2.7	1.8	1.0	1.2	.58	20	4.7	22	9.6	.81	.12	.40
21	5.7	2.9	1.9	1.0	.8	.55	21	3.1	79	8.1	.62	.12	.40
22	5.5	2.8	1.9	1.0	.7	.49	22	395	20	7.1	.57	.12	.38
23	5.2	2.7	1.5	1.1	.7	.49	23	195	12	6.5	.51	.12	.33
24	4.8	2.7	1.5	1.1	.7	.49	24	29	8.5	5.7	.46	.12	.31
25	4.5	2.6	1.5	1.1	.6	.48	25	17	6.8	4.9	.40	.12	.26
26	4.4	2.5	1.5	1.2	.8	.89	26	11	5.9	4.3	.40	.12	.25
27	4.4	2.3	1.6	1.1	.9	.51	27	8.1	5.3	3.6	.40	.12	.25
28	4.2	2.2	1.4	1.0	.9	.91	28	6.8	4.9	3.4	.37	.12	.20
29	4.1	2.2	1.3	1.0	—	.89	29	6.6	6.2	2.9	.33	.12	.21
30	3.9	2.2	1.4	1.0	—	.64	30	26	5.9	2.7	.33	.11	.20
31	3.6	—	1.5	1.0	—	.62	31	—	10	—	.31	.10	—
Total	212.5	91.2	56	35.0	22.0	18.69	Total	846.61	363.8	1508.3	41.02	4.83	30.17
Mean	6.85	3.04	1.81	1.13	.79	.60	Mean	28.2	11.7	50.3	1.32	.16	1.01
Max	12.0	4.0	2.4	1.5	1.2	.91	Max	395	79	835	6.1	.27	13.0
Min	3.6	2.2	1.3	1.0	.60	.40	Min	.25	2.9	2.7	.31	.10	.09
AC-FT	421	181	111	69	44	37.00	AC-FT	1680	722	2,990	81	9.6	60

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