Chemical Quality of Water In the Walnut River Basin, South-Central Kansas

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1982

Prepared in cooperation with the Kansas State Department of Health, Environmental Health Services, Topeka, Kansas



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By ROBERT B LEONARD

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GLOSSARY

- Base runoff (base flow) Sustained or fair-weather runoff In most streams, base runoff is composed largely of ground-water effluent
- Cfs-day. The volume of water represented by a flow of 1 cubic foot per second for 24 hours
- Chemical discharge (load) The weight of dissolved chemical constituents passing a stream section in unit time
- Direct runoff. The runoff entering stream channels promptly after rainfall or snowmelt

Milliequivalents per liter (me/l) A unit for expressing the concentration of chemical constituents in terms of the interacting values of the electrically charged particles, or ions, in solution

- Hardness. The water property attributable to the presence of alkaline earths, mainly calcium and magnesium
- Milligrams per liter (mg/l) A unit for expressing the concentration of dissolved chemical constituents by weight as milligrams of constituents per liter of solution

Percent sodium. The ratio, expressed in percentage, of sodium to the sum of the positively charged ions (calcium, magnesium, sodium, and potassium), all ions, in milliequivalents per liter

Perennial stream. A stream which flows continuously

pH The negative logarithm of the concentration of hydrogen ions, in moles per liter It is lower than 7 in acid solutions and higher than 7 in basic solutions
Pollutants. Foreign substances that impair the usefulness of the water
Runoff. That part of the precipitation that appears in surface streams

Salinity. The dissolved-mineral content or total concentration of solids in solution

Specific conductance. A measure of the ability of water to conduct an electric current It is expressed in micromhos per centimeter at 25°C

Water discharge. The rate of flow of a stream, includes dissolved solids and suspended sediment transported in the water

Water type. The character of the water with respect to its ionic constituents It indicates the anion and cation present in the highest concentrations, in milliequivalents per liter

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CHEMICAL QUALITY OF WATER IN THE WALNUT RIVER BASIN, SOUTH-CENTRAL KANSAS

By ROBERT B LEONARD

ABSTRACT

Improper disposal of oil-field brine and other wastes has adversely affected the naturally diverse chemical quality of much of the water in the Walnut River basin, south-central Kansas

The basin is an area of about 2,000 square miles in the shape of a rough triangle with its apex toward the south The Whitewater River, a principal tributary, and the Walnut River below its junction with the Whitewater River flow southward toward the Arkansas River along courses nearly coincident with the contact of the Chase and overlying Sumner Groups of Permian age The courses of many minor tributaries are parallel to a well-developed joint system in the Permian rock

Thick interbedded limestone and shale of the Chase Group underlie the more extensive, eastern part of the basin Natural waters are dominantly of the calcium bicarbonate type Shale and subordinate strata of limestone, gypsum, and dolomite of the Sumner Group underlie the western part of the basin Natural waters are dominantly of the calcium sulfate type Inflow from most east-bank tributaries dilutes streamflow of the Walnut River, west-bank tributaries, including the Whitewater River, contribute most of the sulfate

Terrace deposits and alluvial fill along the stream channels are assigned to the Pleistocene and Holocene Series Calcium bicarbonate waters are common as a result of the dissolution of nearly ubiquitous fragments of calcareous rock, but the chemical quality of the water in the discontinuous aquifers depends mainly on the quality of local recharge

Concentrations of dissolved solids and of one or more ions in most well waters exceeded recommended maximums for drinking water Nearly all the ground water is hard to very hard High concentrations of sulfate characterize waters from gypsiferous aquifers, high concentrations of chloride characterize ground waters affected by drainage from oil fields Extensive fracture and dissolution of the Permian limestones facilitated pollution of ground water by oil-field brine and migration of the polluted water into adjacent areas Ground water containing more than 1,000 mg/l (milligrams per liter) dissolved solids and more than 100 mg/l chloride is common near oil fields but is exceptional elsewhere 2 CHEMICAL QUALITY OF WATER, WALNUT RIVER BASIN, KANSAS

The concentration of nitrate in about 25 percent of the sampled well waters exceeded the recommended maximum for drinking water High concentrations of nitrate generally were associated with shallow aquifers, local sources of organic pollution, and stagnation

Sodium and chloride are the principle ionic constituents of oil-field brine but are minor constituents of natural surface waters or shallow ground water in the basin. The ratios of the concentrations of sodium to chloride in brine from different oil fields varied within a narrow range from a mean of 0.52. Concentrations of chloride exceeding 50 mg/l in streamflow and 100 mg/l in ground water generally signified the presence of oil-field brine if the sodium-chloride ratios were less than 0.60. Higher sodium-chloride ratios characterized relatively rare occurrences of high concentrations of the ions that might have originated in evaporite minerals or in sewage

The concentration of chloride during low flow of the major streams generally increased, and the sodium-chloride ratio decreased, in a downstream direction from about 0.65 near the headwaters to about 0.51, which is characteristic of oil-field brine. The changes were most abrupt where polluted ground-water effluent augmented low streamflow adjacent to old oil fields. With increased direct runoff, the sodium-chloride ratio normally increased, and these ions constituted a smaller percentage of the dissolved-solids load.

Annual runoff decreased progressively from above normal to below normal during water years 1962–64 Higher concentrations of the ions in streamflow persisted for longer periods during the periods of low runoff, but higher concentrations of the ions corresponded to lower rates of daily mean discharge when annual runoff was highest

The concentrations of dissolved solids in low flow commonly exceeded 500 mg/l in the Walnut River and 1,000 mg/l in the Whitewater River Tributaries draining old oil fields were the principal sources of oil-field brine that made up as much as 70 percent of the dissolved-solids load of the Walnut River upstream from the junction with the Whitewater River

The Whitewater River contributed a disproportionately large part, in relation to its drainage area, of the dissolved-solids, sulfate, and chloride loads of the Walnut River Most of the water and sulfate in the Whitewater River originated upstream from a proposed damsite near Towanda, but a large part of the chloride encountered in concentrations up to about 700 mg/l near the mouth of the Whitewater River originated downstream from the damsite.

Streamflow at Towanda was unsuitable for domestic use or for irrigation most of the time during water years 1962-64 Relations of the concentrations of the ions to specific conductance and to water discharge varied widely from year to year

The concentration of dissolved solids in the Walnut River generally decreased progressively downstream from the mouth of the Whitewater River to Winfield The drainage area of the Walnut River at Winfield is about 95 percent of the basin During the 1964 water year, the concentration of dissolved solids at Winfield exceeded 1,000 mg /l about 50 percent of the time, the concentration of sulfate exceeded 250 mg /l about 40 percent of the time, and the concentration of chloride exceeded 250 mg /l about 60 percent of the time Most of the sulfate was of natural origin

Pollution control markedly reduced the concentrations of chloride at corresponding rates of discharge after 1955 However, concentrations of sodium and chloride were far higher, and sodium-chloride ratios were lower, than those that

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prevailed before extensive development of the oil fields More than half of the annual load of chloride at Winfield during the 1964 water year consisted of residual salt from improper brine-disposal practices in the past

The rate at which chloride was carried from the basin far exceeded the rate at which the near surface supply could be replenished under existing disposal practices. The rate of chloride removal increased disproportionately with the amount and rate of runoff With continued effective pollution control, the concentrations of sodium, chloride, and dissolved solids should progressively decrease. The rate of decrease and the concentrations of the major ions in streamflow depend mainly on the amount, rate, and distribution of precipitation, on water and land use, and on control of streamflow by proposed impoundments

INTRODUCTION

The Walnut River, a tributary of the Arkansas River, drains an area of about 2,000 square miles in the eastern part of south-central Kansas (fig 1). Boundaries of the Walnut River basin, which includes most of Butler County, the central part of Cowley County, and small parts of six adjoining counties, roughly form a triangle with its apex toward the south. The basin is about 75 miles long from north to south and about 40 miles wide in its northern part.

PURPOSE

Soon after the discovery of oil in 1914, improper disposal of oil-field brine and other industrial wastes caused rapid deterioration of many water supplies in the Walnut River basin The investigation described in this report was made from October 1961 to September 1964, after a decade of extensive cooperative effort toward pollution control by the petroleum industry and regulatory agencies of the State of Kansas The purposes for the investigation were as follows

- 1 To determine the chemical quality of ground and surface water.
- 2. To identify and evaluate the principal factors, natural and manmade, that caused variations and fluctuations in the chemical quality of water in the basin
- 3. To develop methods of investigation that could be applied to similar problems elsewhere

The purposes were achieved subject to limitations imposed by the range and availability of the data. Definitions of those limitations and of needs for more information are implicit purposes of the investigation. The information summarized herein is needed for the most efficient development of available water supplies and for evaluation of the effects on water quality of continuing programs of pollution abatement and of proposed streamflow control. CHEMICAL QUALITY OF WATER, WALNUT RIVER BASIN, KANSAS



FIGURE 1.—Index map showing location of the Walnut River basin (shaded area), south-central Kansas.

RESULTS OF PREVIOUS INVESTIGATIONS

The results of a reconnaissance-type water-quality investigation in the Walnut River basin from 1899 to 1908 showed that most of the water was then suitable for domestic and agricultural use (Parker, 1911). Most of the subsequent investigations have dealt with classic problems of oil-field pollution in Kansas (Jones, 1950). After the discovery of oil south of Augusta in 1914, annual oil production in Butler County increased to a maximum of about 35 million barrels in 1918. Refineries, five of which were still operating during this investigation, were built at El Dorado, Potwin, Arkansas City, and Augusta, as

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petroleum supplanted agriculture as the main source of income. Even as the demand on existing water supplies for municipal and industrial use increased, direct discharge of oil-field and refinery wastes into surface waters sometimes naturally high in dissolved solids caused rapid deterioration of water quality Many ground-water supplies were polluted by seepage of brine from so-called evaporation ponds, drainage channels, and improperly maintained oil wells.

By 1921 the cities of Winfield, Augusta, Douglass, and El Dorado were forced to abandon the Walnut River as a source of municipal water supply and to construct wells and reservoirs at considerable expense. Refineries were forced to obtain auxiliary supplies.

Water-quality studies made by the Kansas State Board of Health (now the Kansas State Department of Health) from 1939 to 1951 revealed that the polluted condition of streamflow in the basin was not due to one city or industry but to a combination of the wastes from oil fields, refineries, and cities (Kansas State Board of Health, 1952). Results of chemical analyses of periodic samples of streamflow taken by Board of Health personnel from 1949 to 1960 (Kansas State Board of Health, 1960) indicated that pollution abatement by the Kansas State Department of Health, the Conservation Division of the State Corporation Commission, municipalities, and the petroleum industry apparently reduced the degree of pollution of streamflow, but that the water was still of poor quality at many stream sites. Bayne (1962) showed that the chemical quality of ground water in the southern part of the basin was directly related to the geology and to localized brine pollution The present investigation conforms to recommendations by the Kansas Water Resources Board (1960) for more comprehensive and detailed collection and analysis of chemical-quality data.

COOPERATION

This investigation was the first basinwide study made as part of a cooperative program of water-quality investigations begun in 1961 by the Kansas State Department of Health and the U.S. Geological Survey.

This study was under the general direction of D. M. Culbertson, formerly district engineer, U.S. Geological Survey, Quality of Water Branch, Lincoln, Nebr., and J. L. Mayes, director and chief engineer, Environmental Health Services of the Kansas State Department of Health Personnel of the Division of Water Resources of the Kansas State Board of Agriculture and of the Kansas Water Resources Board assisted in some phases of the project

Special acknowledgment is due B F Latta, director and chief geologist of the Oil Field Section, and R. E O'Connor, district geologist, Wichita, of the Kansas State Department of Health for valuable suggestions and information about oil-field-brine pollution

DATA COLLECTION AND ANALYSIS

The nature and concentration of dissolved solids in water from more than 450 wells, 55 augered observation wells, and about 25 springs were determined by chemical analyses to relate the quality of ground water to the use, geology, topography, proximity to sources of pollution, and to the quality of adjacent surface water. Water from some sources was analyzed periodically to relate any changes in chemical quality to time, water level, and discharge. Whenever possible, wells were pumped or bailed to ascertain that the sample was representative of water around the well bore. The discharges of some springs were measured and analyzed to determine the extent of their contributions to the water and chemical discharge and dissolved-solids load of the river and its tributaries.

Four basinwide combined seepage and salinity surveys and two similar surveys of a selected reach of the Whitewater River were made to determine the chemical quality of base runoff of the Walnut River and its tributaries over a wide range of discharge at more than 90 sites during the same 2-day periods. The results of these surveys, combined with salinity surveys of base runoff in major watersheds, defined qualitatively and quantitatively the principal sources of the dissolved-solids load of the Walnut River. The results also provided a framework for relating the chemical quality of surface water in the basin to that of ground water.

Monthly or more frequent measurements of water discharge and chemical quality were made at two stations on the Whitewater River and at five stations on the Walnut River to relate variations and fluctuations in the chemical quality of streamflow to meteorological variations, to the geologic and hydrologic characteristics of the corresponding drainage areas, and to the degree of oil-field-brine pollution of ground water in the areas. Measurements were commonly made at all stations within a 2-day period to permit comparison of the concentrations of the ions at one station with those at another at about the same time. Data also were collected intermittently at these and other sites in the basin when additional data were needed to describe exceptional conditions of drought or flood. Methods of concurrent sampling and measurement of streamflow were normally in accordance with procedures accepted by the U.S Geological Survey (Rainwater and Thatcher, 1960; Corbett and others, 1943 to ensure that each sample represented streamflow in the cross section.

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The station on the Whitewater River at Towanda near the site of a proposed dam (US Army Corps of Engineers, 1964) is equipped with continuous stage and conductivity recorders The recorded data were combined with results of chemical analyses of streamflow to describe variations in chemical quality with time and water discharge, the magnitude and nature of the dissolved-solids load during water years 1962–64, and the effect of streamflow at Towanda on the chemical quality of streamflow at downstream sites

Most of the chemical analyses and concurrent measurements of water discharge pertinent to this report are included in basic-data reports published by the U.S. Geological Survey and the Kansas State Department of Health References to the published data are included in the text. This large volume of pertinent data is compiled as maps, charts, and graphs designed to describe salient features of water quality and to be of practical use to planning and regulatory agencies

CRITERIA FOR CLASSIFYING WATER

Chemical quality of water in this report refers to dissolved chemical constituents and physical properties such as conductance, hardness, and temperature that determine the suitability of the water for various uses. The diverse chemical quality of water in the Walnut River basin, the different standards pertinent to the many uses of the water, and the predominance of partial analyses warrant only general classification of water in this paper

The suitability of water for most uses decreases as the concentration of dissolved solids or the salinity increases. A system based on the concentration of total dissolved solids (Irelan and Mendieta, 1964) is useful for general classification of water in the basin.

Classification	
Fresh water	Dissolved solids (mg/l)
Excellent	$<\!250$
Good	250-500
Fair	500-1, 000
Saline water	
Slightly saline	1, 000–3, 000
Moderately saline	3,000-10,000
Very saline	10, 000–35, 000
Brines	>35, 000

Concentrations of dissolved solids in water of the basin range from 100 mg/l (milligrams per liter) in some surface water during periods of high runoff to about 200,000 mg/l in some oil-field brines. Most of the ground water and base runoff used for domestic and livestock supply is fairly fresh or slightly saline. Although livestock may drink

moderately saline water without ill effects (California State Water Pollution Control Board, 1952, p. 247), the maximum recommended concentration of dissolved solids for human consumption is 500 mg/l (US Public Health Service, 1962)

The U.S Public Health Service (1962, p 7) recommends the following maximum concentrations of chemical constituents for drinking water

Substance			
Cor	ncent	ration	i (mg/l)
Total dissolved solids	500		
Sulfate (SO ₄)	250		
Chloride (Cl)	250		
Nitrate (NO ₃)	45		
Iron (Fe)		3	
Fluoride (F)	1	8–1	7
Manganese (Mn)		05	
¹ Depends on temperature			

Water in which the concentrations of any constituents exceed the recommended standards noted above is not necessarily unsuitable for domestic use, although it may have some undesirable characteristics. The concentrations of one or more of these constituents in many apparently satisfactory domestic supplies in the basin exceeded the recommended standards However, the presence of individual constituents, particularly nitrate and fluoride, in concentrations exceeding the recommended maximum necessitates further investigation and possible abandonment of some sources of drinking water. Many well waters in the basin contain excessive concentrations of nitrate.

Alkaline earths, mainly calcium and magnesium, cause hardness in water. Hard water may be unsuitable for industrial use because of its tendency to form scale. It is undesirable for domestic use because it forms insoluble compounds with soap. Hardness values are reported in this report in milligrams per liter in terms of calcium carbonate.

The U.S Geological Survey uses the following classification ·

Classification	
Soft	urdness (as mg/l CaCOs) 60 or less
Moderately hard	61-120
Hard	121-180
Very hard	181 or more

Most of the water in the basin is classified as hard to very hard. Carbonate hardness includes that part of the hardness which is equivalent to the carbonate and bicarbonate present in the water. Noncarbonate hardness, which is difficult to remove by ordinary watertreatment processes, is the remainder. A high degree of noncarbonate hardness is characteristic of waters from gypsiferous aquifers in the western part of the basin The specific conductance, normally expressed in micromhos per centimeter at 25°C, is a measure of the ability of water to conduct an electric current. Specific conductance was measured for all samples during the investigation, because it is an inexpensively and rapidly determined index of the chemical quality of water. Its magnitude depends on the concentration and activity of the individual ionic constituents, but it is roughly proportional to the concentration of dissolved solids for most waters in the basin.

The concentrations of ionic constituents, in milliequivalents per liter, can be converted to percentages of total anions or cations. By convention, water has been classified in terms of the principal anion and cation, each of which composes over 50 percent of the total anions or cations. In this report, the predominant anion and cation are used to describe water type, even though each may represent less than 50 percent of the total anions or cations

The pH is a measure of the acidity of a solution The pH is lower than 7 in acid solutions and higher than 7 in basic solutions. The measured pH in the Walnut and Whitewater Rivers ranged from 64to 84

Irrigation waters are normally classified in terms of the total concentrations of soluble salts (salinity hazard), relative proportion of sodium to other cations (alkali hazard), and the concentration of boron and other elements that may be toxic Relatively small, but unmeasured, quantities of raw river water are used for irrigation during periods of drought. The results, which depend largely on the soil type, crop, and concentration of individual constituents at the diversion site, normally are poor because of high salinity. The maximum known concentrations of boron in streamflow of the Walnut and Whitewater Rivers were less than 0.4 mg/l, an amount probably harmless to all but the most sensitive forms of plant life.

FACTORS AFFECTING THE CHEMICAL QUALITY OF WATER

Rainfall contains relatively minor amounts of chemical constituents before it passes over and through soil and rock of the earth's crust The natural chemical quality of ground and surface water is determined chiefly by the solubility of the minerals, distribution of soluble rock with which the water comes in contact, and the dilutant effect of precipitation. At many sites, the quality has been altered by chemical wastes or by changes in the hydrologic regime resulting from the activities of man.

AREAL GEOLOGY

Diversity in the chemical quality of water in the Walnut River basin is determined largely by the distribution, chemical composition,

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geologic structure, and hydrologic characteristics of the soil and rock. The description of the areal geology that follows is based on reports by Fath (1921) and Bayne (1962), on reconnaissance mapping by the Ground-Water Branch of the U.S. Geological Survey, and on observations made in the field by the writer

Bedrock exposures consist of marine sedimentary rocks assigned to the Chase and Sumner Groups of Permian age (pl. 1). Unmapped outcrops of similar lithology and limited extent along the extreme east boundary of the basin may represent the upper part of the Council Grove Group, also of Permian age (J. M. McNellis, geologist, oral commun., 1964).

The Permian rocks are overlain by unconsolidated sediment, principally of Pleistocene age, which forms upland terraces and valley fill as much as 100 feet thick in the broad stream valleys. Except in the headwaters, the major streams in the basin generally follow meanders entrenched in alluvial flood-plain deposits. The average height of the banks is about 20 feet. Except during periods of high flow, the channels are a series of pools separated by riffles, and the resistant bedrock that causes the riffles commonly is exposed in one bank.

The Walnut River falls about 290 feet between the northernmost monthly data collection site on the West Branch (about 25 mi north of El Dorado) and the mouth at Arkansas City The channel length is about 110 miles, versus a straight-line distance of about 58 miles The Whitewater River is slightly less sinuous.

THE CHASE GROUP

The Chase Group, which forms the shallow bedrock of the eastern part of the basin, consists of limestone $(CaCO_3)$, dolomitic limestone $(CaCO_3 + MgCO_3)$, dolomite $[CaMg(CO_3)_2]$, cherty limestone $(CaCO_3 + SiO_2 \cdot 2H_2O)$, and shale. The base of the unit nearly coincides with the east boundary of the basin The contact with the overlying Summer Group nearly coincides with the west edge of the Walnut River valley from Arkansas City to Augusta and of the Whitewater River valley from Augusta to the north boundary of the basin.

The principal shallow aquifers in the basin are limestones in the Chase Group. Extensive fractures and the dissolution of these carbonate rocks (fig. 2) favor rapid recharge and migration of ground water which contains calcium, magnesium, and bicarbonate released by water containing carbon dioxide from the atomsphere. Where the soil cover is thin and permeable or has been removed during oil-field operations, pollutive oil-field brine can gain easy access to groundwater supplies (fig 3) through fractures and solution channels, but its vertical movement is restricted by interbedded shale.



FIGURE 2.—Barneston Limestone of the Chase Group in the watershed of the West Branch Walnut River north of El Dorado, Kans., sec. 27, T. 25 S., R. 5 E.



FIGURE 3.—Thin soil mantle over fractured limestone of the Chase Group in sec. 8, T. 25 S., R. 5 E. Mantle permits rapid interchange of ground and surface water.

The name "Flint Hills" (Schoewe, 1949), applied to the topographic province which includes the eastern part of the basin, is derived from the gray chert or flint ($SiO_2 \cdot 2H_2O$) characteristic of some limestones of the Chase Group. The chert is relatively insoluble in most natural waters in the basin; therefore, concentrations of silica are normally less than 15 mg/l in surface water and less than 30 mg/l in ground water. The undulating topography with locally high relief is caused by differential erosion of the carbonate rock and shale of the Chase Group. Deep incision of aquifers by tributaries and the resultant high relief cause relatively rapid drainage

THE SUMNER GROUP

The Sumner Group consists of shale and subordinate beds of limestone (CaCO₃), gypsum (CaSO₄•2H₂O), and dolomite [CaMg(CO₃)-] Halite, or table salt (NaCl), is found in parts of the Sumner Group elsewhere but not in the Walnut River basin Except for limited outliers north of Augusta, the Sumner Group underlies only those areas west of the Walnut and Whitewater Rivers. Because the rock is generally more homogeneous and less resistant to erosion than i ock of the Chase Group, relief in the area of outcrop tends to be more subdued

Natural waters from the Summer Group normally contain much more sulfate and somewhat more magnesium than those from the Chase Group. With the exception of cavernous gypsum deposits, some of which are highly productive aquifers, rock of the Summer Group is generally less permeable than that of the underlying Chase Group; therefore, migration of ground water through it tends to be slower.

TERRACE DEPOSITS AND ALLUVIUM

The terrace deposits and alluvial fill that overlie the Permian bedrock consist mainly of clay, silt, sand, and gravel of continental origin that are assigned to the Pleistocene and Holocene Series (Bayne, 1962). Nearly all surface water in the Walnut River basin has made contact with these deposits; therefore, the nature, solubility, and baseexchange capacity of the constituent minerals affects the water quality.

The porosity and permeability of these sediments varies locally with wide variation in grain size. Aquifers are discontinuous horizontally and vertically and are normally subject only to local recharge. Soils tend to be thick, heavy, and poorly drained in the river valleys, whereas they tend to be thin and variable in permeability in the uplands

Sediments deposited by the Walnut River and its tributaries consist mainly of locally derived material including pebbles of limestone and chert. The water in the sediments is characteristically hard, but high concentrations of sodium and chloride in some areas indicated incursion into the aquifer of oil-field brine from polluted streamflow, from leaky oil-well casings, or from unsealed disposal ponds. High concentrations of sulfate in the water in sediments in the western part of the basin are derived mainly from gypsum in the adjacent Permian rock. Water supplies from shallow wells in these sediments are particularly susceptible to localized organic pollution.

Terrace deposits of the Arkansas River in a small part of the basin south of Winfield are principally arkosic. Much of the water in the deposits contains high concentrations of dissolved solids. The component minerals are relatively insoluble; therefore, the high concentrations are attributed to the chemical quality of the recharge.

Base-exchange reactions between mineralized waters and the abundant clays in the surficial deposits probably affect the relative concentrations of sodium, calcium, and magnesium in some waters Such reactions are assumed to have reached equilibrium near long-term sources of brine pollution, where the concentrations of these ions are high, but low relative concentrations of sodium in turbid surface runoff during periods of high flow may indicate alteration of low concentrations of these ions by reactions with suspended clay particles.

Further study of the effect of clay minerals on water quality in the basin is warranted, although the total effect is probably much less than that of soluble minerals.

GEOLOGIC STRUCTURE

Geologic structure affects the rate and direction of migration of ground and surface waters and the distribution of sources of mineralization in the basin. The courses of the Whitewater River and of the Walnut River south of Augusta are parallel to the north strike of the underlying rock. The courses of many major tributaries are generally concordant with a series of northeast-trending joints in the eastern part of the basin and with their complements in the west. Solution holes in the carbonate rocks are common; subsidence and collapse of some strata from dissolution of underlying rock caused local structural discontinuities which determined the courses of some streams. Many springs in limestone issue from joints which appear to provide the major avenues of migration for shallow ground water (fig. 4).



FIGURE 4.—Spring, typical of many that issue from fractured limestone aquifers in the basin, in sec. 15, T. 25 S., R. 5 E.

Regional dip toward the west favors rapid downdip drainage of the shallow limestone aquifers of the Chase Group toward the rivers. Conversely, the regional dip impedes rapid easterly drainage from gypsiferous strata of the Sumner Group which support perennial flow of sulfate-rich water to the rivers from the western part of the basin during periods of low precipitation. Structural domes and depressions in highly developed oil-field areas in Butler County (Fath, 1921) interrupt the gentle westerly dip of the bedrock and provide gradients controlling migration of polluted ground water through shallow aquifers within or across surface-water divides.

METEOROLOGY

Long- and short-term meteorological changes cause major fluctuations in the chemical quality of surface water in the basin. Extended droughts have caused shortages of ground and surface water (Kansas Water Resources Board, 1960). When the amount of water available for dilution of pollutants was diminished, the shortages were accentuated by deterioration of the chemical and sanitary quality of the water. Evaporation and transpiration further depleted the water supply and altered its chemical characteristics.

PRECIPITATION AND RUNOFF

The rate of runoff normally increased with the rate and amount of precipitation, but the concentration of dissolved solids in streamflow normally varied inversely with the water discharge. The magnitude and composition of the dissolved-solids load of streamflow in the basin at any time depended largely on long- and short-term variations in precipitation.

Mean annual rainfall in the basin is about 32 inches, about two-thirds of which occurs during the period April through September. Total precipitation at most stations was about 40 percent above normal during the 1961 water year, which preceded the project, and near normal during the 1962 water year. Total precipitation for the 1963 water year and the first half of the 1964 water year (October 1962 through March 1964) was the least of record since 1887 in east-central and southeast Kansas. The resultant drought was relieved in April 1964 (U.S Weather Bureau, 1964).

The chemical quality of runoff from some adjacent drainage areas differed widely; therefore, the distribution of precipitation affected the chemical quality of runoff at downstream stations. Heavy precipitation in the basin commonly occurred during localized convective storms of short duration. For example, because of a single localized storm, annual rainfall at Augusta during the 1964 water year exceeded that at El Dorado, about 10 miles to the northeast, by about 5 inches Annual rainfall at El Dorado was below normal; that at Augusta was above normal (fig 5A).

The investigation was conducted during a period of decreasing annual runoff Total precipitation at the stations shown in figure 5Bwas greater during the 1964 water year than during the 1963 water year, but the rate of streamflow and the annual runoff of the Whitewater River at Towanda and the Walnut River at Winfield reached a minimum during the 1964 water year (fig. 6). The relations of the chemical quality of streamflow to the rate and amount of runoff during a period of uniform or increasing annual runoff may differ.

EVAPOTRANSPIRATION

Evapotranspiration (evaporation plus transpiration) is a major factor causing low streamflow and high concentrations of ions in streamflow during about 40 percent of the average year, when the weather is hot, dry, and windy During the growing season, April through November, large quantities of water are evaporated from the surface of water and moist soil and are transpired by vegetation The concentration of dissolved solids in the residual water increases.

15

16



A

1



FIGURE 5.—Total annual precipitation at selected stations (A), and cumulative total monthly precipitation at El Dorado (B) during water years 1961–64.



FIGURE 6—Duration curves of daily mean flow for the Walnut River at Winfield and Whitewater at Towanda for water years 1962–64 Arrows indicate salinity survey

Phreatophytes, including willow, elm, and hardwood trees that border the stream channels, and crops planted on the flood plains selectively remove nitrate, phosphate, and potassium and relatively small quantities of other ions from the soil and ground water, but the remaining water contains increased concentrations of the ions not required for the plants' metabolism. These plants also intercept ground water moving toward the streams and can induce withdrawal of water from the streams, thereby decreasing the rate of streamflow.

OIL-FIELD BRINE

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Oil-field brine-saline waters brought to the surface as a result of petroleum exploration or production-is the principal source of manmade pollution of water in the basin. In some oil wells, the ratio of brine to oil brought to the surface is as high as 25 to 1, but almost all the brine is now (1964) returned to deep oil-producing strata through injection wells (B F Latta, chief geologist, Oil Field Section, Kansas State Department of Health, oral commun., 1964) There, it poses no immediate threat to the usable water resources of the area, and in many places it serves to maintain pressure in the producing formation and to displace oil which could not otherwise be recovered (Johnston and Castagno, 1963). However, concentrations of sodium and chloride that far exceed those that existed prior to the discovery of oil and the ratios of the ionic constituents to each other indicate the presence of oil-field brine in much of the ground and surface water in the basin Most of the oil-field brine is attributable to improper oil-field operations in the past.

The chief ionic constituents of oil-field brine in the basin are, in order of decreasing concentrations. Chloride (Cl), sodium (Na), calcium (Ca), magnesium (Mg), and sulfate (SO₄) The concentration of chloride in 45 samples of oil-field brine representing nearly random geographic and stratigraphic distribution ranged from about 10,000 to 140,000 mg/l (Rall and Wright, 1953) It exceeded 90,000 mg/l in more than half of the samples The ratios of the concentrations of the major cationic constituents to the concentrations of chloride were virtually constant, despite wide differences in the concentration of chloride (table 1).

The actual and relative concentrations of sodium and chloride are useful indexes of brine-pollution of water in the basin Both ions are derived principally from oil-field brine, although minor amounts are present naturally or are attributable to sewage The arithmetic mean ratio of the concentration of sodium, in milligrams per liter (including negligible amounts of potassium), to that of chloride is about 0.52 for

	All samples (45 analyses)		Samples with <90,000 mg/l chloride (29 analyses)	Samples with >90,000 mg/l chloride (16 analyses)
	Mean ratio	Weighted- mean ratio 1	Mean	ratio
Sodium-chloride Calcium-chloride Magnesium-chloride Sulfate-chloride	0 522 074 022 026	0 5105 0769 0229 0115	0 5328 0710 0220 0396	0 5017 0793 0234 004

TABLE 1 — Mean and weighted-mean ratios of the concentration of selected constituents to the concentration of chloride in oil-field brine in the Walnut River basin

¹ Weighted, with respect to the concentration of chloride

oil-field brine in the basin; the maximum is about 0.57. The standard error of the mean sodium-chloride ratio weighted with respect to chloride (0.5105) determined from the 45 available analyses is only 0.008 (Leonard, 1964a). The sodium-chloride ratio in natural waters normally exceeded 0.60, the ratio in waters containing oil-field brine normally was lower.

In streamflow, the higher ratios normally were associated with concentrations of chloride less than 30 mg/l. For example, analyses of streamflow of the Walnut River at Winfield before the discovery of oil in 1914 (Parker, 1911, table 154, p 296) indicate that the concentration of chloride rarely exceeded 30 mg/l and that the ratio of sodium to chloride varied from about 1.1 to 4.1 During the present investigation, the concentration of chloride in some samples exceeded 500 mg/l, and the ratios varied from about 0.44 to 0.60.

On the basis of concentration-discharge relations and data obtained prior to the discovery of oil in the basin, concentrations of chloride in excess of 50 mg/l in streamflow and 100 mg/l in ground water generally were attributed to oil-field brine if the sodium-chloride ratios were less than 0 60. Most of the time, the concentration of natural chloride was less than 20 mg/l chloride in the Walnut River upstream from the mouth of the Whitewater River and less than 30 mg/l chloride downstream.

Calicum and magnesium constituted relatively constant proportions of the ions in oil-field brine; however, these constituents in most ground water and streamflow were derived principally from dissolution of limestone, gypsiferous shale, and gypsum. Sulfate was normally a minor constituent of oil-field brine, but most of the sulfate in waters of the basin was derived from gypsum and gypsiferous shale. Locally high concentrations of sulfate in ground water from oil-field areas in which gypsiferous strata are absent were attributed to oxidation of hydrogen sulfide associated with some of the oil. The sulfate-chloride ratio in brine normally varied inversely with the concentration of chloride (table 1). The ratio in natural unpolluted water in the basin is commonly greater than 1 During periods of low flow, sulfate-chloride ratios were as high as 11 in unpolluted tributaries but as low as 0 03 in those draining oil fields.

Unpublished reports have implicated refineries in oil-field-brine pollution of streamflow. Concentrations of fluoride exceeding the recommended standards for drinking water were encountered in and downstream from refinery outfalls on the Walnut River during surveys of base runoff, but the effect of the measured contributions of most ions on the concentration of dissolved solids in the main stem was negligible. The concentration and amount of dissolved solids in the treated effluent from refineries were sometimes less than in the upstream diversion.

MUNICIPAL AND AGRICULTURAL WASTE

Concentration of about two-thirds of the nearly 72,000 residents of the basin in four major cities caused concomitant concentration of wastes. Municipal sewage was locally a major source of organic and inorganic pollutants in streamflow in parts of the basin

Low streamflow in some reaches of the Walnut and Whitewater Rivers contained significant quantities of sodium, chloride, nitrate, phosphate, fluoride, and boron attributed to sewage Concentrations of nitrate that exceeded the recommended standards for drinking water are attributed mainly to the oxidation of nitrogeneous wastes. The nitrate and phosphate, both plant nutrients, maintained a heavy algal bloom in some reaches that caused wide diurnal fluctuations in the content of dissolved oxygen during periods of low flow in the summer Foam from non-biodegradable detergent was noted at mainstem sites downstream from sewage effluents

Agricultural wastes include the major components of fertilizers potassium (K), phosphate (PO_4), and nitrate (NO_3). Runoff from feedlots in the Whitewater River subbasin contained varying proportions of these constituents; the nitrate, as in sewage, results from oxidation of soluble nitrogen compounds (Smith and Miner, 1964). High concentrations of nitrate in water from farm wells normally indicated local pollution by nitrogenous wastes from livestock, fertilizer, or sewage.

IMPOUNDMENT

Farm ponds, watershed structures, and municipal and State lakes detain potentially dilutant runoff; however, their net effect on the chemical quality of the Walnut River probably is negligible. There are no major reservoirs in the basin, although several have been proposed (Kansas Water Resources Board, 1963; U.S Army Corps of Engineers, 1964) Possible effects of streamflow control are described in context with other characteristics of specific drainage areas in succeeding sections of this report

CHEMICAL QUALITY OF GROUND WATER

The concentrations of dissolved solids, nitrate, sulfate, or chloride in most sampled ground waters exceeded recommended standards for drinking water (pl 1) Some of the concentrations of dissolved solids shown on plate 1 are approximate values calculated by multiplying the specific conductance by 0.65

The concentrations of major ions, except nitrate, in samples taken during construction of augered observation wells normally increased with depth The concentrations shown on plate 1 are for water from the completed wells. Other pertinent analyses appear in "Chemical Quality of Public Water Supplies of Kansas" (Kansas State Department of Health, 1965a) and in a report on the geology of Cowley County by Bayne (1962) Only salient features are discussed herein

Chemical analyses of the discharge of 17 springs are listed in table 7 (analyses 79–96). Selected analyses on plate 2 are presented as ionic concentration diagrams (Collins, 1923) to illustrate their relations to the geology, the location of oil fields, and the chemical quality of adjacent base runoff.

RELATION TO GEOLOGY

Calcium, magnesium, and bicarbonate ions from limestone constitute a large part of the dissolved solids of natural origin Calcium and sulfate from gypsum in the Sumner Group are the principal ions in nearly all ground waters that contained over 1,000 mg/l dissolved solids but that were not polluted by oil-field brine. In several wells in the western part of the Whitewater River subbasin, the concentration of sulfate alone exceeded 1,000 mg/l Locally high concentrations of sulfate in well waters in the upper part of the Chase Group were caused by recharge from areas of gypsiferous rock assigned to the overlying Sumner Group, by induced withdrawal of river water, or by oxidation of sulfurous petroleum waste Concentrations of sulfate exceeding 100 mg/l in well waters remote from oil production near the east boundary of the basin probably indicate penetration by the wells of gypsiferous shale in the Council Grove Group, which crops out east of the basin Although the U.S Public Health Service recommends a maximum concentration of 250 mg/l, the California State

22 CHEMICAL QUALITY OF WATER, WALNUT RIVER BASIN, KANSAS

Water Quality Control Board (1963) reported that concentrations of as much as 500 mg/l sulfate are not necessarily detrimental for domestic water supplies or stock waters (p. 277).

RELATION TO OIL-FIELD-BRINE POLLUTION

Ground water containing over 1,000 mg/l dissolved solids including over 100 mg/l chloride was characteristically from aquifiers in or adjacent to oil fields (pl. 1). Characteristic sodium-chloride ratios normally confirmed the presence of oil-field brine. Residual brine salts were present in the shallow ground water and as incrustations on the soil in some of the oldest abandoned oil fields, although improper disposal practices generally have been discontinued.

Brine can escape from production or injection wells through poorly cemented corroded casings to pollute water in shallow aquifers. Much of the brine is highly corrosive; the average life of steel casings in many wells was only about 12 years. The pressure in at least two injection formations in the El Dorado field was reportedly high enough to support flow at or near the surface (Kansas State Department of Health, written commun., 1963).

Discharge from the spring shown in figure 7 chemically resembled dilute oil-field brine (analysis 86, table 7; pl. 2). Similar springs com-



FIGURE 7.—Discharge from spring, in sec. 26, T. 25 S., R. 5 E. (Butler County), contained gas and oil and more than 3,000 mg/l of chloride.

monly denoted poorly plugged abandoned oil wells, many of which were properly plugged after 1950 for pollution abatement. Bubbles of gas, a strong odor of hydrogen sulfide, and discharge of oil may implicate two abandoned oil wells shown on a map of the El Dorado oil field by Fath (1921).

Polluted ground water can emerge at the surface far from the source of pollution. For example, floating crude oil and progressively higher salinity during the last 20 to 30 years caused abandonment of the spring represented by analysis 79 (table 7, pl 2) for domestic water supply Discharge from a spring (analysis 80, table 7) which drains the same limestone aquifer at approximately the same elevation about 200 yards to the east remained potable According to residents, there had been no drilling for oil within half a mile of the springs. Local variations in the fracture pattern leading from abandoned oil wells to the northeast probably caused the observed differences

High concentrations of chloride in many of the wells in the Whitewater River subbasin showed the effects of localized oil-field-brine pollution (pl. 1). In February 1963, the concentration of chloride ranged from 226 to 10,900 mg/l in water samples from auger holes drilled in the SW1/4 sec. 36, T. 24 S., R. 3 E, adjacent to two abandoned brine-disposal ponds in the headwaters of a small tributary The ponds were abandoned in 1955. Water from another auger hole, about 600 feet from the ponds, contained 23,950 mg/l chloride, probably from another source. Ground water containing high concentrations of chloride moved down the drainage gradient from the ponds toward the tributary and was replaced by fresher ground water upgradient. A sample of water from the tributary taken about 800 feet downstream from the ponds contained 2,950 mg/l chloride, despite dilution by snowmelt Bryson, Schmidt, and O'Connor (1966) attributed the high concentrations of chloride to residual brine salts leached from the soil and shale in the pond area

The Barneston Limestone, which contains brine-polluted ground water in the El Dorado and adjacent oil fields, extends westward over several extensively drilled domes, from the Walnut River into the Whitewater River subbasin east of Towanda (pl. 1). Chloride-rich ground water from the limestone composed a large part of base runoff in the Walnut River north of Augusta, in the Whitewater River south of Towanda, and in Stearns Creek north of Towanda

Most of the chloride in the Towanda municipal wells near the east bank of the Whitewater River west of Towanda (pl. 1) evidently migrated through the Barneston Limestone. The chemical quality of the well water varied with rates of pumping, location, and antecedent precipitation and generally deteriorated as the pumping rate increased and precipitation decreased.

The chloride concentration in the discharge from a spring (analysis 78, table 7; pl. 2) issuing from the Towanda Limestone Member of Doyle Shale southeast of the wells ranged from 1,110 to 2,090 mg/l in five samples taken during the 1962 and 1963 water years The spring is the main source of base runoff in tributary RM 14.2, where measured concentrations of chloride near the mouth ranged from 1,360 to 2,540 mg/l High concentrations of chloride in waters from nearby wells in unconsolidated flood-plain deposits (pl 1) probably originated from the same source.

NITRATE IN GROUND WATER

The US Public Health Service (1962) recommends that the concentration of nitrate not exceed 45 mg/l The presence of an excessive concentration in drinking water may result in cyanosis of infants (blue babies) to whom the water is fed. At present, there is no economical method for removing excessive amounts of nitrate from water. The locations of well waters containing 40 mg/l nitrate or more are indicated on plate 1; only a slight increase in the concentration of nitrate caused by boiling the water or changes in the well or aquifer could be injurious to health. The concentration of nitrate in water from about 25 percent of the sampled wells exceeded the recommended maximum Nitrate exceeded 45 mg/l in 129 wells in Butler County, 74 of which were for domestic use. It exceeded 90 mg/l in 72 wells, 40 of which were for domestic use

Water in shallow aquifers, water that was stagnant or infrequently pumped, and (or) water close to sources of pollution by animal waste characteristically contained high concentrations of nitrate. This observation is generally consistent with the findings of Metzler (1958), who described stratification of nitrate in ground water in six study areas in north-central Kansas. There, the concentration of nitrate commonly decreased rapidly with depth below the water table He concluded that the nitrates originated at or near the ground surface and "that nitrogenous materials of animal origin, especially sewage and manure, may be the principal source of nitrates or act as the chief stimulant to nitrate production" (p. 5).

Local pollution by nitrogenous organic wastes from the surface seems to be the main cause of high concentrations of nitrate in well waters in the basin The concentration of nitrate in tributary base runoff was characteristically lower than in ground water from adjacent wells Restricted lateral movement may be a dominant characteristic of ground waters locally containing high concentrations of nitrate, but some nitrate may have been removed by plantlife during migration of the ground water to the streams

CHEMICAL QUALITY OF SURFACE WATER

The chemical quality of most streamflow in the basin fluctuated widely; therefore, no single chemical analysis was necessarily typical for an extended period of time. The relations of concentrations and percentages of chemical constituents to each other and to water discharge and time at data collection sites shown on plate 2 are based on a series of measurements made over a wide range of water discharge from about October 1961 to October 1964.

CHEMICAL QUALITY OF BASE RUNOFF

Four basinwide combined seepage and salinity surveys during periods of base runoff were made in Butler and Cowley Counties on December 7-8, 1961; April 24-25 and November 1-2, 1962; and October 9, 1963 The results are described in greater detail in another publication (Leonard, 1964b). Two surveys of the Whitewater River between Towanda and Potwin were made on August 30, 1962, and March 21, 1963 A survey of one reach of the Walnut River was made on August 16, 1963, to check apparently contradictory data from previous surveys.

Detailed descriptions of measuring sites are included in "Surface Water Records of Kansas" (U S Geological Survey, 1962, 1963, 1964b) and locations of main-stem sites and tributary watersheds are shown on plate 3 The sites are numbered in terms of their location in river miles upstream from the mouth of the main stem Chemical analyses of the streamflow at each site are included in tables 8 and 9

The surveys were made over a range of water discharge representing conditions from above-normal precipitation to drought. The December 1961 survey represented conditions of high base runoff and falling stage (M. W. Busby, written commun., 1963). Most vegetation was dormant, and evaporation was negligible because of low wind velocities and temperatures. The October 1963 survey represented conditions of drought (figs 5, 6) and preceded the first killing frost High temperature, low humidity, and abundant vegetation probably caused significant water losses by evapotranspiration. The other surveys represented intermediate conditions.

MAIN STEM OF THE WALNUT AND WHITEWATER RIVERS

Changes in the concentrations of total dissolved solids, sulfate, and chloride in corresponding reaches of the Walnut and Whitewater Rivers were relatively similar during all except the October 1963 sur-

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vey, when many tributaries were dry (figs. 8, 9). During that survey, the concentrations of the various ionic constituents in streamflow at most stations were higher than during the other surveys and were near the maximum recorded during the entire investigation. The effects of manmade effluent on the dissolved-solids load of the main stem were accentuated. The concentration of nitrate in the main stem ranged from less than 1 to about 50 mg/l in the Walnut River and from less than 1 to about 10 mg/l in the Whitewater River. The maximums occurred downstream from sewage effluents.

Streamflow at most main-stem sites during the October survey was unsatisfactory for irrigation because of combined salinity and sodium hazards. During the other surveys, it was generally suitable for use only on soils from which accumulated salts are leached periodically.

DISSOLVED SOLIDS

The concentration of dissolved solids during the surveys exceeded 500 mg/l at all stations on the main stem of the Walnut River except at RM (river mile) 109.8 north of El Dorado and at RM 102.6 downstream from the mouth of the East Branch (fig. 8). With few exceptions it exceeded 1,000 mg/l in the main stem of the Whitewater River (fig. 9).

On October 9, 1963, the concentration of dissolved solids exceeded 1,000 mg/l at all main-stem stations, except RM 109.8 in the headwaters of the Walnut River and RM 1.8 near its mouth at Arkansas City. The concentration was generally lower at Winfield than that at main-stem stations upstream. The maximum was 2,710 mg/l at RM 26.2, on the main stem of the Whitewater River between Potwin and Towanda.

HARDNESS

The water at all main-stem stations was very hard (p 8) Total hardness (as calcium carbonate) ranged from 246 to 684 mg/l in the Walnut River upstream from Augusta, from 619 to 1,290 mg/l in the Whitewater River, and from 389 to 712 mg/l in the Walnut River downstream from Augusta.

BICARBONATE

The concentrations of bicarbonate ion, the chief source of alkalinity in water, ranged from 132 to 644 mg/l in the main stem of the Walnut River and from 254 to 412 mg/l in the main stem of the Whitewater River. Bicarbonate commonly represented the smallest percentage of total anions in the main stem of the Walnut or Whitewater Rivers, but it was the predominant anion in tributaries where neither gypsiferous strata nor oil-field brine affected the dissolved-solids load.



FIGURE 8—Concentrations of total dissolved solids, sulfate, and chloride at data-collection sites on the main stem of the Walnut River during surveys in water years 1962–64


FIGURE 9—Concentrations of total dissolved solids, sulfate, and chloride on the main stem of the Whitewater River during surveys in water years 1962-64

SULFATE

Sulfate concentrations at main-stem sites in the Walnut River were less than 250 mg/l, except during the October and August 1953 surveys at Gordon (RM 71.2) and the October 1963 survey at Douglass (RM 58.5), both downstream from the confluence with the Whitewater River. During the October 1963 survey, most of the streamflow at both stations came from the Whitewater River and west-bank tributaries underlain by gypsiferous rock of the Sumner Group.

Upstream from the junction with the Whitewater River, sulfate in the Walnut River comprised a maximum of about 12 percent of the total anions, compared with 28 percent downstream from the junction. The sulfate upstream is attributed chiefly to refinery and sewage effluent, oxidation of abundant hydrogen sulfide in oil-field brine, and migration of small quantities of sulfate-rich ground water across the drainage divide between the Walnut and Whitewater Rivers.

The concentration of sulfate in the main stem of the Whitewater River ranged from 231 mg/l during the March 1963 survey to 840 mg/l during the October 1963 survey. The lower value was the only concentration less than 250 mg/l at main-stem sites in the Whitewater River during any of the six surveys Concentrations normally decreased downstream from the headwaters to the confluence of the West Branch of the Whitewater River, a major source of the sulfate load of the main stem (fig. 9). Downstream from the West Branch, the concentrations of sulfate decreased toward the mouth, where they ranged from 303 to 382 mg/l at station 07–1471 (RM 0.8). Sulfate was the predominant anion. It constituted about 40 percent of the total anions in the Whitewater River during all but the October 1963 survey, when it decreased from more than 60 percent in the headwaters to about 30 percent downstream because of the increase in chloride ion.

CHLORIDE

The maximum concentration of chloride in the main stem of the Walnut River was 1,220 mg/l at the mouth of the West Branch at El Dorado (RM 103 2) during the October 1963 survey. The concentration exceeded 250 mg/l at that site during all surveys. Streamflow of the unpolluted East Branch, near the site of the proposed El Dorado dam (U.S. Army Corps of Engineers, 1964), diluted streamflow of the West Branch The concentration of chloride downstream from the mouth of the East Branch to Gordon increased as a result of seepage and runoff from areas polluted by oil-field brine, except during

the October survey, when there was no measurable flow at the mouth of the East Branch and most tributaries were dry

Near the junction, the concentration of chloride in the Whitewater River exceeded that in the Walnut River. Perennial sources of olfield brine adjacent to the reaches of the Whitewater River between RM 31 3 and 26 2 and between Towanda (RM 144) and Augusta (RM 08) raised the concentration at the downstream ends to values exceeding 250 mg/l.

Chloride normally predominated in base runoff in the Walnut River, except in the headwaters and in a short reach downstream from the mouth of the East Branch. Chloride was normally subordinate to sulfate in the Whitewater River, except near the mouth, but it constituted about 60 percent of the anions downstream from Potwin during the October 1963 survey.

OIL-FIELD-BRINE POLLUTION

The sodium-chloride ratios in base runoff generally decreased downstream with increasing concentrations, from about 0.65 near the headwaters of both rivers to about 0.51, which is characteristic of oil-field brine (table 2) Sewage and industrial effluent containing sodium and chloride caused local incongruities in the ratios. The concentration of potassium, included with sodium in calculating the ratios, rarely exceeded 5 percent of the concentration of sodium. The ratios at most sites decreased with decreasing rates of water discharge as an increasing proportion of the streamflow was derived from perennial sources of pollution.

The percentages of the dissolved-solids load attributable to oil-field brine at the main-stem stations shown in table 2 normally increased with decreasing water discharge. The percentages ranged from about 17 percent for the Whitewater River at Towanda during the November 1962 survey to about 70 percent for the Walnut River at Augusta during the October 1963 survey The percentages are based on the assumption that the concentration of chloride derived from natural sources was 50 mg/l. Chloride in excess of 50 mg/l is attributed to oilfield brine

The concentration of each of the other ions attributed to oil-field brine is the product of the excess chloride and the corresponding ratio in table 1. Concentrations of chloride in samples taken under similar

TABLE 2 — Percentages of the dissolved-solids load attributable to oilfield brine during salinity surveys in the Walnut River Basin, December 1961 to October 1963

Data-collection site	Date of survey		Water discharge (cfs)	Concen- tration of chloride	Sodium/- chloride ratio	Percentage of dissolved- solids load attributed to oil-field brine		
				(mg/l)		(1)	(2)	
	w	alnut	River			<u> </u>		
Augusta, 07–1469, RM 81 3	Dec Apr Nov Aug Oct	1961 1962 1962 1963 1963	145 64 0 78 4 10 0 4 19	192 222 136 369 655	0 57 58 56 53	35 37 26 57 71	43 44 34 63 74	
Gordon, RM 71 2	Dec Apr Nov Aug Oct	1961 1962 1962 1963 1963	304 144 165 40 1 23 0	231 278 286 426 560	53 52 52 50 50	31 36 38 47 52	36 41 43 51 56	
Douglass, 07-1475, RM 58 5	Dec Apr Nov Oct	1961 1962 1962 196 3	380 204 208 24 6	205 239 255 510	56 50 56 49	30 33 36 53	36 38 41 56	
Winfield, 07–1478, RM 22 6	Dec Apr Nov Oct	1961 1962 1962 1963	668 310 232 25 2	172 203 227 300	53 52 53 52	25 30 34 40	32 36 40 45	
	Whi	tewate	er River					
Towanda, 07-1470 7, RM 14 4	Dec Apr Aug Nov Mar Oct	1961 1962 1962 1962 1963 1963	90 6 48 4 16 4 42 9 41 8 6 54	204 246 281 199 201 510	55 53 55 63 51 51	20 24 27 17 21 43		
Augusta, 07–1471, RM 0 8	Dec Apr Nov Aug Oct	1961 1962 1962 1963 1963	113 58 0 52 6 24 0 9 35	267 336 320 474 700	0 52 50 50 50	27 - 34 - 31 - 46 - 57 -		

[RM, river miles upstream from mouth]

¹ 50 mg/l chloride attributed to natural sources ² 20 mg/l chloride attributed to natural sources

conditions before the discovery of oil in the basin were much less than 50 mg/l therefore, the percentages of the load attributed to brine probably are low (Leonard, 1964a). Slightly higher percentages based on a natural concentration of 20 mg/l chloride for the Walnut River are also shown in table 2

RELATIVE MAGNITUDE OF CHEMICAL DISCHARGE FROM MAJOR SOURCES

Major sources of the chemical load in base runoff included tributary inflow, discharge of springs and seepage of ground water directly into the main stem, and municipal and industrial outfalls. The daily load (or chemical discharge) is the quantity of dissolved solids carried by streamflow past a station or into impoundment during a day. It was calculated for each source as follows.

Load (tons per day) = $K \times daily$ mean water discharge (second-ft) $\times daily$ mean concentration (mg/l) (1)

1

4

where K is a constant approximately equal to 0.0027. To evaluate the effect of individual contributions of water and ions on the quality of base runoff in the main stem, the daily runoff and chemical discharge at all stations during each basinwide survey were calculated as percentages of similar quantities measured in the Walnut River at Gordon (RM 71.2) and (or) the Whitewater River at Towanda (07-1470.7). The results are summarized in table 3. When the percentage of chemical discharge, the net inflow raised the concentration at the reference site.

TRIBUTARY STREAMS

Salinity surveys of low streamflow were made along major tributaries to obtain data on the chemical characteristics of unpolluted water and to localize and define the relative magnitude of sources of pollution. Whenever possible, stable streamflow at all stations in a watershed was measured and sampled during a single day. The results, combined with data from miscellaneous measurements and analyses of the discharge of springs and streamflow under nearly similar hydrologic conditions, are shown graphically on plate 2. Analyses and additional data collected at some of the sites are listed in table 7.

Base runoff unaffected by manmade pollution was normally of the calcium bicarbonate type in watersheds underlain by rocks of the Chase Group and of the calcium sulfate type in watersheds underlain by rocks of the Sumner Group. The concentration of sodium and chloride increased appreciably near and downstream from some oil fields, which indicates either direct discharge of wastes into the streams or, more commonly, local pollution of shallow ground water.

			[Negat	ve figures	s indicate	loss of v	vater or c	hemical lo	bad from	stream]						
Survey date		Decembe	r 7–8, 1961	L	April 24-25, 1962				N	lovembe	r 1–2, 1962	2	October 9, 1963			
	Dis- charge	Dis- solved solids	Sulfate (SO4)	Chlo- ride (Cl)	Dis- charge	Dis- solved solids	Sulfate (SO4) 1	Chlo- ide (Cl)	Dis- charge	Dis- solved solids	Sulfate (SO4) 1	Chlo- ride (Cl)	Dis- charge	Dis- solved solids	Sulfate (SO4)	Chlo- ride (Cl)
					U	pstream	from Go	rdon				- 1 <u>, </u>	·			
Tributaries																
Perennial Other 1	$\begin{array}{c} 11 \\ 54 \\ 7 \end{array}$	16 3 43 4	178 455	$\begin{smallmatrix}18&2\\33&3\end{smallmatrix}$	$\begin{array}{c} 12 & 5 \\ 71 & 9 \end{array}$	199 675	26 8 90 7	18 2 42 8	$\begin{array}{c} 11 & 3 \\ 55 & 2 \end{array}$	203 511	31 6 67 8	20 4 24 4	$\begin{array}{c} 27 & 0 \\ 21 & 5 \end{array}$	454 132	467 280	$42 \begin{array}{c} 2 \\ 7 5 \end{array}$
Total	66 1	59 7	63 3	51 5	84 4	87 4	3 117 5	61 0	66 5	71 4	99 4	44 8	48 5	58 6	74 7	49 7
Net seepage																
Whitewater River Walnut River	153 180	26 8 12 6	267 100	24 5 22 7	14 94	53 41	-199	22 0 13 3	89 242	135 181	-61	17 4 36 9	18.1 28 3	17 7 23 3	$\begin{array}{c} 10 \ 4 \\ 13 \ 5 \end{array}$	21 6 30 3
Total	33 3	39 4	36 7	47 2	10 8	94	-19 9	35 3	33 1	31 6	-14	54 3	46 4	41 0	23 9	51 9
Industrial and municipal effluents and diversions																 0
Refinerles Sewage	-6 12	$-1 \\ 1 0$	3	5 8	- 1 49	- 4 36	$egin{array}{c} 1 & 2 \\ 1 & 2 \end{array}$	$\begin{array}{c} 1 & 0 \\ 2 & 7 \end{array}$	$-1 \ 2 \ 1 \ 6$	44 14	7 13	$-\frac{2}{11}$	$-{2 \atop 7}{7 \atop 8}$	-4852	$ \begin{array}{r} -3 & 5 \\ 4 & 9 \end{array} $	-5^{2}_{36}
Total	6	9		13	48	32	24	37	4	-30	20	9	51	4	14	-16
Total at Gordon	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
					Gordo	on downs	itream to	Winfield								
Tributarles Net seepage	85 3 4 34 4	41 9 37 2	$\begin{smallmatrix}22&7\\12&0\end{smallmatrix}$	36 0 27 6	69 9 45 4	³ 28 3 8 46 0	3 19 3 3 29 9	3 20 8 3 36 4	25 6 15 0	14 8 2 4	11 3 8 0	98 18	69 26	33 - 330	$03 \\ -260$	$08 \\ -421$
Total at Winfield	219 7	179 1	134 7	163 6	215 3	174 3	149 2	157 2	140 6	117 2	119 3	11 6	109 5	70 3	80 3	58 7

TABLE 3.—Contributions of water and selected ions from various sources as percentages of measured water and chemical discharge of the Walnut River at Gordon (RM 71 2) during salinity surveys in the Walnut River basin, December 1961 to October 1963

¹ Tributary runoff not attributed to measured springs or to municipal or industrial effluent
 ² Percentage greater than 100 percent caused by apparent sulfate loss in main stem
 ³ No samples collected at Rock Creek in April 1962
 ⁴ Includes discharge of known but unmeasured minor tributaries

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YIELD INDEXES OF TRIBUTARY WATERSHEDS

Tributary inflow measured near the confluence with the main stem is attributed to the watersheds shown on plate 3, although migration of some ground water across surface-water divides occurs in the limestone terrane. Net seepage is attributed to the remaining areas adjacent to the main stem. To compare the relative pollutive effects of the drainage areas during each survey, the percentage of water or chemical discharge contributed by each watershed is divided by the percentage of area of that watershed, and both percentages are referred to similar quantities for the Walnut River at Gordon (RM 71.2) The quotient is a dimensionless number termed the "water- or constituent-yield index." In the form of an equation

$$Y_{1eld index} = \frac{Percentage of discharge}{Percentage of area}.$$
 (2)

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Water-yield indexes refer to relative rates of water discharge; constituent-yield indexes refer to relative rates of chemical discharge.

The drainage area of 1,056 square miles at Gordon includes most of the measured sources of pollution and is about half the total area of the basin Yield indexes greater or less than 1 indicate that the corresponding drainage areas contributed a disproportionately greater or lesser amount of water or of chemical load per unit area than the entire drainage area of the Walnut River at Gordon. When the constituentyield index exceeded the water-yield index for a watershed, inflow from the watershed raised the concentration of the constituent at Gordon.

The approximate magnitude of maximum-yield indexes, all referred to Gordon, are shown graphically on plate 3 Dashed heavy boundary lines denote those watersheds that contributed a disproportionate amount of water to the main stem during the drought in October 1963. Solid heavy boundary lines denote watersheds where the concentration of the indicated ion in tributary inflow exceeded that in the main stem upstream from the mouth. These lines normally delineate watersheds where the constituent-yield indexes exceeded 1 and the concentration of the indicated ion in tributary runoff was high. In isolated cases, these lines indicate relatively low concentrations of the ion in the main stem at the mouth of the tributary (for example, sulfate in tributaries of the Walnut River upstream from Augusta)

Watersheds that contributed a disproportionately large percentage of the streamflow or chemical load of the Walnut River at Gordon (yield indexes >1) constitute a relatively small part of the drainage area of the basin Perennial springs with small surface drainage areas (for example, RM 105 9, pl 3) normally had exceptionally high maximum water- and constituent-yield indexes because they were relatively important sources of the dissolved-solids load of the main stem during periods of low flow.

The relative proportions of water and load contributed by various tributaries to the main stem during the period of drought in October 1963 commonly differed greatly from those contributed at other times. In October 1963, perennial sources upstream from Gordon contributed 45 percent of the chemical load at that station but only about 20 percent during the other surveys (table 3). Conversely, tributaries draining the more extensive eastern part of the basin, underlain mostly by limestones of the Chase Group, contributed a much smaller proportion of the total discharge of the lower reaches of the main stem in October 1963 than during periods of higher streamflow.

High sulfate-yield indexes characterize drainage areas underlain by gypsiferous rock of the Summer Group in the western part of the basin. High chloride-yield indexes characterize areas of past oil production. High dissolved-solids-yield indexes characterize watersheds for which either the chloride- or the sulfate-yield indexes, or both, are exceptionally high. Although yield indexes for other ions are not shown, those areas with high sulfate indexes normally have high calcium-yield indexes, those with high chloride indexes have high sodium indexes. The dissolved-solids indexes are characteristically low for tributary runoff unaffected by gypsum or oil-field brine. Such runoff normally improves the chemical quality of streamflow in the main stem.

Some of the highest yield indexes shown apply to areas adjacent to the Walnut and Whitewater Rivers and downstream from tributary data-collection sites These areas are underlain chiefly by flood-plain deposits that are readily susceptible to mineralization by oil-field and refinery wastes, fertilizer, polluted influent streamflow, and ground water from adjacent bedrock Seepage of ground water from these areas into the main stem made up a large part of the dissolved-solids load of the main stem during periods of low flow.

SEEPAGE

The calculated net seepage gain or loss in a reach of the main stem is the algebraic difference between the change in water discharge at successive main-stem stations and total tributary contributions to the included reach. If Q_A and Q_B represent daily mean water discharge, in cubic feet per second, at successive main-stem stations A and B in downstream order, and Q_1 and Q_2 represent the daily mean discharge of tributaries 1 and 2 into the reach AB, net seepage, S, for the reach is defined by the following equation

$$S = (Q_B - Q_A) - (Q_1 + Q_2). \tag{3}$$

A positive value for S represents a net seepage gain, in cubic feet per second; a negative value represents a net loss

Net seepage gains and losses in daily mean chemical load, L, were computed from discharge measurements and chemical analyses from an equation analogous to equation 3 above.

$$L = K(Q_B C_B - Q_A C_A) - K(Q_1 C_1 + Q_2 C_2), \qquad (4)$$

where L represents the net gain or loss of load (or chemical discharge), in tons per day, C represents the concentration of a given constituent, in milligrams per liter; K is a constant equal to 0 0027, and subscript designations A, B, 1, and 2 are similar to those in equation 3

The calculations are based on the assumptions that inflow and outflow in the reach are at equilibrium and that all tributaries and diversions were measured A losing reach during one survey sometimes was a gaining reach during another.

The Walnut and Whitewater Rivers were generally effluent (gaining) streams during the surveys; net seepage gains in water discharge were greater than net seepage losses in number and in magnitude. Most net seepage gains in a reach of the main stem consisted mainly of ground water and its dissolved-solids load that migrated into the channel from aquifers adjacent to the reach and downstream from tributary stations. Some net seepage gains included unmeasured tributary inflow Net seepage losses included unmeasured diversions, channel leakage, and effects of evapotranspiration

Most net seepage losses in water discharge represented less than 4 percent of the measured discharge at the downstream end of each reach, well within the range of acceptable errors, however, a net seepage gain or loss in water discharge accompanied by a loss in one ionic constituent and a gain in another normally constituted evidence of the interchange of ground and surface water or of unmeasured diversions

Cumulative net seepage gains and losses in water discharge and in loads of sulfate, chloride, and total dissolved solids during the surveys are shown as percentages of similar quantities for the Walnut River at Gordon (RM 71.2) in table 3 and in terms of yield indexes on plate 3. To facilitate comparison, seepage directly into the Whitewater River is considered part of cumulative net seepage in table 3, not as part of the surface-water contribution of the Whitewater River as shown in a previous report (Leonard, 1964b). Cumulative net seepage into the Walnut and Whitewater Rivers upstream from Gordon ranged from 10.8 percent of the water discharge at Gordon during the April 1962 survey to 464 percent in October 1963. Seepage into the Walnut River upstream from Gordon (RM 109.6 to 71.2) exceeded seepage into the Whitewater River (RM 38.1 to 0.8) during all surveys. The quantity of dissolved solids in seepage into the Walnut River exceeded that into the Whitewater River only during the periods of low base runoff in November 1962 and October 1963

The percentage of the sulfate load at Gordon attributed to seepage varied from a loss of about 20 percent during the April 1962 survey to a gain of about 37 percent during the December 1961 survey During all surveys except that in December 1961, the percentage of water discharge attributed to seepage into the Whitewater and Walnut Rivers exceeded the percentage of sulfate load, therefore, seepage reduced the concentration of sulfate in the Walnut River at Gordon

The pollutive effect of seepage on the main stem of the Walnut River was greater with respect to chloride than to the other constituents Chloride from seepage constituted from 35 to 54 percent of the chloride load at Gordon and exceeded percentages for water discharge during all surveys. During the surveys in November 1962 and October 1963, when seepage was the major source of chloride at Gordon, the amount of chloride in seepage into the Walnut River far exceeded that into the Whitewater River, but the concentration of chloride in the smaller volume of net seepage into the Whitewater River was higher than that into the Walnut River during all surveys.

The chloride load attributed to effluent ground water (perennial sources plus cumulative net seepage, table 3) ranged from about 54 percent of the chloride load at Gordon in April 1962 to about 94 percent in October 1963 Most chloride originated in areas with high chloride-yield indexes (pl 3) where the natural chloride load was negligible. Direct release of oil-field brine from present (1965) operations is apparently absent or negligible; therefore, effluent ground water containing residual brine salts evidently was the main cause of high concentrations of chloride in low streamflow

The causes of calculated losses in water and chemical discharge in a reach are difficult to assess. They could be caused by a lack of equilibrium between inflow and outflow, by unmeasured diversion, by channel leakage to replace ground water withdrawn by wells or abundant phreatophytes adjacent to the channel, or by chemical reactions.

During all but the December 1961 survey, when a falling stage may have caused apparent losses in several reaches, the surveys were made when inflow and outflow of water in each reach upstream from Gordon were nearly at equilibrium. During periods of exceptionally low flow, streamflow measured at the lower end of a reach might have entered the reach many days prior to the surveys, when conditions were dissimilar to those measured at the upstream site. A tracer-dye study in June 1963 showed that part of the low streamflow and its dissolvedsolids load were detained in pools on the main stem for periods longer than the duration of each survey Large net losses in water and chemical discharge between Douglass and Winfield during the October survey (table 3) may exemplify this situation

Contributions to underflow upstream from main-stem measuring sites may have caused some losses. Compensatory gains downstream may have represented emergence of the underflow Tributary inflow to flood-plain deposits downstream from tributary stations caused other losses Because of the time required for migration through stream deposits and because of changes in composition during migration, the quantity and chemical quality of the measured streamflow and emergent underflow probably differed.

Losses in the chemical load caused by evaporation of water from the main stem probably were negligible Most of the sulfate and chloride salts remained in solution under the conditions prevailing during the surveys, although minor amounts of evaporites were deposited in moist soil along the banks of some streams during periods of exceptionally low flow.

Losses or gains caused by reactions involving dissolved chemical constituents in the main stem probably were negligible compared with those representing actual movement of dissolved solids and the water that acted as their vehicle. The chloride ion was stable, although some sodium may have been removed by base exchange with fine-grained sediments Calcium carbonate, observed as scale associated with algal growths on some submerged objects, probably precipitated as the algae removed carbon dioxide from the water. Some sulfate, nitrate, and phosphate probably was used by plant life The presence of hydrogen sulfide in some bottom sediments may signify reduction of sulfate by bacteria—a reaction that might affect adversely the quality of impounded water in the proposed Towanda reservoir

MUNICIPAL AND INDUSTRIAL EFFLUENT

Measured refinery effluents and diversions affected total discharge and chemical load at Gordon less than measured municipal sewage effluents (table 3), but some of each were locally detrimental to the quality of the water in the main stem (table 8) Municipal sewage effluent constituted a maximum of about 8 percent of the water discharge and 5 percent of the chemical discharge of the Walnut River at Gordon during the October 1963 survey. Municipal sewage effluent generally reduced the concentration of total dissolved solids in the main stem but provided nutrients for excessive algal growth in some reaches.

CHEMICAL QUALITY OF RUNOFF FROM MAJOR SUBDIVISIONS OF THE BASIN

Chemically dissimilar streamflow of the Whitewater River significantly altered the chemical quality of the Walnut River. The differences provided a basis for subdividing the basin into three units the watershed of the Walnut River upstream from the mouth of the Whitewater River (about 425 sq mi); the Whitewater River subbasin (about 520 sq mi), and the Walnut River downstream from the mouth of the Whitewater River (about 1,050 sq mi.). Characteristics of the chemical quality of runoff from each of the units under conditions ranging from drought to flood and their relation to causal factors in the respective drainage areas are summarized in downstream order in this section

Ranges in the concentrations of selected ions and corresponding ranges in water discharge are listed in table 4. The shape of profiles of the concentrations of sulfate, chloride, and, to a lesser extent, dissolved solids in concurrent samples at the stations cited are generally similar to those for base runoff (figs 8, 9) except during periods of extreme fluctuation in water discharge

Relations of specific conductance, of percentages of anions and cations (water type), and of approximate concentrations of selected ions to instantaneous water discharge are summarized graphically by curves for each station. At most stations, the relation of specific conductance to water discharge differed from year to year. The specific conductance of individual samples from selected stations are plotted to illustrate the range and distribution of the data. Most of the samples were taken on the more frequent days of constant flow or recession, therefore, the curves best describe streamflow under conditions that prevailed most of the time.

WALNUT RIVER UPSTREAM FROM THE MOUTH OF THE WHITEWATER RIVER

Fractured Barneston Limestone of the Chase Group crops out on the surface or underlies a large part of the drainage area of the Walnut River upstream from the mouth of the Whitewater River. It also occurs as float in most stream courses; therefore, the dissolved-solids load in runoff unaffected by oil-field brine consists principally of calcium and bicarbonate ions and has minor quantities of magnesium and of other ions The western part of the subbasin, an area of exten-

TABLE 4 — Ranges and maximums for water d	ischarge, concentrations of	selected rons, and chemical	properties of streamflow i	in the Walnut
•	River basin during water	years 1962-64		

					Maximums (mg/l)								
Station name and No	Drainage orea (sq mı)	Water discharge (cfs)	Specific conductance (micromhos per cm at 25° C)	Dissolved solids (mg/l)	Sulfate (mg/l)	Chloride (mg/l)	Total hardness (mg/l as CaCO ₃)	Sodium- chloride ratio	pH	Ni- trate	Boron	Fluo- ride	Phos- phate
		·	Walnut River i	ipstream fro	m White	water Rive	2 r						
Cole Creek near De Graff (07-1465 7) 1 East Branch Walnut River near El Do- rado (07-1466) 1	30 151	0 1-800 2-2,000	160-600 170-670	93380 105405	3 3-4 3 10-36	5-24 7-27	60-388 106-307	0 31-2 60 64-1 38	7 2-8 2 7 4-8 3	16 3 8	0 18 21	055	05
West Branch Walnut River near El Do- rado (07-1468) 2	47	1-400	160-1, 320	104-706	5-47	8-270	72-430	54- 80	7 1-8 4	62	18	5	6
Walnut River at Haverhill Road near El Dorado (07-1468 5) Walnut River near Augusta (07-1469)	376 451	3 5–2, 100 2–1, 750	2703, 300 2102, 750	1701, 860 1031, 670	10290 12190	20-870 18-700	120-534 84-512	55- 68 51- 60	64-81 60-84	97 75	38 34	$\begin{smallmatrix}2&2\\1&7\end{smallmatrix}$	13 72
			White	water River	subbasın					<i>i</i> .			<u></u>
Whitewater River ai Towanda (07-1470 - 7) ²³ ≽hitewater River at Augusta (07-1471) ²³	425 517	4-4, 500 8-2, 650	170-2, 800 300-3, 200	1101, 750 1801, 900	20-600 30-510	8-540 23-730	68-1, 129 112-1, 056	0 49- 65 48- 56	7 1-8 3 7 1-8 2	89 71	0 44 36	$\begin{smallmatrix}1&3\\2&2\end{smallmatrix}$	6 9 1 5
		Walr	ut River down	nstream from	n Whitew	ater River							
Walnut River near Douglass (07-1475) ² . Timber Creek near Wilmot (07-1476) ¹ Walnut River at Winfield (07-1478) ² ,	1, 346 63 1, 872	22-7, 100 01-9 6 20-5, 200	210-2, 850 360-690 240-2, 620	146–1, 800 300–407 160–1, 640	13-440 10-25 16-380	15–520 31–78 17–590	94–925 144–296 88–834	0 48- 65 30- 56 50- 60	7 1-8 3 7 5-8 1 7 0-8 3	19 5 3 13	0 32 18 34	$\begin{array}{c}0&8\\&3\\1&0\end{array}$	19 3 11

¹ Data collected intermittently ² Data collected monthly or more frequently ³ Maximum discharge with complete analysis of concurrent sample

sive oil-field development (Fath, 1921) and improper waste-disposal before effective measures of pollution control were adopted, is a source of severely polluted ground water.

Diversions and effluents of refineries on the West Branch of the Walnut River and on the Walnut River and the municipal sewage plant, all at or near El Dorado, altered the chemical quality of streamflow at downstream sites (table 8).

WEST BRANCH WALNUT RIVER Base Runoff

During the surveys of base runoff, the concentration of sulfate, chloride, and dissolved solids at the mouth of the West Branch Walnut River at El Dorado (RM 103 2) exceeded concentrations at every station on the main stem of the Walnut River upstream from the confluence with the Whitewater River The concentration of chloride exceeded that at all stations on the Walnut River, and the concentration of dissolved solids (consisting largely of chloride) exceeded that at other main-stem sites during all but the survey on November 1, 1962. Figure 8 shows a nearly linear increase of about 2,100 mg/l dissolved solids and over 1,000 mg/l chloride in about 6.6 river miles from the upstream station (RM 109 8) to the mouth during the October 1963 survey, when the chloride concentration at the mouth was ride were in a range of concentration similar to that in ground water adjacent to the west bank of the stream

The drainage area of the West Branch, about 78 square miles, includes oil fields that had been extensively developed by 1919 (Fath, 1921). The fields, topographically and structurally higher than the channel of the West Branch, were a source of brine-polluted runoff before and during the investigation. The West Branch contributed about 7 percent of the total chloride load at Gordon during the October 1963 survey, when the chloride concentration at the mouth was 1,200 mg/l and a maximum of about 18 percent during the December 1961 survey, when the chloride concentration at the mouth was about 400 mg/l.

Most of the dissolved-solids load, consisting mainly of sodium and chloride, originated downstream from periodic data-collection site 07–1468.5. In October 1963, most of the chloride load at the mouth was derived from tributaries RM 106.6 and 105 9 (pl. 3) Streamflow of tributary RM 105.9, consisting mainly of discharge from a spring about 100 yards upstream from the mouth (fig 7), carried a daily load equivalent to over 80 percent of the chloride load of the West Branch at its mouth. The concentration of chloride was 3,060 mg/l, similar to that in August 1963 (analysis 86, table 7; pl. 2).

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WEST BRANCH WALNUT RIVER NEAR EL DORADO

(07-1468, RM 1098)

Data were collected monthly at station 07–1468, which was also the upstream station on the main stem during the combined seepage and salinity surveys. The concentrations and the range in concentrations of sulfate, chloride, and dissolved solids normally were less than those in concurrent samples at all other monthly stations

Calcium and bicarbonate were the principal cations at rates of discharge greater than about 1 cfs (cubic foot per second) (fig 10) Sodium and chloride were predominant at lower rates of discharge The sodium-chloride ratio increased from about 0.54 at 0.1 cfs to about 0.80 at about 100 cfs.

EAST BRANCH WALNUT RIVER

The East Branch Walnut River drains an area of about 268 square miles underlain mainly by limestone of the Chase Group The proposed El Dorado dam would regulate most of the runoff, which is apparently unaffected by oil-field brine. Part of the runoff in two major tributaries, Satchel and Bemis Creeks, is impounded for municipal supply in El Dorado Lake and Lake Blue Stem, respectively. Water is withdrawn near the mouth during periods of drought Data describing unregulated streamflow were collected intermittently at sites on Cole Creek near DeGraff (07–1465.7) and on the East Branch near El Dorado upstream from Satchel Creek (07–1466) (See pl. 2.)

BASE RUNOFF

Low streamflow at all stations on the East Branch was calcium bicarbonate type water of low concentration (analysis 10–15, table 7) Inflow from the East Branch significantly diluted base runoff in the Walnut River upstream from Augusta. During the October 1963 salinity survey, there was no measurable flow at the mouth of the East Branch Dissolved-solids concentration in the main stem downstream from the mouth was much higher than during the other surveys, when the East Branch contributed about 25 percent of the water discharge but less than 6 percent of the dissolved solids at Gordon (fig. 8; table 8).

COLE CREEK NEAR DEGRAFF

(07 - 14657)

Cole Creek was dry during much of the 1964 water year Calcium and bicarbonate were the principal ions at all rates of discharge (fig 11). Low, equal, and uniform percentages of sulfate and chloride indi-



FIGURE 10 — Relations of the percentages of major ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at West Branch Walnut River near El Dorado (07-1468) during water years 1962-64



FIGURE 11—Relations of the percentages of major ions, specific conductance, and time to water discharge at Cole Creek near DeGraff (07-14657) during water years 1962-64

cated the absence of gypsum or oil-field brine in the subbasin. Sodiumchloride ratios were greater than 1 at all but the highest rates of discharge, when some sodium may have been removed by suspended clay

EAST BRANCH WALNUT RIVER NEAR EL DORADO

(07 - 1466)

The range and variations in specific conductance and in concentrations of ions in the East Branch Walnut River near El Dorado (fig 12, table 9) generally were similar to those in Cole Creek because the geologic and cultural setting is similar Calcium and bicarbonate predominated at all rates of water discharge. Consistently high sodiumchloride ratios and low concentrations of ions show that oil-field-brine pollution was insignificant

Concentrations of dissolved solids at station 07–1466 were normally lower and the range smaller than at other stations on the Walnut River On the basis of the available data, the water impounded in the proposed El Dorado reservoir would be hard (over 100 mg/l as $CaCO_3$) but would meet accepted standards for drinking water.

WALNUT RIVER AT HAVERHILL ROAD NEAR EL DORADO (07-1468 5, RM 95 9)

Brine-polluted ground water migrates downdip, toward the Walnut River, between El Dorado and Haverhill Road from a large area that includes the extensively drilled structural domes on the west and the westerly dipping strata on the east. The reach receives runoff from much of the El Dorado oil field and effluent of the muncipal sewage plant and both refineries at El Dorado

BASE RUNOFF

Constant Creek (RM 1002), a major west-bank tributary, contributed from 22 to 55 percent of the chloride load at station 07–1468.5 during the surveys of base runoff, the maximum was contributed in October 1963 The headwaters he in a structural saddle in the Barneston Limestone between the Oil Hill and Boyer domes, which had been extensively drilled for oil by 1919 A spring (fig. 13; analysis 90, table 7, pl. 2), near the structurally and topographically lower southeastern part of the saddle, was the major source of oil-field brine in Constant Creek during periods of low flow. Oil, which was evidently flushed from joints and solution cavities in the Barneston Limestone, was skimmed from the emergent ground water by a local entrepreneur, but some escaped into Constant Creek during periods of heavy rainfall



FIGURE 12 — Relations of the percentages of major ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at East Branch Walnut River near El Dorado (07–1466) during water years 1962–64

CHEMICAL QUALITY, RUNOFF FROM BASIN SUBDIVISIONS 47



FIGURE 13.—Polluted spring in the watershed of Constant Creek, sec. 3, T. 25 S., R. 5 E. (Butler County). Discharge contained oil and oil-field brine.

During the April 1962 salinity survey, the concentration of chloride near the mouth of an unnamed west-bank tributary (RM 96.5) was 2,090 mg./l. The chloride load was equivalent to over 7 percent of the chloride load at Gordon. During the period of drought in late 1963, the concentration of chloride near the mouth was high. Crusts of salt were deposited in the headwaters, but the chloride load was insignificant.

The maximum concentrations of fluoride (2.2 mg./l.) and boron (0.38 mg./l.) at Haverhill Road exceeded those at any periodic datacollection site on the main stem of the Walnut River (table 4). Higher concentrations of fluoride and of boron were measured at refinery outfall RM 100.0 and at the municipal sewage outfall RM 100.6, respectively (table 8).

Maximum concentrations of nitrate (97 mg./l.) and phosphate (13 mg./l.) at Haverhill Road exceeded those at other monthly stations (table 4). These plant nutrients, attributed mainly to sewage, maintained a heavy algal bloom that caused wide diurnal fluctuations in the content of dissolved oxygen during periods of low flow in hot weather. In October 1963, when the concentration of nitrate at Haverhill Road was 53 mg./l., the concentration of nitrate in sampled effluent of the El Dorado sewage plant about 4.7 miles upstream was 40 mg./l. and the concentration of phosphate was 46 mg./l. The higher concentrations of nitrate in the river probably were caused by oxidation of nitrite and ammonia from this source.

VARIATIONS AND FLUCTUATIONS

Despite dilution by streamflow of the East Branch, the concentrations of chloride and dissolved solids in all samples and the concentration of sulfate in most samples at station 07–1468.5 exceeded those in concurrent samples upstream at station 07–1468, north of El Dorado

Sodium and chloride were the principal ions at rates of discharge less than about 40 cfs. The sodium-chloride ratio increased from 0.55 at a discharge of about 4 cfs to 0.68 at about 1,000 cfs but decreased slightly at higher rates of discharge when brine salts were flushed from surface storage or shallow aquifers. Calcium and bicarbonate were the principal ions at rates of discharge greater than about 150 cfs (fig. 14). Magnesium and sulfate each constituted a relatively constant 10 to 20 percept of the cations and anions, respectively.

WALNUT RIVER NEAR AUGUSTA

(07-1469, RM 813)

During periods of low flow, the concentrations of sulfate, chloride, and dissolved solids at station 07–1469 normally were lower than those upstream at Haverhill Road, but at higher rates of discharge the concentrations were higher as a result of polluted tributary inflow Maximum concentrations of fluoride and nitrate at both stations exceeded those at all other monthly or intermittent stations, and they were the only stations at which the pH of sampled streamflow was less than 7 (table 4). These characteristics probably were caused by combined municipal and industrial effluent.

BASE RUNOFF

The drainage area of the Walnut River at station 07–1469 is about 43 percent of that upstream from Gordon. During three of the combined seepage-salinity surveys, streamflow at the station contributed from 44 to 48 percent of the streamflow and contained from 26 to 32 percent of the dissolved-solids load, about 9 percent of the sulfate, and from 23 to 40 percent of the chloride at Gordon (RM 71.2). During the period of drought in October 1963, concentrations of major ions were higher than during the other surveys (fig 8), but streamflow at the station constituted only about 18 percent of the streamflow and contained about 16 percent of the dissolved solids, 5 percent of the sulfate, and 21 percent of the chloride measured at Gordon.





Most of the chloride was derived from perennial sources; therefore, the percentage of decrease in the chloride load with decreasing water discharge was less than that for the other loads The part of the dissolved-solids load attributable to oil-field brine during the surveys ranged from 26 percent in November 1962 to 71 percent in October 1963 (table 2)

Sutton Creek (RM 95.8) contributed from 10 to 13 percent of the chloride load of the Walnut River at Augusta during all but the October 1963 survey, when it was nearly dry (pl. 3). The concentration of chloride in Sutton Creek during the surveys ranged from 1,340 to 1,500 mg/l (table 8). The stream intercepts surface and shallow ground-water runoff from the Barneston Limestone on the southwest flank of the Boyer dome, a structure that was extensively drilled before the advent of effective pollution control (Fath, 1921) All analyses of well waters in the watershed show the effects of brine pollution.

Turkey Creek (RM 90.6) contributed from 5 to 10 percent of the chloride load at Augusta during all except the October 1963 survey, when it was dry. Chloride replaced bicarbonate as the predominant anion in low streamflow between stations 16 and 17 (pl. 2), where the channel is adjacent to areas of oil-field development

Cumulative net seepage into the Walnut River contributed from 12 to 32 percent of the streamflow at Augusta In October 1963, when concentrations in the main stem reached a maximum, cumulative net losses in total solids and sulfate ion accompanied a smaller chloride gain. During the other surveys, as much as 32 percent of the sulfate and 28 percent of the dissolved-solids and chloride load at Augusta were attributed to seepage Selective losses in sulfate in the 8-mile reach upstream from the site at Augusta during all surveys probably represent migration (or withdrawal) of water from the channel and replacement by water containing a lower concentration of sulfate, but the losses could have been caused by sulfate-reducing bacteria.

VARIATIONS AND FLUCTUATIONS

Relations of percentages of the ions to water discharge at Walnut River near Augusta are normally well defined (fig 15) The curves in figure 15 show progressive dilution, with increasing water discharge, of polluted sodium chloride type base runoff by calcium bicarbonate type direct runoff Sodium and chloride were the predominant ions at rates of discharge up to about 70 cfs. The sodium-chloride ratio varied from 0.51 to 0.54 in the range from 2 to about 130 cfs but exceeded 0.60 at



FIGURE 15—Relations of the percentages of major ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at Walnut River near Augusta (07-1469) during water years 1962-64

high rates of discharge. Sulfate made up only about 10 percent of the anions, and magnesium varied from about 9 to 15 percent with increasing discharge.

WHITEWATER RIVER SUBBASIN

Sulfate from gypsum is a major constituent of most ground and surface water in the Whitewater River subbasin Nearly all untreated water, except in streamflow at high rates of discharge, is very hard. The hardness derived from gypsum is of the noncarbonate type (in combination with sulfate); therefore, it is not readily removed by ordinary methods of treatment.

Ground water and base runoff containing over 1,000 mg/l dissolved solids are common because of the combined effects of gypsum and of oil-field brine in shallow aquifers Manmade contributors to the dissolved-solids load of the Whitewater River included numerous small oil fields, refineries at Potwin and Augusta, feedlots and livestock pens near Potwin and Towanda, and sewage plants at Potwin, Towanda, and Augusta.

WHITEWATER RIVER AT TOWANDA

(07-14707 RM 144)

Station 07–1470.7 is near the site of the proposed Towanda dam (U S. Army Corps of Engineers, 1964), which would impound runoff from about 80 percent of the drainage area of the Whitewater River subbasin The chemical quality of water at the site is of considerable interest to local, State, and Federal agencies; therefore, more data from this site were collected, and these data are treated here in somewhat more detail than data from other sites in the Walnut River basin. Analyses of samples collected at semimonthly or more frequent intervals were combined with continuous records of stage and specific conductance (fig. 16) to relate variations in chemical quality to time and water discharge.

BASE RUNOFF

About 75 percent of the water discharge, nearly all the sulfate, about 70 percent of the dissolved-solids load, and 50 percent of the chloride load in base runoff of the Whitewater River at its mouth originated upstream from the monthly data collection site at Towanda (07–1470.7, RM 14.4)

The West Branch of the Whitewater River (RM 170, table 9) contributed from 37 to 79 percent of the sulfate load and from 25 to nearly 50 percent of the water discharge and dissolved-solids load at



FIGURE 16.—Continuous conductivity recorder and gage on the Whitewater River at Towanda (07-1470.7) Photographed at flood stage.

Towanda. High concentrations of calcium and sulfate derived from gypsum characterize water from nearly all tributaries and springs in the watershed (analyses 1–6, table 7; pl. 2), which composes about 43 percent of the drainage area at Towanda. The West Branch contributed a greater percentage of the water discharge than of the chloride load; therefore, its contribution lowered the concentration of chloride at Towanda.

During six seepage-salinity surveys, the percentage of the dissolvedsolids load at Towanda attributed to oil-field brine varied from about 17 percent during the November 1962 survey to 43 percent during the period of drought in October 1963 (table 2). The calculations were based on an estimated natural concentration of 50 mg/l of chloride.

During all surveys, except the one made during the period of drought in October 1963, about 50 to 60 percent of the chloride load at Towanda originated upstream from the confluence with the West Branch. In October 1963, only 30 percent of the chloride load originated upstream from the confluence. At that time, Stearns Creek (RM 16.3; table 7, analysis 77; pl. 2), downstream from the confluence, contributed 54 percent of the chloride load and only 12 percent of the water discharge at Towanda. During the four basinwide surveys, net seepage into the reach between Potwin (RM 31.3) and Towanda (RM 14.4) composed from 18 to 52 percent of the chloride load at Towanda. Seepage of severely polluted ground water (pl. 1; analyses 71–74, table 7, fig 10) into the subreach RM 31.3 to 26.2 was equivalent to from 18 to 26 percent of the chloride load at Towanda Seepage downstream from station RM 26.2 composed up to about 30 percent of the chemical and water discharge at Towanda The proposed Towanda reservoir would inundate some of the apparent sources of seepage and would raise the ground-water table adjacent to the reservoir. Lower gradients toward the stream probably would reduce the rate of inflow of polluted ground water.

VARIATIONS AND FLUCTUATIONS

Limestone is less soluble than gypsum, but limestone composes a large part of the rock that underlies the drainage area of the Whitewater River at or near the surface. As the rate of runoff increased, calcium bicarbonate type runoff from limestone superseded calcium sulfate type runoff as a dilutant for polluted sodium chloride type ground-water effluent (fig. 17)

Calcium was the predominant cation at all rates of water discharge. The concentration of sulfate exceeded that in concurrent samples at all other monthly stations in the basin, and sulfate was the predominant anion in a range of discharge from about 4 to about 100 cfs. The percentages of sodium and chloride decreased, and the sodium-chloride ratio increased from about 0 49 at about 5 cfs to about 0.65 at about 1,800 cfs, as direct runoff diluted brine-polluted base runoff.

The specific conductance (and ionic concentration) corresponding to a given rate of discharge depended mainly on the rate and distribution in time of antecedent runoff A plot of points representing corresponding values of daily mean discharge and conductance on consecutive days consisted of a series of noncoincident loops—each loop representing a rise in stage followed by a longer recession During each rise, the specific conductance corresponding to a given rate of discharge normally was higher than during the subsequent recession. The relationship varied widely during each year and from year to year

The combined streamflow-conductance duration curves shown in figure 17 for water years 1963 and 1964 are based on daily mean values obtained from continuous stage and conductivity records. The curve for the 1962 water year is based on daily mean discharge from continuous stage records and relations of instantaneous values of specific conductance to water discharge for individual samples The curves conform generally to scatter diagrams relating discharge to specific conductance for individual samples.



FIGURE 17—Relations of the percentages of major ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at Whitewater River at Towanda (07-14707) during water years 1962-64

The water type varied with the rate of water discharge Therefore, the concentrations of individual ions corresponding to given values of specific conductance also varied as the rate of water discharge varied. Relations of the median concentrations of selected ions to the corresponding value of specific conductance, classed according to water discharge at the time of sampling, are shown by the curves in figure 18.

The curves for calcium and sulfate show slightly higher values in the midrange of water discharge and lower values at low rates of discharge than those drawn by visual fit or by least squares neglecting the rate of discharge Curves for the other ions correspond closely to curves drawn by other methods None were rectilinear over the entire range of the data, although the concentration of dissolved solids, in milligrams per liter, was nearly equal to the product of the specific conductance and a constant of 0.67.

SUITABILITY FOR USE

The relations of the concentrations of selected ions to specific conductance for individual samples of streamflow (fig 18) are combined with duration curves of daily mean specific conductance (fig 17) to show the approximate amount of time during which the concentration of a selected 10n, or 10ns, and (or) rate of water discharge exceeded given values during each water year. For example, a concentration of 1,000 mg/l of dissolved solids corresponded to a specific conductance of about 1,540 micromhos. According to the duration curve of specific conductance for 1963 (fig. 17), this conductance was exceeded about 78 percent of the year, or about 285 days, when the water discharge was less than about 40 cfs. Similarly, because a concentration of 250 mg/l of sulfate corresponded to a specific conductance of about 1,390 micromhos, this concentration-the maximum recommended for drinking water-evidently was exceeded about 83 percent of the time during the 1963 water year. Higher concentrations prevailed for longer periods of time during the 1964 water year, when total runoff was less; therefore, unregulated streamflow at Towanda was unsatisfactory for municipal or domestic use most of the time.

The salinity hazard to irrigation is high when the specific conductance exceeds 750 micromhos and is very high when it exceeds 2,250 micromhos (U.S. Salinity Laboratory, 1954, p. 25). The salinity hazard was high during about 85 percent of the 1962 water year, when water discharge was less than about 300 cfs, and during about 95 percent of the 1963 and 1964 water years, when the water discharge was less than about 100 cfs (fig. 17). It was very high during about 8 percent of the 1963 water year and 40 percent of the 1964 water year, when the water discharge was less than about 15 cfs.



FIGURE 18—Relations of the concentrations of selected ions to specific conductance, Whitewater River at Towanda (07–14707), October 1961 to September 1964

427-145 0-72-5

The sodium-adsorption-ratio normally increased as the specific conductance increased The sodium (alkali) hazard was low during all but about 7 percent of the 1964 water year, when the discharge was less than about 6 cfs The low sodium hazard is mainly the result of relatively high concentrations of calcium and magnesium, not low concentrations of sodium.

THE CHEMICAL QUALITY OF TOTAL RUNOFF AT TOWANDA

Total runoff at Towanda decreased from about 104,600 cfs-days during the 1962 water year to 20,600 cfs-days during the 1964 water year. Calculated values for the specific conductance and concentration of selected ions in total monthly, quarterly, and annual runoff during water years 1962–64 are shown in table 5. The values shown are approximate discharge-weighted means that describe hypothetical concentrations of ions in the mixture if all runoff during each period were impounded and thoroughly mixed and if the effects of such factors as evaporation were neglected.

A disproportionately large part of the annual runoff passed station 07–1470.7 during relatively infrequent periods when the water discharge and specific conductance fluctuated widely For days during which fluctuations were extreme, discharge-weighted values for coriesponding increments of subdivided days were computed by simultaneous subdivision of the records. The time-weighted daily mean specific conductance generally exceeded the discharge-weighted value; therefore, the values for specific conductance shown in table 5 generally are lower than the time-weighted values published annually in basic-data reports

The relations of specific conductance to the concentration of specific ions and to daily mean discharge normally were neither constant nor linear; therefore, the discharge-weighted mean concentrations of sulfate and chloride shown in table 5 for 1963 and 1964 were calculated by summation of the products of the daily mean discharge and concentrations of the ions corresponding to the daily mean values of the specific conductance

During the 1962 water year, continuous conductance records were not available, but a reasonable estimate of the discharge-weighted annual mean specific conductance (table 5) was calculated using the combined streamflow-conductance duration curve (fig. 17) The estimate is based on the assumption that the specific conductance of each increment of annual runoff that passed the station at a given rate of discharge was equal to the value corresponding to that rate of discharge in the duration curves The approximate concentrations of in-

	Total discharge (cfs-days)			Specific conductance (micromhos per cm at 2°C)			Dissolved solids (mg/l)			Sulfate (mg/l)			Chloride (mg/l)		
Water year.	1962	1963	1964	1962	1963	1964	1962	1963	1964	1962	1963	1964	1962	1963	1964
October November December		1, 530 1, 300 1, 128	796 381 417		1, 600 1, 920 1, 900	1, 363 2, 144 2, 532		1, 080 1, 240 1, 230	950 1, 380 1, 645		330 408 405	265 425 405		175 240 235	147 315 455
First quarter		3, 958	1, 594		1, 794	1, 856		1, 170	1, 208		383	360		210	283
January February March		1, 107 1, 118 2, 617	468 469 449		2,060 1,660 990	2, 269 2, 091 2, 354		1, 330 1, 110 630	1, 490 1, 350 1, 550		420 345 175	430 420 430		285 185 107	360 295 395
Second quarter		4, 842	1, 386		1, 302	2, 237		895	1, 460		250	456		140	338
A pril May June		841 871 1, 213	2, 948 5, 478 7, 079		2, 120 1, 680 970	860 630 533		1, 370 1, 120 615	530 390 320		425 350 173	150 100 76		305 185 105	92 65 53
Third quarter		2, 925	15, 505		1, 510	630		1,030	395		305	94		163	65
JulyAugust Septemher		25, 681 672 635	341 316 1, 519		310 2,000 1,890	2, 225 2, 059 823		220 1, 280 1, 220	1, 450 1, 340 510		35 415 403	430 420 145		25 265 233	342 285 88
Fourth quarter		26, 988	2, 176		387	1, 223		235	782	•	47	207		35	161
Annual 1 Do 2 Do 3				721 .	742 678	895 787	461	495 415	570 490	. 125	132	151	. 79 _	82	110
Annual yield	104, 596	38, 713	20, 661												
Annual load (thousand tons per year).							130 2	51 7	31 8	35 3	13 8	84	22 3	86	6 1

TABLE 5—Approximate annual chemical load, and discharge-weighted mean specific conductance and concentrations of selected ions for the Whitewater River at Towanda (07-1470 ?) during water years 1962-64

Based on summation of daily mean values of water discharge and specific conductance
 Based on duration curves of daily mean values of water discharge and specific conductance
 Based on intermittent samples and continous records of streamflow

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dividual ions in each increment were then determined from the relations shown in figure 18.

As a test, the method was applied to data for the 1963 and 1964 water years The estimated values were somewhat lower than those based on continuous conductance records (table 5).

The annual chemical load (or chemical discharge) decreased from 1962 to 1964 as the annual yield (or water discharge) decreased The discharge-weighted annual mean concentrations of the ions were highest and higher concentrations of the ions persisted for longer periods of time when the annual yield was smallest. However, the specific conductance of total annual runoff differed by less than 200 micromhos from year to year because runoff at high rates of discharge (low specific conductance) constituted a larger proportion of the annual yield when the annual yield was smaller (table 5)

The station at Towanda is near the site of a proposed reservoir; therefore, rough calculations showing the effect of streamflow at the site on the concentrations of the ions at downstream stations may have practical significance During the October 1963 survey of base runoff a period of drought—the concentrations of dissolved solids, chloride, and sulfate in streamflow at Gordon (fig 8) and Towanda (fig. 9) far exceeded the recommended standards for drinking water (U.S. Public Health Service, 1962). During the November 1962 survey, the concentrations of chloride and dissolved solids at Gordon and of dissolved solids and sulfate at Towanda exceeded the recommended values.

If there had been no flow at Towanda during the surveys, the concentration of sulfate in the Whitewater River downstream from the station would have been lower, but the concentrations of chloride and dissolved solids would have been higher. The concentrations of sulfate and dissolved solids at Gordon would have been lower than those measured, but the concentration of chloride would have been slightly higher.

If the concentrations of sulfate, dissolved solids, and chloride in streamflow at Towanda had been equal to those calculated for total runoff during the 1964 water year, the rate of discharge at Towanda needed to reduce the concentration of dissolved solids to 1,000 mg/l and of sulfate and chloride to 250 mg/l in the Walnut River at Gordon during the October 1963 survey would have been about 20 cfs for dissolved solids, 7 cfs for sulfate, and 39 cfs for chloride. The rate of discharge needed to reduce the concentration of chloride to the standard recommended for drinking water during both surveys would have far exceeded those needed to reduce the concentrations of the other selected ions to the standards. A rate of about 59 cfs would have been required to reduce the concentration of chloride at Gordon to the recommended maximum of 250 mg/l during the November 1962 survey. The values cited probably would not apply to releases from an actual impoundment, because evaporation and other factors affecting water quality have been ignored. However, the values indicate that retention and mixing of the antecedent storm runoff and substantial releases would have been essential to maintain water quality within the recommended standards in and downstream from a hypothetical reservoir at Towanda at the time of the surveys.

WHITEWATER RIVER AT AUGUSTA

(07-1471, RM 08 Whitewater, RM 806 Walnut)

Streamflow of the Whitewater River at Augusta includes drainage from nearly all sources of water and chemical load in the Whitewater subbasin Effluent from a refinery and the Augusta sewage plant entered the Whitewater River between station 07-1471 and the junction with the Walnut River about 0.8 mile downstream The effluent represented a relatively negligible part of the measured water discharge and chemical load at downstream stations on the main stem during the salinity surveys (table 8)

BASE RUNOFF

The drainage area at station 07–1471 is about 49 percent of the drainage area of the Walnut River at Gordon During the surveys of base runoff, water discharge of the Whitewater River subbasin measured at the station was equivalent to from 30 to 40 percent of the water discharge of the Walnut River at Gordon but up to about 70 percent of the sulfate load and about 50 percent of the chloride and dissolved-solids load at Gordon

Most of the sulfate in the Whitewater River at Augusta originated upstream from Towanda During the April and November 1962 surveys, the sulfate load at Towanda exceeded that downstream at Augusta, but the water discharge and the loads of chloride and dissolved solids at Towanda were less Similar selective losses in the sulfate load in the reach between Towanda and Augusta were calculated for 18 of the 36 concurrent sets of data, although the loss for three of the sets represented less than 2 percent of the sulfate load at Augusta. Unmeasured withdrawals in the reach or bacterial reduction of sulfate in ponded reaches downstream from the Towanda sewage effluent (RM 13.8) are probable causes of the losses

The concentration of sulfate and the sulfate load of inflow from Indianola (Dry) Creek (RM 12) (pl 3) were much less than those from geologically similar drainage areas of west-bank tributaries, because base runoff containing high concentrations of sulfate from the headwaters was impounded and diluted in Santa Fe Lake. The impounded water would probably become unsuitable for domestic use if dilutant direct runoff were curtailed by drought.

During the salinity surveys, tributary flow plus seepage into the reach between Towanda and Augusta contributed from 15 to 29 percent of the streamflow and from 35 to 49 percent of the chloride load of the Whitewater River at Augusta. The drainage area of the reach represents only about 18 percent of the drainage area at the downstream site; therefore, the contribution of chloride per unit area is disproportionately high (pl. 3) Net seepage gains in the reach contributed 33 percent of the chloride load in October 1963. Results of the surveys and the presence of saline seeps, springs, and well waters show (pl. 2) extensive brine pollution of shallow ground water in watersheds on the east bank.

Chemical analyses of streamflow and ground water before 1914 (Parker, 1911) indicated that the concentration of chloride in the Whitewater River at Augusta attributed to natural sources did not exceed 50 mg/l. On that basis, oil-field brine constituted from 27 percent of the dissolved-solids load during the December 1961 survey, when the concentration of chloride was 267 mg/l, to 57 percent during the October 1963 survey, when the concentration was 700 mg/l (table 2) Corresponding percentages at Towanda were less; therefore, the increase in load from oil-field brine in the intervening reach exceeded the increase from natural sources

VARIATIONS AND FLUCTUATIONS

Ranges of measured water discharge and concentrations of ions for the Whitewater River at Augusta are shown in table 4 and figure 19. The concentrations of sulfate in all concurrent samples were lower at Augusta than at Towanda. The concentrations of chloride and of dissolved solids exceeded those at Towanda, except during infrequent periods of high runoff, when brine-polluted inflow to the intervening reach composed a small part of the total.

Calcium was the predominant cation at rates of discharge greater than about 11 cfs; sodium was the predominant cation at lower rates of discharge Magnesium constituted about 20 percent of cations.

Sulfate was a subordinate anion at all rates of discharge at Augusta, although it was a predominant anion upstream at Towanda At Augusta, chloride predominated at rates of discharge less than 200 cfs, when most of the samples were taken; bicarbonate predominated at infrequent, higher rates of discharge. The sodium-chloride ratio increased from about 0.48 at about 10 cfs to 0.56 at about 2,600 cfs as polluted ground-water effluent was diluted with surface runoff.



FIGURE 19—Relations of the percentages of major ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at Whitewater River at Augusta (07-1471) during water years 1962-64
WALNUT RIVER DOWNSTREAM FROM THE MOUTH OF THE WHITEWATER RIVER

Runoff from 907 square miles, about 46 percent of the area of the Walnut River basin, enters the main stem of the Walnut River between the mouth of the Whitewater River and Winfield (fig. 1)

Thick limestones assigned to the Chase Group dip gently westward toward the Walnut River, which flows near and generally parallel to the contact with the overlying Sumner Group (pl. 1). These rocks underlie over 80 percent of the drainage area; therefore, the geohydrologic characteristics of the area are more similar to those of the northeastern part of the basin than to those of the Whitewater subbasin.

All east-bank tributaries between Gordon (RM 71.2) and Winfield (07-1478, RM 22.6) drain watersheds underlain by rock of the Chase Group. These tributaries contributed about 35 percent of the total flow at Winfield during the December 1961 salinity survey but only 4 percent during the October 1963 survey, when most were dry. Westbank-tributary watersheds, underlain by rocks of the Summer Group, contributed a more constant percentage of base runoff.

During surveys of east-bank tributaries, base runoff was of the calcium bicarbonate type near the headwaters. The concentration of dissolved solids increased only slightly, but the proportion of sodium and chloride and the chloride load normally increased appreciably downstream from some oil fields (pl. 2) as a result of pollution of shallow ground water. Base runoff in west-bank tributaries was dominantly of the calcium sulfate type, but chloride constituted a significant part of the dissolved-solids load in Four Mile (RM 73.4) and Stewart Creeks. Unlike the east-bank tributaries, the concentration of dissolved solids normally decreased downstream with the inflow of less mineralized water from the upper part of the Chase Group. The high proportion of magnesium encountered in some of these tributaries is probably from the Nolans Limestone of the Chase Group, which consists largely of dolomite $[CaMg(CO_3)_2]$ (Runnels and Schleicher, 1956).

WALNUT RIVER NEAR DOUGLASS

(07-1475, RM 585)

Streamflow of the Walnut River near Douglass is principally a variable mixture of the chemically dissimilar streamflow of the Walnut and Whitewater Rivers upstream from Augusta. With few exceptions concurrent concentrations of sulfate, chloride, and dissolved solids at Douglass were less than those in the Whitewater River at Augusta and greater than those in the Walnut River at Augusta. The concentration of sulfate was always greater than in the Walnut River at Augusta. When the concentration of chloride in the Walnut River at Augusta was less than about 450 mg/l, the concentration at Douglass was normally higher; when the concentration exceeded 450 mg/l at Augusta, the concentration at Douglass was generally much lower The concentration of dissolved solids at Douglass normally exceeded that of the Walnut River at Augusta, except during periods of low flow when the concentration of chloride at the upstream site was exceptionally high.

BASE RUNOFF

Under conditions of drought (October 1963), the streamflow and chemical load of the Walnut River at Augusta was equivalent only to about 17 percent of the water discharge and dissolved-solids load, 5 percent of the sulfate load, and 22 percent of the chloride load at Douglass. At the same time, quantities equivalent to about 40 percent of the streamflow and sulfate load and 50 percent of the chloride and dissolved-solids load at Douglass were measured on the Whitewater River at Augusta. The sulfate load of perennial Four Mile Creek (RM 43 4) was nearly equal to that of the Whitewater River at Augusta was less, but the load of sulfate, chloride, and dissolved solids was greater, than that of the Walnut River at Augusta

In the Walnut River near Douglass, the percentages of the dissolvedsolids load attributed to oil-field brine ranged from about 30 percent during the December 1961 survey, when the water discharge was 380 cfs and when the chloride concentration was 205 mg/l, to about 53 percent during the October 1963 survey, when the water discharge was 24.6 cfs and the chloride concentration was 510 mg/l (table 2)

Streamflow of the Little Walnut River (RM 63.6) normally diluted streamflow of the main stem The watershed of the Little Walnut River, which constitutes about 20 percent of the drainage area upstream from Douglass, contributed from about 3 to 28 percent of the water discharge but only 0.8 to 15 percent of the dissolved-solids load at Douglass during the surveys. The location of the dam for the proposed Douglass reservoir on the Little Walnut River east of Gordon (U.S. Army Corps of Engineers, 1964) is shown on plate 2 As was typical of runoff from watersheds underlain by rock of the Chase Group, streamflow of the Little Walnut represented a disproportionately small percentage of streamflow of the main stem during periods of low flow, although the water was chemically suitable for domestic use.

During all surveys, net seepage into the reach (including 0.8 mile of the Whitewater River) between Augusta and Gordon (RM 71.2), about midway between Augusta and Douglass, augmented the streamflow and chloride load of the main stem. Net seepage was equivalent to about 22 percent of the streamflow at Gordon during the October 1963 survey and about 37 percent of the chloride load during the November 1962 survey. However, net losses of sulfate amounting to from 2 to 9 percent of the load at Gordon were measured in April and November 1962 and were confirmed by a special survey of the reach in August 1963. Measurements at an intermediate station (RM 79.3), about 1 mile downstream from the mouth of the Whitewater River, during the special survey showed that net sulfate gains in the upstream part of the reach were offset by greater losses downstream

Small net seepage losses in sulfate load accompanied net gains in water discharge between Gordon and Douglass during the April 1962 and October 1963 surveys During the October survey, the measured loads of chloride and total solids at Douglass were 3 to 5 percent smaller than at Gordon, although the water discharge was about 7 percent larger. Unmeasured withdrawls of river water and inflow of ground water of lower sulfate concentration in the reach probably caused the apparent discrepancies.

VARIATIONS AND FLUCTUATIONS

Ranges and variations in water discharge and concentrations of ions for the Walnut River near Douglass are shown in table 4 and figure 20 Calcium predominated over sodium at rates of discharge greater than about 40 cfs Sodium decreased from about 45 to about 20 percent with increasing water discharge. Magnesium constituted about 20 percent of the cations.

The percentage of chloride decreased with increasing discharge from about 60 percent of the anions at 22 cfs to about 40 percent at 1,000 cfs Bicarbonate predominated at higher rates of discharge Sulfate constituted about 20 percent of the anions in most samples The sodiumchloride ratio increased with increasing discharge from about 0.48 to 0.65.

The computed load of sulfate for concurrent samples of streamflow of the Walnut River at Augusta normally was equivalent to only about 5 to 10 percent of the sulfate load at Douglass; the sulfate load of the Whitewater River at Augusta was about 66 percent of the sulfate load



FIGURE 20—Relations of the percentages of major ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at Walnut River near Douglass (07-1475) during water years 1962-64

at Douglass. Relations of concurrent loads of chloride at the three stations were more variable The magnitude of the combined chloride loads of the Walnut and Whitewater Rivers at the Augusta stations normally was nearly equal to the chloride load at Douglass during periods of exceptionally low flow but was only about two-thirds of the load at higher rates of discharge The source of the other third, evidently carried in direct runoff, was not determined

The chloride load of the Whitewater River normally exceeded that of the Walnut River at Augusta when the discharge at Douglass was less than about 100 cfs As water discharge increased, the chloride load of the Walnut River at Augusta increased more rapidly than that of the Whitewater River, despite the larger area of the Whitewater River subbasin Salts from residual oil-field brine evidently are more abundant in normal or excessive runoff from the more extensive old oil fields in tributary watersheds of the upper Walnut River than from similar areas in the Whitewater River subbasin

TIMBER CREEK NEAR WILMOT

(07 - 1476)

Streamflow of Timber Creek near Wilmot consists of runoff from about 63 square miles underlain by rock of the Chase Group. Samples were taken intermittently until February 1963, then monthly until the recorded streamflow decreased to zero in August 1963 (U.S. Geological Survey, 1963). There was essentially no flow until April 3, 1964, when the drought was temporarily broken Streamflow again decreased to zero in June, where it remained through August 25, 1964.

The sampled water was satisfactory for domestic use on the basis of chemical quality, but the stream is not a reliable source of water supply during periods of drought Concentrations and relative proportions of the major ions varied only slightly with water discharge (fig 21) The water was of the calcium bicarbonate type; other ions composed less than 25 percent of the cations or anions The concentration and relative proportion of chloride were slightly higher downstream from small areas of oil development than at other sites (analyses 45–48, table 7; pl. 2)

Low streamflow downstream from the confluence of Dutch Creek with Timber Creek generally contained higher proportions of sodium and chloride than that upstream (analyses 49–51, table 7; pl. 2). During the salinity surveys, base runoff from the drainage area of Dutch Creek at site RM 25.8 (about 160 sq. mi.) ranged from the equivalent of 23.4 percent of the streamflow and 9.3 percent of the chloride load of the Walnut River at Gordon to zero.



FIGURE 21 — Relations of the percentages of major ions, specific conductance, and time to water discharge at Timber Creek near Wilmot (07-1476) during water years 1962-64

WALNUT RIVER AT WINFIELD

(07-1478, RM 226)

The drainage area of the Walnut River at Winfield is about 95 percent of the total area of the Walnut River basin Unless unmeasured sources contribute large quantities of water and dissolved solids to the main stem between station 07–1478 and the mouth, the chemical quality of streamflow of the Walnut River at Winfield is nearly similar to that at the mouth

BASE RUNOFF

During periods of low flow, most tributary inflow between Douglass and Winfield diluted streamflow in the main stem (pl. 3). Yield indexes for sulfate exceeded 1 in the relatively small west-bank watersheds of Eight Mile Creek (RM 52.4) and Pole Cat Creek (RM 49.2). Most of the dissolved solids in base runoff of the Walnut River at Winfield during the combined seepage-salinity surveys originated upstream from Gordon (table 3) Runoff from part of the drainage area downstream from Gordon apparently exceeded that upstream from Gordon during the December 1961 and April 1962 surveys, although total inflow and outflow in the long reach (48 6 miles) probably was not in equilibrium During the October 1963 survey, the load of dissolved solids, sulfate, and chloride at Winfield was less than at Gordon or at Douglass, but the water discharge was about 10 percent greater Seepage into the reach evidently exceeded the quantity of more highly concentrated water diverted from the reach or ponded within it

Variations in the Chemical Quality of Streamflow During Water Years $1962{-}64$

The ranges of water discharge, specific conductance, and concentrations of selected ions for the Walnut River at Winfield are shown in table 4 The concentrations of sulfate, chloride, and total solids at Winfield in all but two concurrent samples of streamflow were equal to or less than those upstream at Douglass. Variations in water type with discharge shown in figure 22 were somewhat similar to those at Douglass Calcium was the predominant cation, except at rates of discharge less than about 50 cfs, when sodium also composed about 40 percent of the cations Magnesium composed about 20 percent of the cations over the entire range.

The proportion of sulfate decreased from about 30 percent of the anions to about 10 percent, and chloride decreased from about 55 to 30 percent, as the percentage of bicarbonate increased with increasing water discharge The sodium-chloride ratio increased from less than 0.50 to about 0.60 with increasing water discharge.

The combined duration curves (fig 22) are based on continuous stage records and on analyses of daily samples The conductance of each sample represents the conductance of streamflow only at the instant of sampling, but the data were treated as if the instantaneous conductance were the daily mean conductance Differences between instantaneous and daily mean conductance and discharge were large during some of relatively infrequent days when extreme fluctuations occurred The combined duration curves probably describe the approximate relations of specific conductance to water discharge for the specified periods better than would curves fitted to the widely dispersed instantaneous data



FIGURE 22—Relations of the percentages of ions, specific conductance, approximate concentrations of selected ions, and time to water discharge at Walnut River at Winfield (07-1478) during water years 1962-64

The duration curves (fig 22), combined with the relations of specific conductance to the concentrations of selected ions (fig 23) show that higher concentrations of the ions in streamflow at Winfield persisted for longer periods of time, as the total annual runoff decreased from the 1962 to the 1964 water year; but higher concentrations corresponded to higher rates of water discharge during the years of greatest yield. The concentrations of dissolved solids in daily samples



FIGURE 23 — Relation of the concentration of selected ions to specific conductance, Walnut River at Winfield, October 1961 to September 1964

exceeded 1,000 mg/l during about 50 percent of the 1964 water year but only about 1 percent of the 1962 and 1963 water years The concentration of sulfate exceeded 250 mg/l during less than 1 percent of the 1962 and 1963 water years and about 40 percent of the 1964 water year. The concentration of chloride exceeded 250 mg/l during about 5 percent of the 1962 water year, about 20 percent of the 1963 water year, and nearly 60 percent of the 1964 water year.

The salinity hazard to irrigation (US Salinity Laboratory, 1954, p. 25) was high during about 75 percent of the 1962 water year and 80 percent of the 1963 and 1964 water years The lower limit of 750 micromhos per cm was exceeded when the water discharge was less than about 1,000 cfs during the 1962 water year, 300 cfs during the 1963 water year, and about 150 cfs during the 1964 water year. The salinity hazard was very high (>2,250 micromhos per cm) during about 20 percent of the 1964 water year, when the water discharge was less than about 35 cfs The sodium-absorption-ratio increased with increasing specific conductance, but it was low except when the salinity hazard was very high.

The discharge-weighted annual mean specific conductance and concentrations of sulfate, chloride, and dissolved solids increased from 1962 to 1964, although monthly values for each year differed widely (table 6). Annual mean concentrations based on discharge-weighted composites of daily samples for the 1963 and 1964 water years are included in the table for comparison.

Comparison of the water and chemical discharge for similar periods in tables 5 and 6 shows that streamflow of the Whitewater River at Towanda near the site of a proposed dam (U.S. Army Corps of Engineers, 1964) normally affected the chemical quality of streamflow of the Walnut River at Winfield adversely.

The relative proportions of the total annual water and chemical discharge at Winfield contributed by the Whitewater River at Towanda normally increased as runoff decreased during the 1962–64 water years. Runoff at Towanda contributed from 20 to 33 percent of the runoff (but more than 50 percent of the sulfate load), from 22 to 26 percent of the chloride load, and from 27 to 39 percent of the dissolved-solids load of the Walnut River at Winfield. The drainage area at Towanda is about 23 percent of the drainage area at Winfield; therefore, it contributed a disproportionately large part of the sulfate load at Winfield.

The discharge-weighted mean concentrations of sulfate at Towanda exceeded those at Winfield; therefore, contributions from Towanda caused the concentration of sulfate at Winfield to increase. During the 1962 water year, the discharge-weighted annual mean specifi

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	Total di	scharge (cf	's days)	Specif (micro	fic conduct mhos per o 25°C)	tance em at	Dissolv	ved solids	s (mg/l)	Sul	fate (m	g/l)	Chl	oride (m	g/l)
Water year.	1962	1963	1964	1962	1963	1964	1962	1963	1964	1962	1963	1964	1962	1963	1964
October November December	112, 200 137, 212 26, 606	9, 880 6, 865 6, 313	1, 557 1, 370 1, 371	391 438 1, 121	910 1, 386 1, 201	1, 922 1, 793 2, 112	240 269 650	529 804 697	1, 170 1, 070 1, 295	34 36 103	88 138 119	256 216 322	44 50 170	127 217 182	368 334 452
First quarter	276, 018	23, 058	4, 298	485	1, 131	1, 942	299	657	1, 185	40	111	265	57	169	373
January February March	43, 598 49, 431 18, 959	8, 266 4, 446 15, 804	1, 420 1, 388 1, 145	676 594 1, 130	1,076 1,322 900	2, 477 2, 175 2, 043	408 360 655	626 770 523	1, 540 1, 340 1, 255	57 50 105	107 134 86	375 340 305	86 73 173	160 207 128	482 425 396
Second quarter	111, 988	28, 516	3, 953	717	1,017	2, 245	430	592	1, 385	59	99	355	92	150	440
April May June	11, 665 5, 860 26, 722	4, 933 10, 882 9, 145	13, 760 10, 789 21, 935	1, 165 1, 353 647	1, 286 1, 083 893	994 649 531	680 785 390	741 628 520	575 395 320	108 133 54	125 105 86	87 55 43	180 220 81	195 166 126	142 81 63
Third quarter	44, 247	24, 960	46, 484	877	1,054	695	515	611	420	75	102	60	122	157	90
= July August September	27, 160 3, 186 48, 381	34, 797 2, 646 3, 234	1, 663 4, 597 3, 213	515 1, 214 445	406 1, 311 1, 110	815 766 1, 144	315 705 275	235 764 659	485 460 660	43 115 37	27 133 120	70 65 105	61 189 51	46 205 178	110 102 175
Fourth quarter.	78, 727	40, 677	9, 473	500	521	903	305	303	530	42	41	78	59	66	128
Annual ¹				572	875 672	905 _ 700 _	345	508 405	542 425	49	82	93		126	137
Do 4					939	942 _		547	560		96	110		145	160
Annual yield.	510, 980	117, 211	64, 208 -												
Annual load (thousand tons per year)							484 2	160 8	94 0	68 8	26 0	16 1	102 4	3 9 9	23 8

TABLE 6 — Approximate annual chemical load, and discharge-weighted mean specific conductance and concentrations of selected ions for the Walnut River at Winfield (07-1478) during water years 1962-64

¹ Based on instantaneous daily samples and continous records of streamflow
 ² Based on duration curves of daily mean values of water discharge and instantaneous specific conductance
 ³ Based on extrapolation of incomplete records
 ⁴ Based on analyses of composited daily samples

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conductance and concentrations of chloride and total solids at Towanda also exceeded those at Winfield. During the 1963 water year, the monthly mean concentrations at Towanda normally exceeded those at Winfield, but the annual means were lower, owing to dilution during short periods of high runoff.

During the drought-ridden 1964 water year, when normally dilutant tributary inflow to the lower Walnut River was depleted, the monthly mean concentration of chloride for 9 months and the annual mean concentrations at Winfield exceeded those at Towanda

VARIATIONS IN BRINE POLLUTION WITH TIME

Ten-day-composite samples of streamflow at Winfield from December 1906 through November 1907 contained a maximum chloride concentration of 29 mg/l and a mean concentration of about 15 mg/l (Parker, 1911, table 154, p. 296). The sodium-chloride ratios varied from about 11 to 41 Although the concentration of chloride in individual samples may have been slightly higher during periods of low flow, somewhat similar conditions probably prevailed until the discovery of oil in the basin in 1914. Intermittent samples (Kansas State Board of Health, 1960) showed that the chloride content of the river increased rapidly after 1917 and that the sodium-chloride ratio decreased to values near 0.51, the ratio for oil-field brine (table 1). The concentration of chloride in several samples exceeded 3,000 mg/l during the 1955 water year. Concentrations up to 600 mg/l and sodium-chloride ratios that ranged from 0.44 to 0.60 during the present investigation denoted continued pollution by oil-field brine. During the salinity surveys of base runoff, the percentage of the dissolvedsolids load attributed to oil-field brine increased from about 25 percent in December 1961 to 40 percent in October 1963, when contributions from perennial sources composed a large percentage of total flow.

Median concentrations of chloride determined from individual analyses made before and during this investigation are related in figure 24 to the corresponding values of daily mean discharge obtained from continuous stage records of the U.S. Geological Survey. The curves are based on median instead of average concentrations to minimize bias by extremes The data used include published and unpublished chloride analyses of semimonthly samples taken by personnel of the Kansas State Department of Health from September 1949 to April 1960 and analyses of samples taken during the present investigation. Reliable data relating the concentrations to the instantaneous rate of water discharge before 1961 were limited; therefore, the relations are useful only for semiquantitative comparison.



FIGURE 24 — Variation with time in the relation of the concentration of chloride ions to the daily mean discharge at Walnut River at Winfield during water years 1950–64

The ranges in concentrations corresponding to a given rate of water discharge were commonly greatest during extended periods of exceptionally high or low flow For example, during the drought of 1956, the concentration of chloride at Winfield varied from less than 500 to over 3,000 mg/l at corresponding rates of discharge in the range 6–16 cfs As pollution abatement became more effective, the range in concentration and the median concentrations of chloride corresponding to a given rate of water discharge generally decreased progressively after reaching a maximum during the years 1954–55

The duration curves in figure 22 show that the specific conductance corresponding to a concentration of 250 mg/l of chloride in daily samples was exceeded only during about 5 percent of the 1962 water year, about 20 percent of the 1963 water year, and nearly 60 percent of the 1964 water year. The percentages increased with decreasing annual runoff The specific conductance exceeded a value corresponding to 500 mg/l of chloride during about 2 percent of the 1964 water year only (fig 23) Analyses of daily samples for chloride showed that all concentrations exceeding 500 mg/l occurred between October 1963 and January 1964, a period of exceptionally low flow during which the maximum concentration was about 600 mg/l.

The relation of 10nic concentrations to water discharge depended largely on antecedent runoff; therefore, the relation differed from year to year. The data collected during water years 1962-64 represent changes in chemical quality of streamflow during a period of decreasing annual runoff. Relations based on data collected during a similar period of uniform or increasing annual runoff may differ. Collection of these data is part of a continuing cooperative program of the Kansas State Department of Health and the U S Geological Survey

The concentration of chloride decreased during periods of increased water discharge, but the rate at which chloride was removed from the basin increased disproportionately with the amount and rate of runoff The calculated annual chloride discharge of the Walnut River at Winfield was about 102,400 tons in 1962, 39,900 tons in 1963, and 23,800 tons in 1964 (table 6) Based on a generous estimate of 50 mg/l for the natural concentration of chloride, about 30–70 percent of the annual chloride loads was from manmade waste, mainly oil-field brine.

According to the Kansas State Department of Health, more than 99 percent of the brine now produced is properly disposed of in injection wells. By the end of 1964, only 54 unsealed earthen ponds in the basin were not connected with injection systems, and these ponds received only small quantities of brine Calculations from unpublished data provided by the Oil Field Section, Kansas State Department of Health (written commun, 1964), show that only about 2,800 tons of chloride as oil-field brine was stored in surface ponds in the basin in 1963 Nearly all was stored temporarily in sealed ponds for injection to deeper aquifers

The rate at which chloride was carried out of the basin in streamflow far exceeded the rate at which the supply in the soil and shallow aquifers was replenished under existing disposal practices Direct releases of oil-field brine to streams have been curtailed, and leakage from existing facilities constitutes a minor part of the chloride load The rate at which the concentrations of sodium, chloride, and dissolved solids in streamflow will decrease depends on the rate at which pollutive salts from inproper disposal operations in the past are flushed from soils and aquifers and diluted by precipitation. The chemical quality of water in the future will depend mainly on the amount, rate, and distribution of precipitation, on water and land use, and on control of streamflow by proposed impoundments

SUMMARY

Wide diversity in the chemical quality of water in the basin is determined largely by the chemical composition, distribution, geologic structure, and hydrologic characteristics of the sedimentary bedrock of Permian age Calcium, magnesium, and bicarbonate released during dissolution of carbonate rock of the Chase Group are characteristic ions in unpolluted runoff from the eastern part of the basin. Gentle westward regional dip impedes rapid drainage from gypsiferous strata of the Sumner Group, which support perennial sulfate-rich runoff from the western part of the basin, including the Whitewater River subbasin. Structural domes and depressions and a well-developed joint system locally control migration of ground water through shallow aquifers within or across surface-water divides. Extensive fracture and dissolution of the limestones permit rapid recharge and migration of ground water and facilitate pollution of ground water by oil-field brine

The quality of ground water in terrace deposits and alluvial fill along stream channels depends mainly on the quality of local recharge; but calcium, magnesium, and bicarbonate from ubiquitous fragments of limestone or calcareous shale mask the effects of baseexchange reactions or oil-field-brine pollution in some of the discontinuous aquifers

Over 99 percent of the oil-field brine from numerous fields in the basin is returned to deep oil-producing strata through injection wells However, the concentrations of sodium and chloride in much of the ground and surface water far exceeded those prevailing before the discovery of oil in 1914 or at similar sites unaffected by oil-field drainage.

The ratio of the concentration, in milligrams per liter, of sodium to chloride is about 0.52 for oil-field brine and is normally greater than 0.60 for natural waters in the basin Concentrations of chloride in excess of 100 mg/l in ground water and 50 mg/l in streamflow were generally attributed to the presence of oil-field brine if the sodiumchloride ratio was less than 0.60. Ground water containing over 1,000 mg/l dissolved solids and over 100 mg/l chloride was normally characteristic only of aquifers in or adjacent to old oil fields

The concentrations of dissolved solids, sulfate, or chloride in most well waters exceeded maximums recommended for drinking water. Nearly all the waters are classified as hard to very hard (>120 mg/l as $CaCO_3$). Calcium and sulfate derived from gypsum were the principal ions in nearly all ground water that contained over 1,000

SUMMARY

mg/l dissolved solids but that was not polluted by oil-field brine. The concentration of dissolved solids, except nitrate, in unconsolidated deposits normally increased with depth.

The concentration of nitrate exceeded the recommended maximum for drinking water (45 mg/l) in about 25 percent of the wells sampled Shallow aquifers, stagnation or infrequent pumping, and (or) proximity to sources of organic pollution characterized well water containing high concentrations of nitrate. The concentration of nitrate in base runoff was characteristically lower than in ground water from nearby wells

Streamflow in the Walnut and Whitewater Rivers changed from a sodium chloride to a calcium bicarbonate type, and the sodium-chloride ratio increased as direct runoff diluted polluted ground-water runoff during periods of rising stage. The normally inverse relation of ionic concentration to water discharge during each water year differed as annual runoff decreased during water years 1962–64.

During four basinwide salinity surveys of base runoff over a wide range of discharge, the concentrations of dissolved solids exceeded 500 mg/l in the Walnut River and 1,000 mg/l in the Whitewater River at nearly all stations Tributary watersheds that contributed a disproportionately large percentage of the chemical load of the main stem constituted a relatively small part of the drainage area of the basin Most of these watersheds are underlain by gypsiferous rock or contain old oil fields

The Walnut River and Whitewater River were generally effluent (gaining) streams. In October 1963, about 94 percent of the chloride load of the Walnut River at Gordon (RM 712) was attributed to effluent ground water (perennial sources plus cumulative net seepage) that contained oil-field brine. Net losses of sulfate in some reaches indicated unmeasured diversions or bacterial reduction of sulfate.

Measured municipal sewage effluent made up as much as 8 percent of the water discharge but made up less than 5 percent of the chemical discharge in base runoff at Gordon The net effect of measured refinery effluents and diversions was less, but they also adversely affected water quality in the main stem near the outfalls

Base runoff at the mouth of the West Branch of the Walnut River at El Dorado (RM 1032) consisted mainly of severly polluted runoff from oil fields in the western part of the subbasin The most severe pollution occurred downstream from station 07–468, north of El Dorado In October 1963, a single spring (RM 105.9) contributed over 80 percent of the chloride load at the mouth of the West Branch, where the chloride concentration was 1,220-mg/l. Runoff from the watershed of the East Branch of the Walnut River diluted streamflow in the main stem Most runoff would be regulated by the proposed El Dorado dam. Calcium and bicarbonate were the principal ions at all rates of water discharge at station 07–1466 and at Cole Creek near De Graff (07–1465.7), a west-bank tributary.

The Walnut River between El Dorado and the station at Haverhill Road (07-14685) receives brine-polluted runoff from part of the El Dorado oil field and effluent from the El Dorado sewage plant and two refineries Maximum concentrations of dissolved solids (1,860 mg/l), chloride (870 mg/l), nitrate (97 mg/l), fluoride (2.2 mg/l), and phosphate (13 mg/l) at Haverhill Road were as high or higher than in concurrent samples collected at other stations in the basin Constant Creek (RM 1002), a source of oil slicks on the Walnut River during periods of high runoff, contributed from 22 to 55 percent of the chloiide load in base runoff at Haverhill Road Most of the nitrate, phosphate, and fluoride are attributed to municipal and refinery effluent.

The chemical quality of streamflow of the Walnut River near Augusta (07-1469, RM 813) closely resembled that at Haverhill Road, but ranges in the concentrations of the major ions were smaller Up to 70 percent of the dissolved-solids load in base runoff was attributed to oil-field brine Sutton Creek (RM 958), which drains a large area underlain by polluted ground water west of the river, was a major source of the brine

The concentrations and loads of sulfate, chloride, and dissolved solids in streamflow of the Whitewater River near its mouth normally exceeded those in the Walnut River upstream from the junction of the two rivers; but during periods of high runoff, the chloride load in the Walnut River was larger. The Whitewater River was the main source of sulfate in the Walnut River. About 75 percent of the water discharge, nearly all the sulfate, and about 50 percent of the chloride load in base runoff of the Whitewater River at its mouth originated upstream from Towanda (07–14707), the proposed site of a dam.

Streamflow at Towanda generally was unsuitable for domestic use or for irrigation during water years 1962–64 The concentration of dissolved solids exceeded 1,000 mg/l more than 70 percent of the time, and the concentrations of sulfate and chloride exceeded 250 mg/l more than 70 and 50 percent of the period, respectively. The salinity hazard to irrigation was high to very high more than 90 percent of the time. Variable relations of concentrations of the ions to water discharge during each year and differences in the relations from year to year

SUMMARY

preclude accurate predictions from available records of the chemical quality of runoff during any single year. Therefore, data collection has been continued.

The West Branch of the Whitewater River (RM 17.0) was the major source of sulfate at Towanda, but its contribution decreased the concentration of chloride in base runoff. Springs in the watershed of Stearns Creek (RM 16.3) contributed up to 54 percent of the chloride load in base runoff at Towanda. Most of the apparent sources of seepage that contributed up to 30 percent of the chemical and water discharge in base runoff at Towanda would be inundated by the proposed Towanda reservoir.

Calculated concentrations of dissolved solids (570 mg/l), sulfate (151 mg/l), and chloride (110 mg/l) for total runoff at Towanda during the 1964 water year exceeded those for the preceding years but were far lower than those prevailing most of the time Retention and mixing of most of the runoff during periods of high discharge would have been needed to maintain concentrations below the recommended maximums for drinking water in an actual reservoir.

Sodium and chloride were the predominant ions in the Whitewater River at Augusta (07–1471, RM 0.8) near its mouth during periods of low flow, when oil-field brine constituted more than 50 percent of the dissolved-solids load. Most of the increase in chemical discharge in the reach between Towanda and Augusta during periods of low flow is attributed to perennial brine-polluted inflow from the east bank Sulfate was a subordinate anion at all rates of discharge. Repeated losses in the sulfate load in the reach between Towanda and Augusta are attributed to unmeasured withdrawals or to bacterial reduction.

Concentrations of sulfate, chloride, and dissolved solids in the Walnut River near Douglass (07-1475, RM 58 5) normally were less than concurrent concentrations in the Whitewater River at Augusta and greater than those in the Walnut River at Augusta. During the drought'in October 1963, when normally dilutant runoff of the Little Walnut River (RM 63.6) and other east-bank tributaries was negligible, about 53 percent of the dissolved-solids load at Douglas was attributed to oil-field brine. At that time, the sulfate discharge of Four Mile Creek (RM 73 4), a perennial west-bank tributary, was equivalent to about 40 percent of the sulfate load at Douglass

The concentrations of sulfate, chloride, and dissolved solids in the Walnut River at Winfield (07–1478, RM 226) generally were lower than those at Douglass. Tributary inflow between Douglass and Winfield, except sulfate-bearing runoff from Eight Mile (RM 524) and Pole Cat (RM 492) Creeks, diluted low flow in the main stem; but the

water at Winfield was unsatisfactory for domestic use or for irrigation during extended periods of low flow The concentration of sulfate exceeded 250 mg/l about 40 percent of the 1964 water year The concentration of dissolved solids exceeded 1,000 mg/l during more than 50 percent of the 1964 water year. The sodium (alkali) hazard to irrigation was low during all but about 7 percent of the 3-year period, but the salinity hazard was high to very high during about 80 percent of the same period

Pollution abatement caused marked reduction in concentrations of chloride corresponding to given rates of discharge at Winfield after 1955, but the concentration of chloride exceeded 250 mg/l during nearly 60 percent of the 1964 water year Concentrations of chloride up to 600 mg/l and sodium-chloride ratios from 0.44 to 0 60 denoted continued pollution by oil-field brine which constituted up to 40 percent of the dissolved-solids load in base runoff Most of the brine was derived from ground water polluted by improper oil-field operations in the past.

During this investigation, annual storage of chloride in surface brine ponds in the basin was equivalent to less than 12 percent of the annual chloride load of the Walnut River at Winfield. The rate at which chloride was carried from the basin by streamflow far exceeded the rate at which it was replenished in the soil and shallow aquifers by existing disposal practices. The chloride load increased disproportionately with the amount and rate of runoff. The concentration of the major ions in streamflow and the rate at which pollutants will be removed depends mainly on the rate and distribution of precipitation, on the construction and management of proposed reservoirs, and on the continued effectiveness of pollution abatement

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TABLE 7 — Chemical analyses of base runoff in tributary

[Results in milligrams per

	Sample No , location (sec-township-range), and date of collection	Dis- charge (cfs) (pl 2)	Silica (SiO ₂)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)	Sulfate (SO4)
-	West Branch Whitewater Rwer										
1	SW14NE14 13-24S-2E,	3 90	12		304	68	37	58	415	0 0	688
2	Gypsum Creek, NE¼SE¼	1 19	11		384	85	32	54	327	0	1, 050
3	25-248-2E, 10-12-62 SE14SW14 17-258-3E,	7 34	13	-	310	70	39	64	407	0	720
4	Wildcat Creek, SW14SW14	3 81	12		2 10	67	29	57	393	0	490
5	20-25S-3E, 10-12-62 Prairie Creek, SW14NW14	148	11		3 94	79	39	52	334	0	1, 030
6	29-25S-3E, 10-12-62 SE¼SW¼ 6-26S-4E, 10-12-62 ¹	18 53	10		200	53	39	66	305	0	442
	Whitewater River										
64	NE¼NE¼ 17-26S-4E, 10-12-62 ¹	43 00	11	-	156	42	84	60	288	0	270
	West Branch Walnut River	0.95	10		01	17	10	0.1	9#1	0	10
(3E/45W/4 3-245-3E, 10-11-62	2 35	12		91	17	12	21	301	0	18
8	NE% NW% 2-208-5E, 10-11-62	8 27	16		57	14	11	48	224	0	24
9	$10-11-62^{1}$	8 72	13		59	13	28	52	215	0	14
	East Branch Walnut River										
10	SE¼SE¼ 15-23S-7E, 10-10-62	4 96	95		38	61	90	35	156	0	82
11	SE¼SE¼ 30-23S-7E, 10-10-62	783	13	-	57	83	10	38	217	0	13
12	SW14SE14 2-24S-6E, 10-10-62	11 61	15		57	93	10	49	220	0	10
12	A Cole Creek, NE¼NW¼ 21-248-6E 10-10-62	3 00	13		50	11	89	51	200	0	14
13	SE¼SW¼ 28-24S-6E,	20 15	15		64	12	90	44	242	0	12
14	$SW_{4}NE_{4}$ 17-25S-6E,	42 45	15	·····	50	11	85	49	207	0	14
15	$SW_{4}NW_{4}$ 1-26S-5E, 10-11-62 1	71 44	16		56	79	8 1	43	198	0	12
	Turkey Creek									•	
16	$NW_{4}NW_{4}29-26S-6E$, 10-19-62	67	12	••••••	70	19	17	25	290	0	26
17	SE¼NE¼ 35-26S-5E, 10-19-62	1 46	13		96	20	133	38	249	0	28
18	SW14NW14 10-27S-5E, 10-19-62	3 79	95		102	22	136	43	327	0	26
10	Lutie Wainut River	20	5 5		75	14	26	~ 2	949	0	16
20	4-25-63 SW1/NW1/ 5-975-7F	2 00	00		06	11	50	20	212	ů	16
20	4-25-63	2 09	00		50	11	10	21	211	0	17
21	4-25-63	5 05	80	•••••	91	15	40	20	201	0	17
22	$1 \times \frac{1}{4} \times \frac{1}{4} = \frac{1}{288} - 5E$, 4 - 25 - 63	784	80		102	17	59	29	290	0	17
23	N $E_{4}^{4}SE_{4}^{4}$ 4-28S-5E, 4-26-63	8 95	85		96	21	64	34	295	0	18
24	Hickory Creek, NW¼SW¼ 15-28S-5E, 4-26-63	650	95		114	17	92	29	295	0	16
25	NW¼SE¼ 19-28S-5E, 4-26-63	16 90	90		99	21	73	31	293	0	20
26	SE¼NE¼ 9-29S-4E, 4-26-63	19 58	95		103	15	68	34	29 3	0	19
27	Unnamed tributary, NW4SW4 34-26S-7E, 4-25-63				. 61	15	19		195		15

watersheds of the Walnut River during water years 1962–64 $\,$

liter, except as indicated]

Phos-		c t-	Specific - conduct	Sodium	Per-	Noncar- bonate	TTand	ed solids at 180°C)	Dissolve (residue	D		_		Chloride
phate (PO ₄)	рН	er t	- ance (micro- mhos per cm at 25°C)	adsorp- tion ratio	cent so- dium	nard- ness as CaCO ₃	Hard- ness as CaCO ₂	Tons per- acre- foot	Mıllı- grams per liter	(B)	trate (O ₃))- 	ride (F)	(Cl)
														•••••••••••••••••••••••••••••••••••••••
03	79	0	1,860	05	7	698	1,040	194	1, 430	041	22	6	06	44
1	78	0	2, 150	4	5	1,040	1,310	2 52	1,850	51	24	6	6	25
t	79	.0	1,910	5	7	727	1,060	2 02	1,480	40	35	6	e	48
2	81	0	1,470	4	7	486	800	148	1,090	38	22	5	5	31
2	79	0	2, 190	5	6	1,030	1,310	2 52	1,850	48	33	7	7	36
3	80	0	1,420	6	10	467	717	140	1,030	36	26	5	5	69
4	79	0	1,470	15	24	326	562	1 27	935	28	27	4	4	174
1	79	ю	590	3	8	9	297	48	356	13	21	4	4	90
8	77	0	430	3	10	16	200	36	264	12	23	4	4	13
8	78	0	540	9	23	24	200	42	312	10	19	4	4	56
2	78	90	280	4	14	0	120	23	166	08	13	3) 3	6 0
8	77	0	390	3	11	0	176	32	232	15	25	3	3	70
4	77	0	390	3	11	0	180	3 2	236	12	26	3	3	8 0
ł	78	0	3 80	3	10	6	170	29	216	10	24	3) 3	8 0
4	78	0	420	3	8	11	209	34	253	13	25	4	4	7
3	77	0	370	3	10	0	170	31	227	13	14	4	4	9
5	78	0	360	3	9	10	172	29	216	10	21	3	3	8
1	80	.0	610	5	13	14	252	47	344	13	28	2	2	13
1	79	0	1, 270	32	47	118	322	1 00	738	15	66	2	2	271
1	81	0	1, 320	32	46	77	345	1 01	740	19	19	2	2	240
1	79	0	590	8	20	46	244	46	338	03	4	1	1	61
2	80	0	800	13	28	62	284	62	456	08	5	1	1	118
2	80	0	760	1 2	26	58	288	59	436	05	4	1	1	96
2	80	0	920	14	28	86	324	72	528	08	4	1	1	140
2	80	0	970	15	30	84	326	74	544	08	9	1	1	148
1	79	0	1, 140	21	36	112	354	86	636	07	4	1	1	204
2	80	0	990	17	32	94	334	78	572	07	4	2	2	162
2	79	0	960	17	31	78	318	75	550	08	4	3	3	147
	82	0	560	6	16	54	214	44	- 322		4.			56

	Sample No, location (sec-township-range), and date of collection	D15- charge (cfs) (pl 2)	Silica (SiO ₂)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)	Sulfate (SO4)
1 27 A	<i>intle Walnut River</i> —Con South Branch Little Walnut River, SW¥ANW¥ 17-27S-7E, 4-25-63				90	11	58		288 .		11
	Four Mile Creek										
28	SW1/SE1/24-27S-2E, 11-14-62	1 29	80		424	76	94	65	207	001	, 116
29	SE¼NE¼ 31-27S-3E, 11-14-62	3 47	11	•••••	376	67	76	62	320	0	884
3 0	NW¼NW¼ 2-28S-3E, 11-14-62	5 01	10	•	294	57	63	57	337	0	650
31	NW14SW14 7-28S-4E,	8 05	12		326	69	68	55	349	0	770
3 2	NW1/SE1/ 17-28S-4E, 11-14-62 1	8 32	12		291	65	82	53	283	0	708
	Eight Mile Creek										
33	SE¼SE¼ 29-28S-3E, 8-2-63	62	16		491	65	56	49	327	0 :	1, 207
34	NW14NE14 3-29S-3E,	54	12		382	60	46	81	271	0	976
35	SW14 SW14 12-29S-3E,	1 01	12	·····	214	52	3 0	69	285	0	510
3 6	NE¼NE¼ 25-29S-3E,	$2 \ 05$	12		131	3 2	21	96	229	0	266
37	$NW_{4}^{2-63}NW_{4}^{1}$ 7-30S-4E, 8-2-63 ¹	1 3 2	12	·····	101	2 3	18	81	166	0	213
	Rock Creek										
38	SW¼NW¼ 15-29S-7E, 8-1-63	10	••••		69	11	9	•••••	. 205	-	10
3 9	NW14NW14 27-298-6E,	86	13		86	12	14	2 0	278	0	15
40	SW4NW4 36-29S-5E,	98	12		79	11	60	34	229	0	17
41	SE¼NE¼ 31-29S-5E,	1 18	11		73	93	52	40	19 3	0	12
42	SE¼SE¼ 10-30S-4E,	1 64	95	•••••	56	10	36	50	173	0	12
43	8-1-63 SW¼NW¼ 21-30S-4E,	2 57	95		56	10	55	49	166	0	14
44	8-1-63 ¹ SW $\frac{1}{4}$ NW $\frac{1}{4}$ 32-29S-5E, 8-1-63	< 10			78	13	61	·	. 185		64
	Timber Creek										
45	$SW_{4}NW_{4}$ 19-30S-7E,	58	55		. 74	12	13	17	276	0	18
46	SEWNEW 4-31S-7E,	1 82	90		. 75	14	10	16	273	0	19
47	NE4SE4 16-31S-5E,	3 00	85		. 88	94	26	25	276	0	18
48	SE¼NE¼ 24-31S-4E,	3 30	8 0		. 88	15	22	25	288	0	17
49	4-24-63 Dutch Creek, NW1/NE1/	347	65		. 82	11	16	25	268	0	15
49.	24-31S-4E, 4-24-63 A Cedar Creek, NW¼ NW¼ 1-32S-4E,	02		· · · · · · ·	. 107	27	9 3		_ 298		28
50	4-26-63 NW $\frac{1}{4}$ SW $\frac{1}{4}$ 2-32S-4E,	7 51	75		. 87	14	25	25	281	0	17
51	4-25-63 NE $48W4$ 21-32S-4E, 4-24-63 ¹	8 56	8 0		. 96	10	45	34	290	0	23
	Stewart Creek										
52	SE¼NE¼ 2-31S-3E, 11-7-63	13	65		. 90	49	70	55	264	0	127
	Posey Creek										
53	NW¼NW¼ 26-33S-4E, 12-5-63	62			. 75	5 19	87		- 342		110

TABLE 7 — Chemical analyses of base runoff in tributary watersheds

See footnotes at end of table

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Chloride	Fluo	Nitrato	Boron	Dissolv (residue	ed solids at 180°C) Horde	Noncar- bonate	Per-	Sodium-	Specific conduct-	nИ	Phos-
(Cl)	ride (F)	(NO ₃)	(B)	Milli- giams per liter	Tons per- acre- foot	ness as CaCO ₃	ness as CaCO ₃	so- dium	tion ratio	(micro- mhos pei cm at 25°C)	pn	(PO4)
104		04		460	63	270	34	32	15	790	79	
175	08	4	51	2, 110	2 88	1, 3 70	1, 200	13	11	2, 490	79	01
134	7	18	54	1, 780	2 42	1, 210	952	12	9	2, 150	76	2
108	6	31	41	1,400	1 91	968	692	12	9	1, 820	79	1
107	7	36	40	1,600	2 18	1, 100	811	12	9	1, 950	79	2
137	6	32	37	1, 500	2 04	99 3	761	15	11	1, 808	80	1
52	9	44	51	2, 150	2 90	1,490	1, 220	75	6	2, 480	74	4
45	8	27	41	1, 730	2 40	1, 200	978	76	6	2, 080	77	3
28	5	58	27	1,040	1 40	748	514	79	5	1, 390	77	4
23	5	44	15	646	88	458	270	88	4	940	75	4
18	5	44	13	496	67	3 46	210	98	4	740	75	8
42				. 328	45	217	49	86	3	520		
32	2	4	07	33 2	45	264	36	10	4	560	77	3
125	2	9	10	446	61	242	54	35	17	790	79	2
112	2	5	10	384	52	220	62	33	15	690	77	2
80	3	4	08	303	41	180	38	30	1 2	540	80	3
115	3	7	10	377	51	180	44	39	18	660	77	2
158				. 526	72	248	96	35	17	850		
10	2	11	05	294	40	234	8	11	4	490	78	2
17	2	9	03	289	3 9	244	20	8	3	480	77	2
55	2	5	05	356	48	258	32	18	7	610	78	2
49	2	8	05	365	50	281	45	14	6	620	79	2
31	2	9	07	305	41	250	30	12	4	530	77	1
217		4		. 740	1 01	378	134	35	22	1, 280	79	
54	2	5	05	361	49	274	44	16	7	6 3 0	79	2
83	3	16	08	43 9	60	280	42	26	12	750	78	6
164	2	4	19	657	89	426	210	26	15	1, 110	80	1
42		9.		502	68	265	0	42	23	710	80	

of	the	Walnut	River	during	water	y ears	1962-	64—(Continued
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427-145 0---72----7

	Sample No , location (sec-township-range), and date of collection	Dis- charge (cfs) (pl 2)	Silica (SiO2)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)	Sulfate (SO4)
_	Badger Creek										
54	SE¼SW¼ 12-33S-4E, 4-24-63				112	3 0	60		327 _		54
	Black Crook Creek										
55	SE¼NE¼ 34-32S-4E, 11-7-63	20 02	12	.	1 3 0	29	257	50	3 20	0 0	58
	Whitewater River										
56	SW14SE14 20-23S-4E,				184	78	3 75		229		280
57	8-29-63 NE¼NW¼ 5-24S-4E,	3 95	12		268	83	172	62	386	0	542
58	Henry Creek, NE¼SW¼	1 64	15		157	52	31	57	425	0	270
59	Averys Creek, SE ¹ / ₄ SW ¹ / ₄	1 48	13	••••	133	45	44	57	376	0	150
60	5-24S-4E, $11-1-62Gillion Creek, NE_{4}^{1/2}NE_{4}^{1/2} 13-25S-3E,$	1 38	13	-	111	42	26	53	337	0	176
61	Unnamed tributary, NW $\frac{1}{4}$ SW $\frac{1}{4}$ 12-25S-3E,	85	11		182	49	203	12	366	0	158
62	Indianola Creek, SW¼ SE¼ 3-27S-3E, 4-11-63	< 02									120
	Santa Fe Lake										
63	NW¼NE¼ 13-27S-3E, 4-11-63						••• •• •				3 0
	West Branch Walnut River										
64	$NE_{4}^{1}NW_{4}^{1}$ 23-25S-5E,	7 15	13		77	20	71	56	261	0	33
65	$\begin{array}{c} 11-1-02 \\ NE\frac{1}{4}NE\frac{1}{4} 2-26S-5E, \\ 11-1-62 \\ 1 \end{array}$	11 06	10	•	90	23	160	68	227	0	45
	Sutton Creek										
66	SW¼NW¼ 4-26S-5E, 10-10-63 ¹	02	-		504	108	2, 527	• ••	13 9 _	• ••	30
	Pole Cat Creek										
67	SE ¹ 4SE ¹ 4 13-30S-3E, 10-9-63	03	90		78	24	15	63	261	0	80
	Muddy Creek										
68	NE¼SE¼ 5-30S-4E, 10-10-63	01	75		85	21	19	45	3 20	0	24
ι	Innamed tributary to Walnut River										
6 9	SW¼NE¼ 21-28S-4E, 8-16-63	2 05			3 64	67	811		. 171		135
	Springs and seeps										
70	$SW^{1}_{4}NE^{1}_{4}$ 13-24S-2E, 10-12-62	20	10	-	642	91	88	68	361	0	1,610
71	$N E \frac{1}{4} N W \frac{1}{4} 25 - 24 S - 3E,$ 2 - 1 - 63			0 19			29		. 381		60
72	$NW_{4}^{-1-3}SW_{4}^{-2}$ 25-23S-3E,	····· •		79		····• ·	. 14		- 34		250
73	$SW_{4}^{-1-5}SW_{4}^{-1}$ 36-24S-3E,				- 77	36	460		- 259		40
74	Shot Hole NW1/NW1/ 11-25S-3E, 11-1-62				- 712	110	459		- 283		1, 700

TABLE 7 — Chemical analyses of base runoff in tributary watersheds

See footnotes at end ot table

Chloride	Fluo	Nitrata	Boron	Dissolve residue	ed solids at 180°C)	Hord.	Noncar- bonate	Per-	Sodium-	Specific conduct-	nH	Phos-
(Cl)	ride (F)	(NO ₃)	(B)	Milli- grams per liter	Tons per- acre- foot	ness as CaCO ₃	ness as CaCO ₃	so- dium	tion ratio	(micro- mhos pei cm at 25°C)		(PO ₄)
148		04		638	87	403	135	24	13	1,060	79	
485	02	9 3	10	1, 160	1 57	444	182	55	53	2, 060	80	01
790		8				780	592	51	58	3, 330	76	
344	5	4	28	1,660	2 26	1,010	694	27	24	2,460	79	1
30	4	26	23	800	1 09	605	257	10	5	1, 160	81	3
99	2	75	18	717	98	517	209	15	8	1, 120	8 1	2
28	4	10	21	571	78	450	174	11	5	880	82	2
455	3	44	16	1, 310	1 78	656	356	40	34	2, 230	78	2
23												
10	•••••						•••••					
133	4	1.0	13	504	69	274	60	36	19	880	77	2
307	3	4 1	18	798	1 09	319	133	52	39	1, 410	75	1
5, 000		•••••	•• •••••		•••••	1, 700	1, 590	76	26 6	14, 300		
17	3	11	13	373	51	293	79	10	4	600	77	2
33	1	5	08	369	50	298	36	12	5	630	77	1
1, 890				3, 520	4 79	1, 180	1, 040	60	10 2	6, 180		
148	10	12	73	2, 920	3 97	1, 980	1,680	9	0	3, 210	71	1
66	2	32		_, •_•		432	120	13	6	.,		•
46	3	17				326	298		3			
745		44				340	128	78	10.8	3. 050	8.0	
870		- 4				2, 230	2,000	31	4 2	5, 170	76	
										, -		

of the Walnut River during water years 1962-64-Continued

	Sample No, location (sec-township-range), and date of collection	Dis- charge (cfs) (pl 2)	Silica (SiO2)	Iron (Fe)	Cal- cium (Ca)	Mag- ne- sium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO ₃)	Sulfate (SO4)
	Springs and seeps—Con							ø		_	
75	SE¼NE¼ 26-25S-3E,						42		425 .		180
76	NW4NE4 31-25S-4E,			- <i>-</i>	122	43	17		386 -		125
77	$SW_{4}SE_{4}$ 5-26S-4E,	•	11		171	50	542	11	254	0 0	122
78	SW14SW14 9-26S-4E,	0 38			296	78	1, 048		383 -		72
79	8-28-63 NW¼NE¼ 33-26S-4E,	23			182	78	455		273 .		30 \
80	$SW_{4}NE_{4}V$ 33-26S-4E, S=20-63	11			77	32	13		361		10 \
81	Flowing well, NW14		75	-	227	79	1, 028	11	183	0	86
82	SEMNW 21-23S-7E,	01			69	24	16		298	0	15
83	8-28-63 NW148E14 15-258-5E,	04			154	56	341		317 .		30
84	8-28-63 SW14SE14 10-24S-7E,	< 01					14		271 .		10
85	3-13-64 NE¼SE¼ 8-25S-6E,	02			87	25	20	-	403	0	80
86	8-28-63 NW¼NW¼ 26-25S-5E,	36			422	115	1, 446		386	0	36
87	8-28-63 NE¼NE¼ 8-26S-5E,		95		199	62	920	39	193	0	48
88	9-19-62 NE¼NE¼ 17-268-5E,		10		21	47	41	24	76	0	82
89	9-19-62 SW14SE14 28-26S-4E,		12		120	39	169	35	305	0	20
90	9-10-62 NW1/2SW1/4 3-26S-5E,				128	21	129		415	0	80
91	11-2-62 SE¼NW¼ 1-27S-5E.				77	13	56		244		17
92	2-17-62 SW1/ANW1/A 30-27S-6E.	_			353	94	1, 330		3 95		32
93	6-22-62 NE4/SW1/ 28-27S-4E.				48	18	575		683		50
04	11-2-62 SWL/NFL/ 33-278-5F				51	27	15		286		17
0.5	2-17-62			-	967	-,	1 042		251	 م	190
90	8-29-63		-		207	10	1,042		100	0	19
96	N W $\frac{4}{4}$ SE $\frac{4}{4}$ 28-308-6E, 9-4-63		12	0.03	104	13	83	5	344	U	14

TABLE 7 — Chemical analyses of base runoff in tributary watersheds

¹ Data-collection site during combined seepage-salinity surveys

Chloride (Cl)	Fluo- rıde (F)	Nitrate (NO3)	Boron (B)	Dissolve (residue) Milli- grams per liter	ed solids at 180°C) Tons per- acre- foot	Hard- ness as CaCO ₃	Noncar- bonate hard- ness as CaCO ₃	Per- cent so- dium	Sodium- adsorp- tion ratio	Specific conduct- ance (micro- mhos pei cm at 25°C)	Phos- pH phate (PO ₄)
20						472	124	16	08	1, 150	
46		89				481	165	7	3	950	7 9
1, 090	02	9	0 61	2, 230	3 03	632	424	65	94	3, 970	77 01
2, 090		15				1, 060	746	68	14 0	7, 260	7 6
1, 070		7				774	550	56	71	3, 840	8 1
27		97			·····	324	28	8	3	610	8 1
2, 140	2	8	32	3, 820	5 20	891	741	71	15 0	6, 610	78 1
27		88				270	26	11	4	530	8 1
755	-	8				614	354	55	60	2, 830	8 0
11	1	19				220	0	12	4		
15		33				320	0	12	5	670	79
3, 060		9.			·····	1, 530	1, 210	67	16 1	9, 680	7 4
1, 840	2	8	76	3, 360	4 57	752	594	73	14 6	5, 930	80 1
67	4	17	12	206	28	72	10	54	21	360	661
409	3	13	56	964	1 31	460	210	44	34	1, 780	80 1
240	•••••	4.	• • • • • • • • •			406	66	41	28	1, 390	7 5
105	2	26		. 440	60	246	46	33	16	740	••••••
2, 700	02	13.		4, 816	6 55	1, 270	946	70	16 3	8, 520	
590		4	-			194	0	87	18 0	2, 950	8 0
11	2	21.		. 270	37	238	4	12	4	470	
1, 960		22.				986	698	70	14 4	6, 690	76_
18	1	16 .	• • • • • • •	365	50	313	31	5	2	600	782

of the Walnut River during water years 1962-64-Continued

² Estimated

TABLE 8 — Chemical analyses of streamflow during combined seepage-

[Results in milligrams per liter, except as indicated

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Sample source and date of collection	Dis- charge (cfs)	Silica (SiO ₂)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicai- bonate (HCO ₃)	Cai- bonate (CO3)
RM 109 8 West Branch Walnut River near El Dorado (07-1468), main-								·
Dec 7. 1961	10 34	70	98	31	60	30	344	0
Apr 24, 1962	7 38		91	28	69.		324	
Nov 1, 1962	657	12 7 5	90 71	20 27	35 86	45 51	271 281	29
RM 109 6, unnamed tributary							-01	
Dec 7, 1961 Apr 24 1962	1 97	65	109	38 42	248	40	320 327	0
Nov 1, 1962	85	75	136	43	296	53	342	0
BM 107 9 upperied tributery 1	11	45	184	71	626	70	271	0
Dec 7, 1961.	040							
Apr 24, 1962	11		62	22			281	
Dec 7, 1961.	13 94	85	112	27	110	32	354	0
Apr 24, 1962	10 70	19	94 77	32	132	5.6	320	
Oct 9, 1963	32	65	97	35	218	56	256	ŏ
RM 106 6, unnamed tributary	1 69	65	095	70	860	5.6	246	0
Apr 24, 1962	1 29		235 315	102			240	
Nov 2, 1962	72	55	377	108	1, 230	10	207	0
RM 106 1, unnamed tributary ¹	11		510	149			111	
Dec 7, 1961	26	80	77	22	21	19	307	0
RM 105 9, unnamed tributary	01		12	10			210	
Dec 7, 1961.	90	13	201	33	464	40	390	0
Nov 2, 1962	53 71	13	339	30 71	1,020	10	422	0
Oct 9, 1963	25	13	424	115	1, 430	14	381	0
Dec 7, 1961.	02							
RM 1050, diversion American Petro-								
Nov 1, 1962	18							
Oct 9, 1963	18	20	324	93	1, 120	13	312	0
fina Refinery ¹								
Apr 24, 1962	30 48		56	13			224	
Oct 9, 1963	30	29	70	18	525	13	232	0
RM104 2, unnamed tributary	0.56	75	208	37	700	6.8	354	. 0
Apr 24, 1962	18		. 198	45			. 295	
Nov 1, 1962	12	60	148 216	38 45	524	74	215 242	0
RM103 2, main-stem site			. 210	10				
Dec 7, 1961	21 72 14 20	60	131 130	31 35	220 266	42	359 31/	0
Nov 1, 1962	11 06	10	. 100	23	160	68	227	0
Oct 9, 1963	76	65	190	51	644	13	244	. 0
Dec 7, 1961	73 54	11	88	15	14	14	310) 0
Apr 24, 1962	34 60 41 44) i 14	. 75	10	12	3 8	- 281 254	• • • •
Oct 9, 1963	(3)	25	63	11	16	38	23	i ŏ
RM102 6, main-stem site	03 34	L 10	90	17	57	33	32	I 0
Apr 24, 1962 5	42 6	<u>.</u>	- 89	16	44		310	; <u>-</u> -
Nov 1, 1962 4	50 2 1 20	2 12	76 160	14 38	39 467	46 10	25) 231	\$0 70
RM 100 8, unnamed tributary 1	1 20		100				20	
Dec 7, 1961	2 83		98 101	13	26	10	320) 0 1
Nov 1, 1962	1 13	14	95	16	17	2 5	308	i 0
Configuration at and of table								

See footnotes at end of table

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RM, river mile upstream from mouth of main stem]

Sulfate (SO4)	Chloride (Cl)	Fluo- 11de (F)	N1- trate (NO ₃)	Boron (B)	Dis- solved solids (iesidue at 180° C)	Hard- ness as CaCO ₃	Noncar- bonate hard- ness as CaCO ₃	Sodium adsorp- tion ratio	Specific conduct- ance (mi- cromhos per cm at 25° C)	рН	Phos- phate PO4
45 50	111 124	02	19	0 13	524 553	372 342	90	14	980 990	76	
39 39	52 142	33	4 6 2	15 13	422 550	306 288	36 58	9 34	710 980	84 75	0 2 1
71 67 71 71	465 490 570 1, 280	2 2 2	$\begin{array}{c} 7 & 1 \\ 3 & 1 \\ & 4 \\ 1 & 7 \end{array}$	27 23 34	1, 130 1, 260 1, 240 2, 490	428 457 516 751	166 236 529		2, 210 2, 230 2, 250 4, 480	76 79 76	 0 1
20 27	15 18		4		² 307 296	245			540 520		
52 49 33 36	201 241 133 445	2 4 3	$\begin{array}{c}1&5\\&&4\\1&0\\2&1\end{array}$	19 13 15	688 786 504 1, 030	390 366 274 386	100 60 176	24 30 19 48	1, 290 1, 390 880 1, 920	78 77 78 78	 2 1
61 58 76 118	1, 800 2, 310 2, 700 4, 050	1 1	10 4 4	27 - 28	3, 400 4, 150 4, 830 7, 050	911 1, 210 1, 380 1, 880	709 1, 210		6, 540 7, 390 8, 340 12, 300	75	 i
37 19	$\frac{15}{23}$	2	$\begin{smallmatrix}2&2\\8&8\end{smallmatrix}$	08	364 318	282 254	30		620 570	76	
21 25 33 44	940 1, 490 2, 050 3, 060	$ \cdots $	- 4 - 4 1 2 9	36 38 42	1, 960 2, 970 3, 890 5, 500	637 844 1, 140 1, 530	317 792 1, 220	· · · · · · ·	3, 920 5, 320 6, 670 9, 480	72 71 70	 1 1
135	4, 080		••••						12, 600		
28 44	405 2, 390		18	42	² 973 4, 360	1, 190	934		1, 670 7, 480	77	····· 1
484 445 540	415 287 451	- 4	4 37	23	1, 480 2 1, 270 1, 770	193 	58		2, 770 2, 230 2, 950	777777	2 9
86 59 72 110	1, 3 20 1, 500 985 1, 100	1 1 	4 4 4	44 - 31 	2, 720 2, 950 2, 020 2, 260	671 679 525 724	381 349		5, 020 5, 290 3, 560 3, 900	77	2
60 64 45 175	410 510 307 1, 220	2 	15 31 41 23	23 - 18 38	1, 052 1, 290 798 2, 550	454 468 319 684	160 1 33 484	45 53 39 11	1, 950 2, 230 1, 410 4, 520	77 75 73	1 2
23 23 18 23	12 14 12 18	2 3 2	53 31 11 17	07 16 08	302 289 280 280	281 248 216 202	27 		570 520 450 450	79 79 77	3 2
31 26 21 137	102 72 69 880	2 3 3	22 15 15 27	15 15 24	481 412 378 1, 910	318 288 246 555	55 39 361	13 4 9 86	927 710 666 3, 430	77 81 73	4
21 26 14	44 51 46	- 2 - 1	$\begin{smallmatrix}4&2\\&4&2\\&1&1\end{smallmatrix}$	10 13	390 428 367	298 318 303	36 	· · · · ·	7 3 0 740 6 3 0	78	

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Sample source and date of collection	Dis charge (cfs)	Silica (SiO2)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO ₃)
RM100 6, municipal sewage effluent, El Dorado								
Dec 7, 1961	6225 217		78	21			259	•••••
Nov 1, 1962	⁶ 1 45							
RM100 3, diversion, Skelly Oil Re- finery	6 70	24	75	18	205	25	193	0
Apr 24, 1962	2 80		93	17			298	
Nov 1, 1962	2 80	12	118	33	354	17	205	
RM100 2, Constant Creek	05	12	110	00	1004		200	
Dec 7, 1961	2 94	90	221	59	828	69	302	0
Nov 1, 1962	82	95	268	86	1,200	13	342	0
Oct 9, 1963 RM 100 1, effluent, Skelly Oil Refinery	44	11	840	117	1, 800	21	293	0
Apr 24, 1962	1 31 66		88	17			285	
Nov 1, 1962	03	5.0				5 Ô	156	
RM 100 0, effluent, Skelly Oil Refinery Dec. 7, 1961	1 83	50	00	00	40	50	100	U
Apr 24, 1962	1 84		59	10			9 8	5 102
Oct 9, 1963. RM 98 1, unnamed tributary	1 34 1 43	14	50	11	224	13	176	Ō
Dec 7, 1961	² 05 ² 05		99	19			205	
Nov 1, 1962	03		- 100				101	
RM 96 5, unnamed tributary	2 05		122	32	-		181	
Dec 7, 1961	1 01	50	237	55 56	890	80	256 261	0
Nov 1, 1962	72	7 0	198	44	684	12	290	0
Oct 9, 1963 RM 96 5, unnamed tributary 1	01	75	162	48	700	13	271	0
Dec 7, 1961.	2 10							
Dec 7, 1961	02							
RM 95 9, Walnut River at Haverhill Road near, El Dorado (07- 1468 5), main-stem site								
Apr 25, 1962	51 80 61 40	13	109 90	15 17	117 76	53	278 281	Ō
Oct 9, 1963	3 52	75	141	34	442	16	132	0
Dec 7, 1961.	1 84	70	194	41	795	98	339	0
Apr 25, 1962	95 00	10	174	44	760	12	327 356	0
Oct 9, 1963	95 05	55	151	38	760	16	324	ŏ
RM 94 2, unnamed tributary ¹ Dec 7, 1961	14 02	85	144	21	191	30	356	0
RM 93 1, unnamed tributary 1								
Apr 25, 1962	² 15 01		163	30			342	
RM 92 5, unnamed tributary		7.0	100	10			207	0
Apr 25, 1962	16		110	19			. 285	0
Nov 1, 1962 Oct 9, 1963	14 2 01		96 109	21 21	193 118	$\begin{smallmatrix}4&3\\3&1\end{smallmatrix}$	264 315	0 0
Dec 7, 1961	129	10	112	15	98	40	295	0
Apr 25, 1962 Nov 1, 1962	539 720		101 82	20 19	131 76	5 5	. 281 254	0
Oct 9, 1963	3 99	10	150	3 6	454	14	200	Ō
Dec 7, 1961	6 66	75	82	17	124	26	259	0
Apr 25, 1962 Nov 1, 1962	$\begin{array}{c} 3 & 84 \\ 2 & 91 \end{array}$	10	96 122	21 20	193	48	332	0

TABLE 8 — Chemical analyses of streamflow during combined seepage-salinity

See footnotes at end of table

								_			
Sulfate (SO4)	Chloride (Cl)	Fluo- rıde (F)	N1- t1ate (NO3)	Boron (B)	Dis- solved solids (residue at 180° C)	Haid- ness as CaCO3	Noncar- bonate hard- ness as CaCO ₃	Sodium adsorp- tion ratio	Specific conduct- ance (mi- cromhos per cm at 25° C)	pН	Phos- phate PO4
² 86 95 76 65	² 185 167 202 33 2	1 3	² 40 32 41 40	0 78	² 740 779 ² 726 926	281 261	103		1, 260 1, 280 1, 230 1, 600	7 0	46
2 29 35 22 92	98 120 66 670	 1 0	5 3 19	47	² 522 570 ² 414 1, 500	302 430	262		870 940 690 2, 590	7 2	20
56 63 60 34	1, 680 2, 360 2, 290 3, 560	1 1 0	4 4 4 4	48 58 56	3, 250 4, 260 4, 220 6, 330	794 965 1, 020 1, 33 0	546 742 240	· · · · · · · · ·	6, 200 7, 780 7, 410 11, 700	74 75 76	 1 1
28 16 21	94 118 183 69		31 8 88	08	² 440 532 ² 708 301	290 164	36		760 920 1, 220 520	75	7
204 135 246	328 300 117 185	28	4 4 3	19	² 912 908 ² 799 864	188 170	26		1,690 1,770 1,480 1,490	72	9
150 128 240 110	17 149 52 690		15		² 313 652 516 1, 480	325 436			540 1, 110 890 2, 600		
116 1 33 101 69	1, 780 2, 090 1, 290 1, 30 0	$\frac{1}{\frac{1}{2}}$	4 4 4	40 5 7 46	3, 420 4, 070 2, 540 2, 520	818 961 675 602	608 437 380		6, 510 7, 230 4, 550 4, 560	74. 77 76	1
65 175	1, 400 760								4, 920 3, 070	 	
49 40 167	213 133 810	4 1 8	97 75 53	18 32	752 550 1, 800	334 294 492	64 384	2 8 1 9 8 7	1, 280 920 3, 210	75 71	9 3 6
111 84 99 76	1, 470 1, 500 1, 350 1, 340	$\frac{2}{1}$	$\begin{smallmatrix}1&0\\&4\\&4\\1&4\end{smallmatrix}$	57 60 60	2, 920 2, 890 2, 740 2, 620	652 615 660 532	374 368 266		5, 570 5, 040 4, 750 4, 740	76 78 75	29
26 20	395 341	2	4	15	980	446	154		1, 830 1, 630	79	
20 26	360 535		4		1, 250	530			1, 760 2, 250		
27 2 3 24 24	380 440 359 238	2 2 2	4 4 7 5	15 27 13	916 1, 090 893 682	332 352 326 358	80 110 100		1, 720 1, 970 1, 600 1, 250	78 78 78 78	1 1 1
52 47 36 178	186 237 141 820	6 4 9	15 71 71 15	19 15 47	642 788 531 1,850	341 334 282 522	99 74 358	23 31 20 87	1, 260 1, 360 910 3, 210	74	6 1 4
34 38 32	217 310 351	3 2	$\begin{smallmatrix}4&4\\6&2\\&4\end{smallmatrix}$	08 19	634 840 940	274 326 386	62 114		1, 200 1, 490 1, 650	77	1

surveys of the Walnut River basin, December 1961 to October 1963-Continued

TABLE 8 — Chemical analyses of s	streamflow during	combined se	epage-salinity
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Sample source and date of collection	Dis- charge (cfs)	Silica (SiO ₂)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)
RM 90 2, unnamed tributary 1 Dec. 7, 1961	0.03							
Apr 25, 1962	01		58	40			332	
Dec 7, 1961	20	60	99	24	47	2 2	332	0
RM 89 2, main-stem site Dec 7, 1961	137	10	109	17	98	42	290	0
Apr 25, 1962 Nov 1, 1962	68 80 71 3		106 93	18 17	136 . 84	5 2	285 288	
Oct 9, 1963	3 56	65	146	34	407	13	198	õ
Dec 7, 1961	99	65	102	58	157	34	337	0
Apr 25, 1962 Nov 1, 1962	59 30	7 5	128 138	76 76	233	5 0	366 383	0
Oct 9, 1963	10	12	77	27	14	27	361	0
Dec 7, 1961.	36	60	80	30	15	22	359	0
Nov 1, 1962	23 22	8 0	38 80	32 32	18	25	269 373	0
RM 85 9, unnamed tributary 1 Dec 7, 1961	31	55	67	32	31	19	359	0
Apr 25, 1962	05	5.5	70	34 37	30	5.0	378	
RM 85 2, unnamed tributary 1	00	00	02	01	00	00	120	°,
Apr 25, 1962.	² 05		44	39			298	
Nov 1, 1962 RM 84 7, unnamed tributary 1	06	60	86	43	23	27	432	0
Dec 7, 1961	14 10		••••••					
RM 83 6, unnamed tributary				00		1 0	200	0
Apr 25, 1962	35		62 85	28 29	14	10	. 368	
Nov 1, 1962 Oct 9, 1963	24 07	12 13	62 88	31 29	14 18	$18 \\ 58$	317 400	0
RM 83 3, unnamed tributary	63	8.0	82	26	52	18	339	0
Apr 25, 1962	49	-10 -	76	26	40	21	325	- 0
Oct 9, 1963	23 15	6 0	70 59	33	40 52	29	305	0
Dec 7, 1961.	11							
RM 81 3 (07-1469), Walnut River near								
Dec 7, 19617	145	-						
Nov 1, 1962	78 4	13	99 99	21	74	4 8	320	0
Aug 16, 1963	8 23 4 19	90 5	88 112	19 31	339	10	185	0
RM 80 6 (07-1471), Whitewater River at Augusta								
Dec 7, 1961	113	13	212	58 66	136	40	412 315	0
Nov 1, 1962	52 6	12	226	64	152	74	386	
Aug 16, 1963	24 0 9 35	75	192 216	57 64	230 339	12 9	285 305	
RM 80 6, effluent, Socony Mobil Re- finery ¹								
Dec 7, 1961	46		-					
Oct 9, 1963	08	40	90	43	970	131	142	8
Augusta								
Dec 7, 1961	1 26 4 54			20		 	527	
Nov 1, 1962	70		- 58	21			195	0
RM 79 3, main-stem site 1	94 #		104	 K0			979	n
Oct 9, 1963	34 5 14 8		104	52 54	325	12	281	Ŏ
RM 78 3 unnamed tributary ¹ Dec 7, 1961	01							
RM 77 2, unnamed tributary ¹ Dec. 7, 1961	04	-						
Api 25, 1962	01	i <u>-</u>	86	25			266	

i.

See footnotes at end of table

Sulfate (SO4)	Chloride (Cl)	Fluo- ride (F)	N1- trate (NO3)	Boron (B)	Dis- solved solids (residue at 180° C)	Hard- ness as CaCO ₃	Noncar- bonate hard- ness as CaCO ₃	Sodium adsorp tion 1atio	Specific conduct- ance (mi- cromhos per cm at 25° C)	pН	Phos- phate PO4
30	13	.							700		
48	13	•••••	31		373	309			640		
38	88	02	15	0 10	481	34 6	74		880	77	
56 48	186 245	6	$^{15}_{53}$	18	642 794	342 338	104	23	1,260 1,370	73	
36 153	146 750	3	62 12	18 36	568 1.690	302 504	66 342	$\begin{array}{c} 2 & 1 \\ 7 & 9 \end{array}$	960 2, 970	77 74	0615
46	370	3	31	07	932	493	217		1,840	76	
66 58	575 560	3	4	15	1,390	632 657	343		2,470 2,350	78	·····i
74	16	4	îî	10	335	303	7		510	77	ĩ
32	13	3	93	07	351	323	29		640 450	78	-
20 34	16	4	44	19	396	331	25		650	8 0	2
40	23	3	31	07	386	298	4		730	77	-
32 30	26 28	4	31	19	402 428	314 356	8		690 740	8 0	ī
25	22								710		.
32 40	29 27	4	$53 \\ 75$	19	354 444	270 3 91	37		630 770	81	2
25 10	$\begin{smallmatrix}13\\8&0\end{smallmatrix}$								580 390		
28	13	3	93	08	312	270	3 2		610	77	
31 26	10 12	3	97 75	16	394 323	331 282	22		660 580	8 0	i
27	12	2	13	12	397	338	10		670	79	4
32 33	79 95	2		08	454 514	312 296	34		880 880	77	
28 31	76 76	3 3	$36 \\ 18$	$ 19 \\ 12 $	459 420	317 282	39 32		830 760	$\begin{array}{c} 7 & 9 \\ 8 & 2 \end{array}$	1
25	450								2,060		
									,		
35 49	192 222		····a 1		² 650 746	338	94	$21 \\ 30$	1, 220 1, 290		
33	136	4	33	18	547	334	72 124	18	970	78	·····
86	655	9	$10 \\ 19$	23	1, 390	407	255	73	2, 520	74	-
297	067	,	- 1	10	1 000	740	490		1 000	7 9	
364	322		15		1, 290	708	400		. 2,140		
$\frac{382}{315}$	320 474	3	18	32 24	1, 420 1, 500	827 713	511 479	•••••	2, 190 2, 450	76	3
303	700	2	7	31	1,840	802	552		3, 110		3
	600			. .	² 2, 740				3, 920	.	
1,000 1,330	540 685	30	128	1 4	² 3, 210 3, 580	401	271		4,590	8 5	2
-,					0,000				0,		
	- 83 123	•	4		² 610	320			1,060		
55	99		23	 	² 592				1,020	7 4	
00	101		11	99	1 990	401	1)		010	1 I 7 E	41
244 231	434 655	4 5	10	24 32	1, 330 1, 670	022	394 		2, 260 2, 840	77	
85	695								2, 860	 .	
90 61	34 70		<u>-</u>			210			800		
01	10		01		4/0	010			. 100		

surveys of the Walnut River basin, December 1961 to October 1963-Continued
Sample source and date of collection	Dis- charge (cfs)	Silica (SiO ₂)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)
RM 73 4, Four Mile Creek								
Dec 7, 1961	22 23	12	213	46	61	34	361	0
Nov 1, 1962	12 20	13	208	56	84	62	346	····
Aug 16, 1963	4 24	12	310	72	82	58	264	Ŏ
Oct 9, 1963	3 58	11	336	67	86	58	285	0
Dec 7 1961	1 20	0.0	238	46	580	74	290	0
Apr 25, 1962	1 <u>20</u> 49		274	60			256	
Nov 1, 1962	68	11	189	39	333	87	271	0
Aug 16, 1963	05		364	67				
Dec 7. 1961	12							
RM 71 2, Walnut River at Gordon,								
Dec 7, 1961	304	12	166	37	117	46	371	0
Apr 25, 1962	144		142	41	144		271	
Nov 1, 1962	165	13	161	35	144	64 77	332	0
Oct 9, 1963	23 0	15	198	53	200	97	251	ŏ
RM 63 6, Little Walnut River	-0 0							
Dec 8, 1961	107	10	90	14	61	24	278	0
Apr 20, 1902	30 24 1	12	80 98	10	61	38	303	0
Oct 9, 1963	81	65	69	11	41	42	229	ŏ
RM 58 5, Walnut River near Douglass								
(07-1475), main-stem site	380	12	140	32	110	39	364	0
Apr 25, 1962.	204		126	38	119		285	`
Nov 1, 1962	208	11	149	32	136	61	332	0
Oct 9, 1963	24 55	5	184	52	243	93	222	0
Dec. 8, 1961	13 1	95	115	27	64	28	386	0
Apr 25, 1962.	5 13		110	29			344	
Nov 1, 1962	1 44	15	102	26	26 10	48	342	22
BM 524 Eight Mile Creek	2 01	10	80	21	19	40	320	0
Dec 8, 1961	11 9	12	170	48	42	29	332	0
Apr 25, 1962	6 38	:	206	49			334	
Nov 1, 1962	3 88	15	245	50	40	48	390	0
RM 49 2. Pole Cat Creek	10	11	201	05	0,		0.2	Ū
Dec 8, 1961.	9 51	85	106	47	3 9	28	244	0
Apr 25, 1962	4 10	- 11 -	147	55 43	33	5.9	359	0
Oct 9. 1963	1 03	90	78	24	15	63	261	ŏ
RM 47 0, Rock Creek 1	10.0			10	50	0.5	051	0
Dec 8, 1961	46 8	190	80	10	52 63	2036	201	0
RM 25 8. Dutch Creek ¹	0.01	10	101	10	00	00	200	Ũ
Dec 8, 1961	71 2	9	78	13	50	24	234	0
Apr 25, 1962	21 30		98	16	54	4 7	295	0
RM 22.6 Walnut River at Winfield	4 84		100	19	04	4 (022	0
(07-1478), main-stem site								
Dec 8, 1961	668	13	144	28	91		373	0
Apr 25, 1962	310	12	114	34 31	100	57	209	0
Oct 9, 1963	25 22	25	141	39	148	85	215	ŏ
RM 18, Walnut River at Arkansas								
City, main-stem site	720	12	141	96	86	34	373	0
Nov 9, 1963	270	12	109	30	104	61	239	ŏ
Oct 9, 1963		. 60	113	26	104	70	212	0

TABLE 8 — Chemical analyses of streamflow during combined seepage-salinity

No flow during some surveys
 Estimated
 Sample taken from below dam Withdrawals of about 5 6 cfs upsteam during survey
 Average of three samples

Sulfate (SO4)	Chloride (Cl)	Fluo- rıde (F)	N1- trate (NO3)	Boron (B)	Dis- solved solids (residue at 180° C)	Hard- ness as CaCO ₃	Noncar- bonate hard- ness as CaCO ₃	Sodium adsorp- tion ratio	Specific conduct- ance (mi- cromhos per cm at 25° C)	pН	Phos- phate PO4
412 623 638 789 804	94 115 136 142 154	05 7 8 6	$\begin{array}{c} 7 \\ 12 \\ 3 \\ 7 \\ 7 \end{array}$	0 21 41 36 36	1, 080 1, 370 1, 440 1, 600 1, 670	720 894 964 1,070 1,110	424 680 854 880		1, 580 1, 840 1, 890 2, 090 2, 190	77 78 76 76	0 1
99 66 135	1, 210 1, 550 780 1, 890	1 2	15 62 4	28 - 30	2, 400 2, 960 1, 640 3, 520	783 930 632	545 410		4, 580 5, 240 2, 930 6, 180	77 77	2
30	400								1, 870		
186 215 172 259 315	231 278 286 426 560	3 7 4 5		30 30 27 30	958 1, 020 1, 010 1, 290 1, 580	566 523 546 612 712	262 274 410 506		1, 780 1, 740 1, 710 2, 210 2, 630	77 78 79 79	5 4 2
24 23 21 19	110 131 124 75	1 1 2	36 15 9 5	08 15 08	466 491 515 351	282 278 310 217	54 62 29		900 860 880 630	79 79 78 78	 1
155 151 148 285	205 239 255 510	2 3 5		21 	846 931 926 1, 410	504 470 504 672	206 2 3 2 490		1, 420 1, 540 1, 530 2, 400	78 77 76	 5 3
49 48 28 24	120 172 46 33	$\frac{2}{2}$	66 53 5 5 5	08 12 08	592 708 448 369	398 394 362 298	82 45 36		1, 110 1, 190 740 630	78 83 77	4 1
370 447 523 600	37 40 40 45	4 4 4	97 62 30 16	19 32 30	884 1, 030 1, 180 1, 250	621 716 846 894	349 522 614		1, 410 1, 440 1, 490 1, 610	77 79 78	 3 6
276 328 231 80	34 44 35 17	- 3 3	$ \begin{array}{r} 8 & 4 \\ 9 & 7 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \end{array} $	18 	656 850 689 373	458 593 516 293	258 222 79		$1,060 \\ 1,240 \\ 1,010 \\ 600$	74 78 77	2 2 2
17 16	99 141	1 1	$31 \\ 4$	08 10	411 529	256 318	50 78		800 920	79 80	2
25 34 27	92 112 102	02 2	66 71 35	0 05	400 504 499	248 310 316	56 52		750 870 850	79 78	6
114 149 146 231	172 203 227 300	2 3 4	$egin{array}{ccc} 4 & 2 \\ & 4 \\ 1 & 5 \\ 5 & 3 \end{array}$	24 24 23	781 826 842 1, 020	474 424 457 512	168 212 225 336	1 8 2 2	1, 330 1, 380 1, 410 1, 710	78 76 78	 3 1
114 117 143	166 208 206	2 3 3	$\begin{smallmatrix}8&0\\&4\\1&1\end{smallmatrix}$	16 21 21	745 729 751	459 396 389	153 200 215		1, 260 1, 240 1, 260	80 74 18	5 5

surveys of the Walnut River basin, December 1961 to October 1963-Continued

³ Sample probably is not representative of streamflow cross section
 ⁶ Average flow
 ⁷ Average of two samples

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TABLE 9 — Chemical analyses of streamflow during combined seepage-salinity

[Results in milligrams per liter, except as indicated

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Sample source and date of collection	Dis- charge (cfs)	Silica (SiO ₂)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)
RM 38 1, main-stem site Dec 7, 1961 Apr 24, 1962 Aug 30, 1962 Nov 1, 1962 Mar 21, 1963 Oct 9, 1963 PM 36.2. PM 36.2.	7 58 4 52 1 79 3 95 3 92 14	90 12 14 95	218 238 273 268 230 318	77 80 79 83 69 82	181 183 146 172 132 88	4 3 6 2 6 1 6 0	390 359 259 386 405 259	0 0 0 0
Image: State State Dec 7, 1961 Apr 24, 1962 Nov 1, 1962 Oct 9, 1963 State RM 35 7, Averys Creek or East Rm 35 7, Averys Creek or East	3 92 2 15 1 64 21	10 15 16	144 136 157 178	53 50 52 54	40 31 27	33 57 53	395 342 425 354	0 0 0
Branch whitewater River Dec 7, 1961 Apr 24, 1962 Nov 1, 1962 RM 31 3, main stem-site Dec 7, 1961	3 90 3 03 1 48 19 35	11 - 13 - 10	134 153 133 189	42 46 45 59	57 - 44 101	33 57 38	337 339 376 368	0 0 0
Apr 24, 1962 Aug 30, 1962 Nov 1, 1962 Mar 21, 1963 Oct 9, 1963 RM 30 9, diversion, Vickers Refinery	14 36 4 42 9 12 10 48 69	13 13 9 5	200 203 222 174 281	64 63 66 45 58	108 94 108 75 62	6 6 6 1 5 7	366 259 395 349 293	0 0 0 0
Dec 7, 1961 Apr 24, 1962 Nov 1, 1962 Oct 9, 1963 RM 30 8, Diagonal or Diamond Creek	1 90 2 14 1 34 1 63		229 253	62 66	51	55	351 290	···· · · · · · · · · · · · · · · · · ·
Apr 24, 1962 Nov 1, 1962 Oct 9, 1963 RM 29 5, Dry Creek ¹	3 06 2 21 1 62 67	13 14 16	303 308 366 420	59 60 62 73	53 48 48	5 0 5 3	278 388 295	0 0 0
Apr 24, 1962 Nov 1, 1962 RM 29 2, Brush Creek Dec 7, 1961 Apr 24, 1962	2 82 1 76 1 33 82 31	90 80	88 123 191 114	38 37 40 68 53	34 34 360	66	300 393 461 442	0 0
Nov 1, 1962 Oct 9, 1963 RM 28 4, unnamed tributary ¹ Dec 7, 1961 Apr 24, 1962	35 17 15 08	9575	82 198	35 64 38	304 630	14 17	361 327 	00
RM 28 4, unnamed tributary 1 Dec 7, 1961 Apr 24, 1962 RM 27 6, unnamed tributary Dec 7, 1961	2 05 2 03 79	3 0	61 141	26 50	196	4 6	454 156	0
Apr 24, 1902 Nov 1, 1962 Oct 9, 1963 RM 26 6, unnamed tributary 1 Dec 7, 1961 RM 26 6, unnamed tributary 1	97 27 2 2 02	10 3 5	216 265	70 85	184 235	77 93	100 110 110	0 0
Dec 7, 1961	2^{2} 01 29 74 19 22 5 40	19	182 230 230	61 55 67	145 167 187	44	315 344 259	0
Nov 1, 1962 Mar 21, 1963 Oct 9, 1963 RM 25 1, Gillion or Four Mile Creek Dec 7, 1961	12 54 13 66 98 3 34	12 13 12 9 0	231 191 354 90	67 54 100 51	140 119 407 39	$ \begin{array}{r} 8 & 8 \\ 7 & 5 \\ 12 \\ 2 & 8 \end{array} $	390 351 300 307	0 0 0 0
Apr 24, 1962 Aug 30, 1962 Nov 1, 1962 Mar 21, 1963 Oct 9, 1963	$ \begin{array}{r} 2 & 28 \\ 42 \\ 1 & 38 \\ 1 & 98 \\ 12 \\ \end{array} $	13 10	98 109 111 107 86	56 49 42 35 55	40 26 26 28	53 37	283 337 354 288	0 0

See footnotes at end of table

surveys of the Whitewater River subbasin, December 1961 to October 1963

Dis-solved Noncar-Specific Fluo-rıde (F) N1-Hard-Sodium Phosbonate hardconductadsorp-Sulfate Chloride Boron pН phate PO₄ trate (NO₃) ance (misolids ness as (SO4) (Cl) (B) CaCO₃ cromhos (residue ness tion at 180° C) as CaCO₂ ratio per cm at 25° C) 1, 500 1, 700 1, 660 1, 660 1, 402 1, 720 $\begin{array}{r}
 2 & 7 \\
 2 & 6 \\
 2 & 0 \\
 2 & 4 \\
 2 & 0 \\
 1 & 1
 \end{array}$ 2, 390 2, 480 2, 350 2, 460 2, 090 2, 190 335 337 290 0 28 860 923 04 2.6 540 446 77.... 523 670 4 4 - --- ----------1,006 794 28 15 542 344 5 4 1,010 694 2 1 429 265 5 6 858 526 84**0** 1,130 160 4 28 918 250 44 4 12 13 742 577 253 ... 1,170 78... ~ - - $\begin{array}{c}
 7 & 1 \\
 2 & 6 \\
 2 & 7 \\
 \end{array}$ 257 1, 140 1, 160 1, 240 280 270 30 732 545 605 -8 1 7 7 23 30 3 43 800 -362 30 886 376 2 16 666 231 1,210 15 12 7 5 13 723 826 507 78..... 160 119 2 223 150 1, 310 1, 120 108 570 ... - $\ddot{2}$ $\overline{2}$ 81 18 99 717 517 209 -1, 130 $\begin{array}{c}
 1 & 6 \\
 1 & 7 \\
 1 & 5 \\
 1 & 5
 \end{array}$ 363 178 8 3 19 714 412 1,840 76. 4 - - - -1, 250 1, 250 1, 222 1, 290 223 1, 860 1, 750 1, 860 412 487 188 178 $\dot{7}62$ 554 501 78 78 766 4 4 . - - -23 13 422 304 214 134 $\begin{array}{c}1&6\\1&3\end{array}$ 825 964 333 1,450 8075 619 644 106 5 1, 360 700 ā 5 28 940 2 363 ² 178 2 1, 130 1,840 42. 491 400 160 1,410 1,300 826 . 1,920 - --- ----- - ----- --- - -1,880 1,700 76 205 - - -......... . <u>5</u> 3 8 902 644 $\overline{2}$ 40 604 106 1,300 1, 430 1, 500 1, 640 1, 850 1, 910 2, 040 2, 240 701 91 5 53 19 998 738 76..... 1, 020 1, 170 1, 350 731 89 õ 7 8 7 6 8 57 850 32 - $\tilde{2}$ 1 1 786 98 1, 040 78 28 1, 910 4 129 3 880 79..... 24 $\mathbf{22}$ 10 497 373 123 - ----149 157 28 34 $\frac{12}{11}$ 521 635 372 472 840 990 79 8 150 - - -3 ī8 1, 890 2, 080 1, 280 2, 810 75 2, 870 3, 140 559 420 5 40 756 378 7 6 80 73 53 814 318 502 32 434 4 66 30 348 1, 980 198 1, 390 310 6 63 757 489 3,860 13 4 75 134 202 1 190 -- --- ---22.... -----236 869 403 1, 430 -- ----..... 60 263 -----1,290 65 13 259 475 ---- --..... 1, 230 1, 280 1, 640 1, 990 $egin{array}{ccc} 3 & 6 \ 1 & 5 \ 3 & 2 \ 4 & 1 \end{array}$ 491 251 8 15 558 430 1,900 7 7 569 234 624 736 32 30 . 758 252 826 920 846 371 1 Ŏ 1, 010 130 2,690 8,750 15 790 2,900 ----- $24 \\ 26 \\ 28$ 93 53 1, 230 704 2,050 2,210 2,380 2,100 364 415 266 4 21 7 8 446 1, 420 1, 576 315 800 -. -- --650 79 79 79 79 74 512 404 1016 378 872 8 36 11 -----4 ----30 1, 410 1, 184 2, 710 532 411 $\begin{array}{c}
 2 & 1 \\
 2 & 0 \\
 4 & 9
 \end{array}$ 301 852 4 4 49 49 1,840 4,250 323 245 $\frac{13}{32}$ 699 566 965 1. 050 1.290 196 217 3 26 603 669 434 182 1,020 1.060 7 8 48 16 49 474 474 242 174 $\begin{array}{c} 7 & 9 \\ 8 & 2 \end{array}$ ----.... - - - -268 35 667 990 -----4 21 176 28 10 571 450 880 8 2 ĩ 126 32 3 14 13 541 598 411 121 860 81 33 910 210 440 ----

RM, river mile upstream from mouth of main stem]

Sample source and date of collection	D1s- charge (cfs)	Sılıca (S1O ₂)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO2)
RM 24 9, unnamed tributary						-		
Dec 7, 1961	2 33	90	157	44	214	34	303	0
Aug 30 1962	1 10		101	00 48	281	• • • • • • • •	271 234	
Nov 1, 1962	85	11	182	49	203	12	366	0
Mar 21, 1963	1 04	75	184	45	192	51	339	Ő
Oct 9, 1963	12		175	57	308		276	• • • • • • • • •
RM 24 4, unnamed tributary	2 10							
RM 23.2. main-stem site	- 10							
Dec 7, 1961	38 50	11	192	56	130	38	388	0
Apr 24, 1962	22 64		190	66	130		356	
Aug 30, 1962	6 64		198	63	191		254	
NOV 1, 1962	16 12	13	213	60	126	84	383	0
Oct. 9, 1963	19 04	12	256	48 74	243	10	268	0
RM 21 5 Rock Creek	1 02		200	.1	210	20	200	Ū
Dec 7, 1961	2 30	95	130	58	75	34	346	0
Apr 24, 1962	1 39		122	68			249	
Aug 30, 1902	07 69		90	40	04	6 7	2/1	
Mar 21, 1963	1 00	12	126	51	62	51	349	ŏ
Oct 9, 1963	04	14	84	35	41	53	320	ŏ
RM 20 9, unnamed tributary 1								
Dec 7, 1961	34	70	78	28	33	46	298	0
Aug 30, 1902	2 01		107	39	4/		. 410	
Mar 21, 1963	- 00	10	65	30	38	4 0	195	19
RM 19 1, main-stem site		-•						
Dec 7, 1961	44 16	11	155	58	130	40	295	0
Apr 24, 1962	24 29		186	66	138	• • • • • • • •	356	•
Aug 30, 1962	17 00	13	201	01 56	102	13	. 217 393	
Mar 21 1963	20 18	12	160	45	92	7 0	337	ŏ
Oct 9, 1963	2 18	6	224	65	206	10	298	Ō
RM 17 9, unnamed tributary 1								
Dec 7, 1961	2 15							• •••••
Apr 24, 1902	17	•••••	202	04			400	
RM 17.6. unnamed tributary	00						••••••	
Dec 7, 1961	2 01							
Aug 30, 1962	07		. 117	51	75		. 371	
Nov 1, 1962	10	14	133	57	83	4 2	412	. U
Mar 21, 1963	04	10	127	57	80	32	308 376	ů N
RM 17.0 West Branch Whitewater	04	17	100		00	40	070	0
River								
Dec 7, 1961	22 45	13	232	72	61	40	298	0
Apr 24, 1962	431 50		266	81			. 320	
Aug 30, 1902	20.68	12	- 242	67	57	8.3	339	0
Mar 21, 1963	20 13	îĩ	209	72	64	60	237	ŏ
Oct 9, 1963	2 73	15	251	55	78	75	329	Ó
RM 16 3, Stearns Creek								
Dec 7, 1961	2 06	75	115	35	169	32	337	0
Apr 24, 1902	48		. 104	41 62	680		- 290 303	
Nov 1, 1962	1 25	11	208	56	540	15	378	0
Mar 21, 1963	2 69	10	136	36	426	9 0	217	, Q
Oct 9, 1963	78	19	334	87	1, 190	25	388	; O

TABLE 9---Chemical analyses of streamflow during combined seepage-salinity surveys

See footnotes at end of table

Sulfate (SO4)	Chloride (Cl)	Fluo- ride (F)	N1- trate (NO3)	Boron (B)	Dis- solved solids (residue at 180° C)	Hard- ness as CaCO₃	Noncai- bonate hard- ness as CaCO ₃	Sodium adsorp- tion ratio	Specific conduct- ance (mi- cromhos per cm at 25° C)	pН	Phos- phate PO4
145 170 172 158 183 210	450 520 565 455 424 635	03	15 4 2 1 5 4 4 2 7	0 15 16 16	1, 240 1, 450 1, 498 1, 310 1, 278 1, 580	572 607 557 656 644 670	324 365 356 366		2, 190 2, 390 2, 440 2, 230 2, 230 2, 700	75 79 78 79	021
45 314 356 421 350 264 382	29 241 257 370 260 205 610	4 4 4 3	84 15 10 19 56 49	16 28 13 23	1, 200 1, 290 1, 432 1, 270 1, 038 1, 830	709 745 753 778 631 942	391 545 464 341 722	2 1 2 1 3 0 2 0 1 8 3 4	740 1, 850 1, 970 2, 210 1, 910 1, 610 2 880	76 78 78 80 72	
130 167 74 110 110 47	210 295 185 294 179 76	2 1 3 2	3 1 4 10 4 4 1 7 26	12 18 15 08	818 1,000 713 921 744 500	563 584 428 627 524 354	279 206 359 238 92		1, 410 1, 660 1, 160 1, 650 1, 290 860	77 78 81 81 76	
31 128 110 54	72 40 36 86	4 4	15 15 4	07 16	378 590 417	310 428 286	66 88 94		710 970 1, 070 730	78 79 84	2
302 340 386 326 231 357	244 274 309 246 204 470	4 	75 31 10 18 29 44	18 19 14 21	1, 120 1, 290 1, 246 1, 230 974 1, 560	625 735 664 732 584 826	383 486 418 308 582	23 22 27 19 14 31	1, 810 1, 970 1, 940 1, 850 1, 550 2, 480	76 76 78 81 74	1 6 3 4 6
420 322 60	530 430 187		62		1, 550	767	· · · · · · · · · · · · · · · · · · ·		2, 900 2, 450 1, 410		
20 162 191 207 223	14 131 142 138 155	3 4 3	89 11 36 97	23 16 16	786 847 845 919	502 566 526 578	198 228 224 270		540 1, 290 1, 420 1, 350 1, 440	8 1 8 0 8 0 8 0 8 0	1 6 2
597 665 566 642 590 485	100 149 157 101 105 169	5 	$\begin{array}{c} 7 & 1 \\ 2 & 2 \\ 1 & 0 \\ 4 & 0 \\ 4 & 0 \\ 1 & 0 \end{array}$	27 41 27 30	1, 270 1, 450 1, 308 1, 380 1, 254 1, 240	875 996 859 972 818 852	631 637 694 624 582		1, 870 1, 990 1, 820 1, 850 1, 820 1, 790	79 80 81 80 78	2 3 3
56 65 142 124 83 247	326 385 1, 330 1, 090 820 2, 300	3 1 2 1	$ \begin{array}{r} 3 & 6 \\ 8 & 0 \\ 1 & 0 \\ 5 \\ 4 \\ 4 \end{array} $	10 51 24 84	884 1, 010 2, 780 2, 350 1, 736 4, 530	431 428 849 749 488 1, 190	155 527 439 310 873		1, 660 1, 810 4, 850 4, 110 3, 260 7, 780	78 75 76 72 72	 1 2 1

of the Whitewater River subbasin, December 1961 to October 1963-Continued

Sample source and date of collection	Dis- charge (cfs)	Sılıca (S1O2)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO ₃)	Car- bonate (CO3)
RM 144, Whitewater River at								
stem site								
Dec 7, 1961	90 57	10	219	60	112		403	0
Apr 24, 1962	48 44	290	206 216	68 62	131		334	
Nov 1, 1962	42 86	15	261	63	101	24	398	0
Mar 21, 1963	41 78	12	203	55	96	61	354	0
RM 14 2. unnamed tributary	0 54	11	234	61	200	11	334	0
Dec 7, 1961	1 27	12	226	52	704	12	390	0
Apr 24, 1962	40 36	10	245 278	68 67	964	17	349 368	
Oct 9, 1963	15	13	362	90	1, 250	18	410	ŏ
RM 138, municipal sewage effluent,								
Dec 7, 1961	01							
Apr 24, 1962	2 30	• • • • • • • • •	150	53			549	
Nov 1, 1962	28 19	31	160	69	320	24	466	
RM 13 1, unnamed tributary			-00					-
Dec 7, 1961	81 74	12	96 88	38 35	23	29	417 388	0
Nov 1, 1962	18	12	97	35	26	4 0	425	0
Oct 9, 1963	2 01		82	44		•••••	344	
Dec 7. 1961	09							
RM 10 8, unnamed tributary 1	07	10		0.0	10	1 7	107	0
Dec 7, 1961	27 2 15	13	96 74	33	13	17	427 344	0
RM 10 8, unnamed tributary								
Dec 7, 1961	2 57		150	46			276	
Nov 1, 1962	1 24	10	216	49	568	94	337	0
Oct 9, 1963	38	14	244	73	780	12	3 22	0
Dec 7, 1961	2 04							
RM 96, unnamed tributary (spring								
fed) Dec 7 1061	64	10	01	30	14	17	405	. 0
Apr 24, 1962	49		86	32			393	
Nov 1, 1962	37	11	88	29	15	18	393 378	0
RM 96, unnamed tributary (spring	09	21	00	00	10	10	010	U
fed)	c 0	10	101	54	200	1 2	246	
Apr 24, 1962	09 58	13	. 197		290	40	. 288	
Nov 1, 1962	47	13	199	63	361	58	344	. 0
Oct 9, 1963	13	16	246	79	481	57	300) U
Dec 7, 1961	1 12	10	72	34	16	16	349) 0
Apr 24, 1962	76	- 12 -	. 58	35	20	3 1	- 329 376) i 0
RM 8 6. unnamed tributary 1	10	12	10		. 20	01	010	, ,
Dec 7, 1961	2 08			05				
Apr 24, 1962	2 06			20				,
RM 8 4, main-stem site						4.0		۰ ^۱
Dec 7, 1961	98 58	12	179 197	58	116	40	- 312 - 342	2 U
Nov 1, 1962	48 62	13	226	62	115	77	386	j 0
Oct 9, 1963	8 36	17	198	56	i 257	11	290	J 0
See footnotes at end of table								

 $T_{\texttt{ABLE}} \ 9 \ - \ Chemical \ analyses \ of \ streamflow \ during \ combined \ see page-salinity \ surveys$

Sulfate	Chloride	Fluo- ride	N1- trate	Boron	Dis- solved solids	Hard- ness as	Noncar- bonate hard-	Sodium adsorp-	Specific conduct- ance (mi-	pН	Phos- phate
	(01)	(r) 	(1103)	(D)	at 180° C)	04003	as CaCO ₃	iatio	per cm at 25° C)		
397 439	204 246	03	53 15	034	1, 2 3 0	79 3 794	463 520	17 19	2,050 2,040	79	
454	281		22		1,412	794	536		2,080	74	
361	201	4	25	22	1, 420	731	441	16	1, 775	79	3
376	510	4	13	32	1, 750	834	560	38	2, 750	76	5
111 102	1,360 1,730	1	$\begin{array}{c} 6 & 6 \\ 6 & 2 \end{array}$	44	2, 750 3, 380	778 891	458		4,960 6,090	72	
95 105	1,930 2,540	1	15	54 54	3,690 4,710	969 1. 270	667 937		6, 470 8, 290	7575	1
100	2,010	-	U	01	4, 110	1,210	307		0, 200		-
181	640		2 1	····	² 2, 020	500			3, 210		
140	342 342		5		1, 420				2, 250		
212	530	4	106	64	1, 690	682	300		2, 740	74	43
47 37	28 32	2	84 42	10	464 428	396 364	54		820 760	78	
39 83	36 46	1	14	18	467 502	386 386	38		820 860	79	2
15	8.0				001				460		
15	14	3	6.6	08	305	375			700	7 8	
23	14		53		350	308			640		
8	675				² 1, 930				2,860	.	
67 87	885 1,180	1	42 5	40	1, 960 2, 410	563 740	464		3, 35 0 4, 270	78	
105	1,600	0	4	57	3, 110	909	645	••••••	5, 590	75	
9	15								530		
22	14	2	97	07	378	350	18		670	77	
20 21	15 15	· ····;·	$97 \\ 84$	16	386 400	346 338	16		680 680	7 8	1
13	13	$\hat{2}$	10	05	386	330	20		640	75	î
33	710	2	53	10	1 520	674	300		2 780	72	
40	970	·····;·	42		1,990	762			3,650		
3 9	1,200	1	7 1 9	37	2, 360	938	474 646		3 , 100 4 , 270	73^{4}	
21	18	2	84	10	346	319	33		620	78	
19 18	17 21	· ···i	62 5	07	332 358	288 322	14		580 630	- o ⁻	1
25	32								640		
23 18	38 33	<i>-</i> -	22		324	280			560 790		
361	218	4	75	24	1, 190	685	429	19	1,850	77	
390 406	261 236	3	$22 \\ 20$	34	1, 300 1, 330	767	503	21	2,040	- 8.0	1 3
313	510	š	i 9	30	1, 580	724	486	4 2	2, 580	73	4

of the Whitewater River subbasin, December 1961 to October 1963-Continued

Sample source and date of collection	Dis- charge (cfs)	Silica (SiO ₂)	Cal- cium (Ca)	Mag- nesium (Mg)	Sodium (Na)	Potas- sium (K)	Bicar- bonate (HCO3)	Car- bonate (CO3)
RM 7 2, unnamed tributary 1								
Dec 7, 1961	² 020							
RM 5 9 unnamed tributary 1			_					
Dec 7, 1961	32	10	83	31	20	26	381	0
Apr 24, 1962	14		72	27			334	
NOV 1, 1962	07	13	70	33	21	2 9	371	U
(forming mall)								
1000110000000000000000000000000000000	19	0.0	173	50	620	5 9	220	0
Apr 24 1062	12	50	230	80	020	0 2	208	0
Nov 1, 1962	05		200	00				
Oct 9, 1963	2 02		412	178			178	
RM 38. mainstem site								
Dec 7, 1961	109 0	12	214	59	132	38	407	0
Apr 24, 1962	49 80	-	186	67	151 .		303	
Nov 1, 1962	50 13	13	229	58	140	74	378	0
Oct 9, 1963	968	15	217	62	295	11	310	0
RM 24, Elm Creek			~~			• •		•
Dec 7, 1961	27	12	98	22	110	30	307	0
Apr 24, 1962	2 20		80	22			312	
DCt 9, 1903	08	22	82	23	90	34	324	U
Dec 7 1061	2 70	14	74	12	10	4 1	242	٥
Apr 24 1062	1 10	14	80	28	10	41	332	v
Oct 9 1963	35	16	87	19	14	4 2	322	0
RM 08 (07-1471). Whitewater River at			0.					
Augusta main-stem site								
Dec 7, 1961	113 0	13	212	58	136	40	412	0
Apr 24, 25, 1962 ⁵	58 00		186	67	162 .		314	
Nov 1, 1962	52 57	12	226	64	152	74	386	0
Aug 16, 1963	24 00	75	192	57	230	79	285	0
Oct 8, 1963	935	15	216	64	339	12	305	0

 ${\tt Table 9--Chemical \ analyses \ of \ streamflow \ during \ combined \ see page-salinity \ surveys}$

¹ No flow during some surveys ² Estimated ³ Average of two samples

Sulfate (SO4)	Chloride (Cl)	Fluo- rıde (F)	N1- trate (NO3)	Boron (B)	Dis- solved solids (residue at 180° C)	Hard- ness as CaCO ₃	Noncar- bonate hard- ness as CaCO ₃	Sodium adsorp- tion ratio	Specific conduct- ance (mi- cromhos per cm at 25° C)	pН	Phos- phate PO4
60	500								2, 160		
28 19 21	23 26 23	03	$5 \ 3 \ 2 \ 2 \ 1 \ 8$	0 08	381 332 378	334 290 310	22 6		680 590 700	79 81	0 1
27 24 13 7 5	1, 320 1, 700 1, 660 4, 280	1	104	13	2, 43 0 3, 160 7, 290	674 903 1, 760	494		4, 520 5, 720 5, 640 12, 500	75	
353 383 398 307	252 298 274 600	4 3 3	$ \begin{array}{r} 6 & 6 \\ 1 & 5 \\ 4 & 0 \\ 1 & 4 \end{array} $	27 30 30	1, 320 1, 340 1, 360 1, 780	776 740 810 796	442 500 542	$ \begin{array}{r} 2 & 1 \\ 2 & 4 \\ 2 & 1 \\ 4 & 6 \end{array} $	1, 960 2, 080 2, 060 2, 960	77 80 76	4
33 29 20	191 1 34 96	2 2	$\begin{smallmatrix}1&9\\6&2\\1&1\end{smallmatrix}$	12 <u>- 13</u>	618 530 462	335 305 299	83 	 	1, 120 960 790	77	3
33 45 43	12 23 14	2 2	$\begin{smallmatrix} 7 & 1 \\ 6 & 2 \\ 9 \end{smallmatrix}$	10 	270 372 374	238 314 295	40 31		470 670 580	75	3
337 366 382 315 303	267 336 320 474 700	4 3 3 2	$71 \\ 10 \\ 18 \\ 4 \\ 7$	19 32 24 31	1, 290 1, 380 1, 420 1, 500 1, 840	768 742 827 713 802	430 511 479 552	2 1 2 6 2 3 3 7 5 3	1, 900 2, 160 2, 190 2, 450 3, 110	78 80 76 76	

of the Whitewater River subbasin, December 1961 to October 1963-Continued

Discharge measurement believed to be erroneous Discharge probably about 23 cfs
 Average of two nearly identical measurements and samples

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