

aquifer. This large number of nodes provides sufficiently detailed resolution for the purposes of this investigation. The model parameters range in accuracy from the well-defined data on aquifer extent, thickness, and outcrops, to relatively poorly defined data on hydraulic conductivity and recharge and discharge. These data adequately define the hydrologic conditions in the model area, and a good model calibration was achieved.

The model was calibrated by comparing the model-calculated potentiometric surface maps with measured potentiometric surface maps and by comparing model-calculated discharge with measured changes in streamflow. The close agreement between the calculated and measured potentiometric surfaces for each aquifer indicates that the model is a good simulator of the steady-state flow system in the aquifers. The water budget calculated by the model also should be a good estimate of the actual water budget for the area and likely is of better accuracy than water-budget information based on field measurements.

It generally is difficult or impossible to make direct field measurements of most components of a water budget. In many instances, the component to be measured is spatially or temporally variable or is inaccessible for measurement. Gain or loss in streamflow may occur in response to ground-water discharging into, or recharging from, a stream. The long-term average gain or loss in streamflow is difficult to measure because of the short-term effects of storm runoff, interaction with flow in alluvial aquifers, evapotranspiration from phreatophytes, and diversions. Gain or loss in streamflow was measured along 71 reaches of selected streams in July, August, and September 1986 (table 3). Pertinent gain-loss data are summarized in table 10 for purposes of comparison with surface-water gain-or-loss data calculated by the steady-state model. The difficulty in relating instantaneous measurements of streamflow to long-term average streamflow are apparent. However, the measured and model-calculated values of gain or loss are of comparable magnitude, which indicates that the model-calculated water budget likely is a reasonable estimate of the actual steady-state water budget.

GROUND-WATER GEOCHEMISTRY

The chemical composition of ground water is the result of geochemical processes that include dissolution of soluble minerals from the soil and aquifer matrix, chemical reactions and ion exchange reactions between dissolved constituents, and precipitation of minerals. The large number of dissolved constituents in water, and the complex geochemical processes that may affect the concentrations of these constituents, make identification of most geochemical reactions difficult even when adequate data are available. In the western part of the study area, ground-water-quality data are few and poorly associated with individual aquifers. In the eastern part of the area, the more numerous chemical analyses associated with specific aquifers enable evaluation of some geochemical processes. The prevalence of these geochemical processes in nature and the similarity of geology, hydrology, climate, and topography, between the eastern and western parts of the study area indicate that geochemical processes identified in the eastern part of the area also likely are occurring the western part of the area, even though data may be lacking.

Table 10.—*Measured and calculated gain or loss in streamflow in the eastern part of the study area*

Stream	Reach (fig. 23)	Date measured	Flow, in cubic feet per second	
			Measured gain (+) or loss (-) in streamflow	Model- calculated long-term average gain (+) or loss (-) in streamflow
Grassy Creek	1-3	07-22-86	+ 0.12	+0.03
		09-15-86	0 0.05	
	3-4	07-22-86	0 0.01	+0.01
		09-15-86	- 0.06	
	4-5	07-22-86	0 0.11	+0.06
		09-15-86	- 0.02	
5-6	07-22-86	- 0.02	+0.06	
	09-15-86	+ 0.03		
Foidel Creek	1-3	09-17-86	+ 0.08	+0.02
Middle Creek	1-2	09-17-86	0.0	+0.08
		09-17-86	+ 0.02	
"S" Creek	2-3	09-16-86	+ 0.02	+0.01
		08-13-86	0 0.02	
	4-5	09-16-86	- 0.02	+0.01
		08-13-86	0.0	
5-6	08-13-86	0.0	+0.01	
	09-16-86	+ 0.01		

About 75 water-quality analyses were available in the study area for U.S. Government observation wells completed in the Williams Fork Formation. About half of these samples were collected during 1980–81; the remaining samples were collected during earlier U.S. Geological Survey studies. In addition, data from about 1,000 chemical analyses of ground water are available from mining companies in the area. Results of most of these analyses have been published in various mine permitting or monitoring documents pertaining to the eastern part of the study area. An additional one-time sampling of domestic wells and springs was conducted by the U.S. Geological Survey in 1977 (Brogden and Giles, 1977). However, these domestic well data are of limited usefulness because of the lack of well-construction data and possible mixing of alluvial and bedrock water in the well.

Dominant Water Types and Distribution

The Twentymile aquifer contains water that primarily is a sodium bicarbonate type. Water in this aquifer commonly has dissolved-solids concentrations that range from 300 to 600 mg/L; the larger concentrations occur in the north-central part of Twentymile Park (fig. 40). Hardness averages about 20 mg/L as calcium carbonate, and the water is classified as soft. Sulfate concentrations generally range from 40 to 140 mg/L.

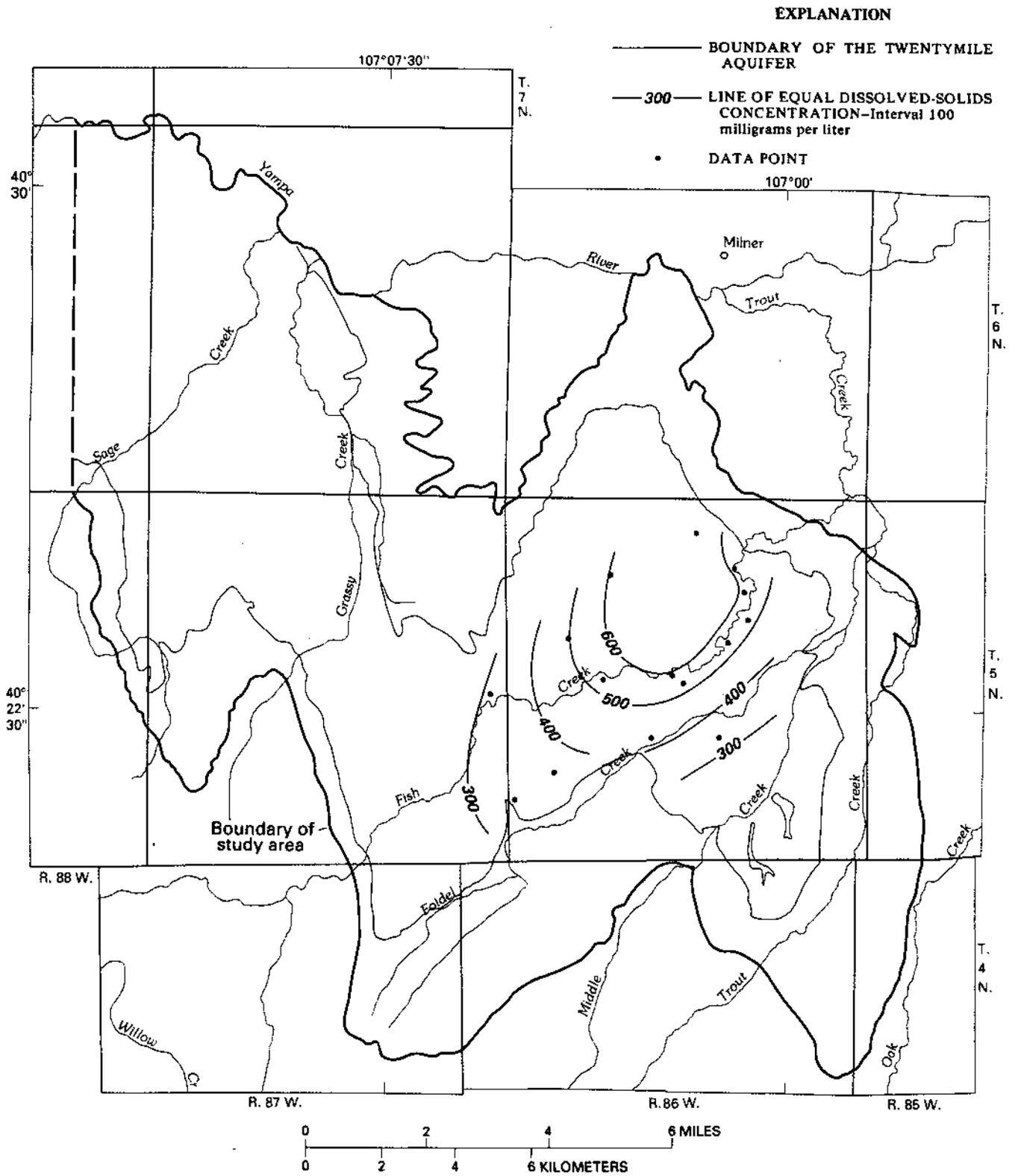


Figure 40.--Dissolved-solids concentrations of water in the Twentymile aquifer in the eastern part of the study area.

Water in the basal Williams Fork aquifer generally is a sodium or calcium bicarbonate type but may be a sulfate type in local areas. Calcium is the predominant cation near recharge areas along the margin of the aquifer. In these areas, calcium plus magnesium concentrations average about 250 mg/L; sodium plus potassium concentrations average about 70 mg/L. As the water moves into deeper parts of the aquifer it becomes a sodium bicarbonate type. Water in the deeper parts of the basal Williams Fork aquifer has calcium plus magnesium concentrations that average about 25 mg/L; sodium plus potassium concentrations average about 280 mg/L. The decrease in calcium plus magnesium concentrations and the concurrent increase in sodium plus potassium concentrations are the result of cation exchange reactions on the clay minerals of marine shales that are interbedded in the aquifer. Cation exchange does not affect water composition substantially until the water has moved about 1 mi into the aquifer (fig. 41). By the time the water has moved about 2 mi into the aquifer, most cation exchange is complete, and the water at greater distances along the flow path retains a relatively uniform sodium-dominant cation composition.

This cation exchange produces a natural softening of the ground water. Near the margins of the basal Williams Fork aquifer, where calcium and magnesium concentrations are large, the water is classified as very hard; the mean hardness is about 960 mg/L as CaCO_3 . In the central part of the aquifer, where the water has undergone cation exchange, the water is classified as soft to hard; the mean hardness is about 70 mg/L as CaCO_3 .

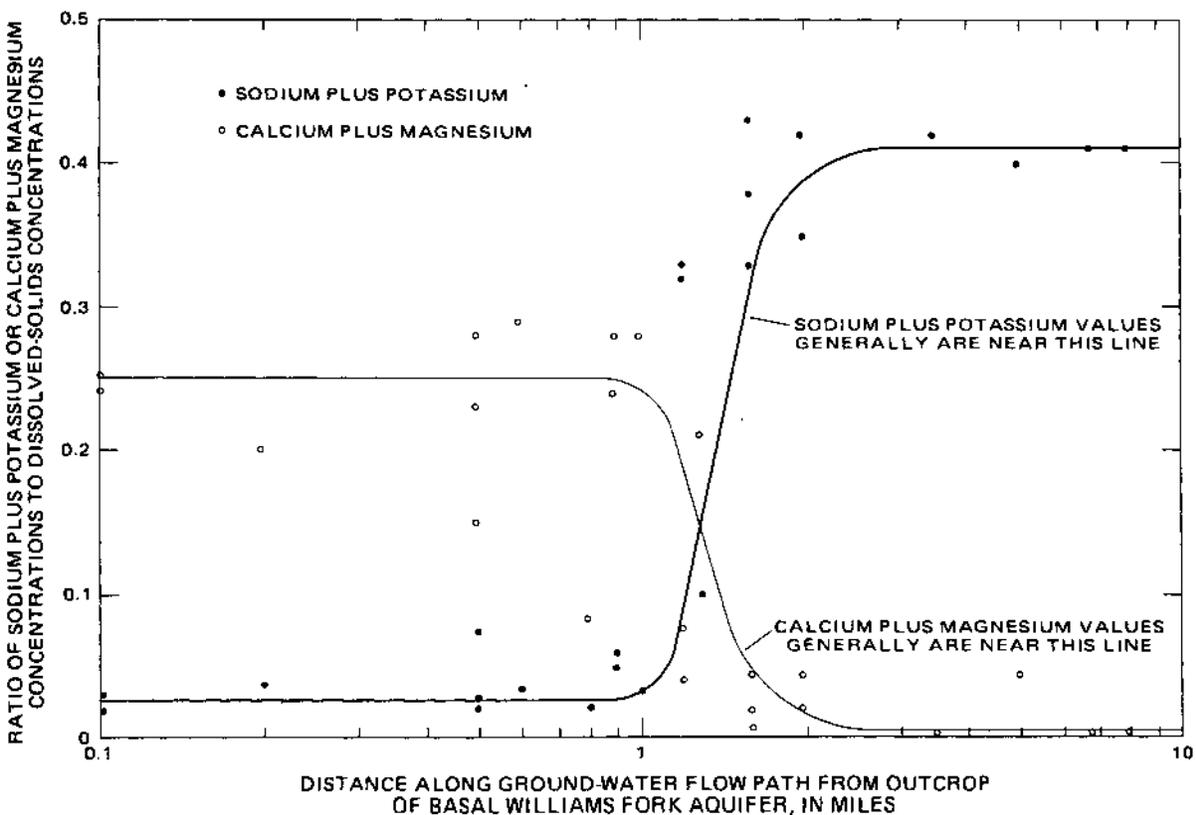


Figure 41.--Change in relative concentrations of cations in the basal Williams Fork aquifer.

In some parts of the basal Williams Fork aquifer, sulfate is the dominant anion in solution. Oxidation of sulfur minerals present in the coal and associated carbonaceous shale and dissolution of gypsum are the likely sources of the dissolved sulfate. Large amounts of sulfate are formed in the oxidizing environment of mine spoils; lesser amounts of sulfate occur in the undisturbed outcrops of the coal-bearing intervals. Ground water containing large natural concentrations of sulfate occurs sporadically along the recharge area near the basin margins. Near areas disturbed by mining, large sulfate concentrations are more prevalent. Sulfate concentrations generally range from 50 to 1,500 mg/L in the mined areas and from 50 to 400 mg/L in the undisturbed areas. The relative concentration of sulfate decreases at greater distance along the ground-water flow path downgradient from mined areas, as shown in figure 42. This decrease likely is caused by a combination of three geochemical processes: (1) Sulfate reduction—the precipitation of sulfate from solution in a reducing environment; (2) dispersion—the mixing and spreading of the water that contains large concentrations of sulfate into the surrounding water that contains small concentrations of sulfate; and (3) limited solute movement—water that contains large concentrations of sulfate has moved only a limited distance away from the mine during the time since mining began.

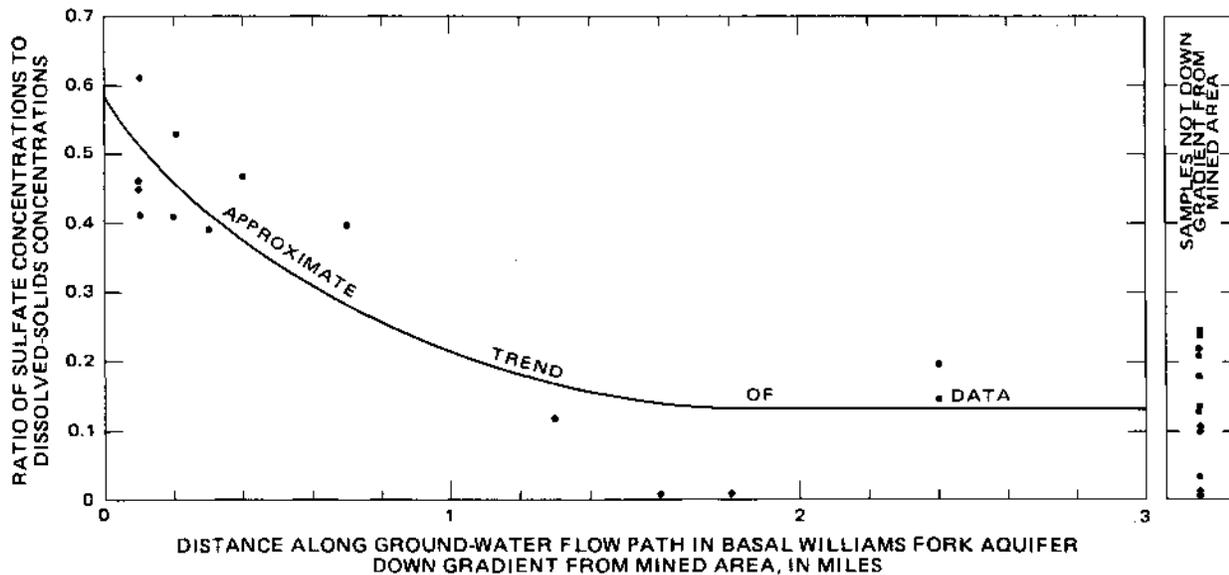


Figure 42.--Change in relative concentration of sulfate in the basal Williams Fork aquifer.

Dissolved-solids concentrations in the basal Williams Fork aquifer generally range from 300 to 1,400 mg/L in those areas where sulfate concentrations are small (fig. 43). Dissolved-solids concentrations larger than 1,000 mg/L are present near the eastern margin of Twentymile Park. In areas where dissolved sulfate concentrations are large (fig. 43), dissolved-solids concentrations may range sporadically from 400 to 3,000 mg/L. The relation between dissolved-solids concentrations and specific conductance also is affected by the anion water type as shown in figure 44. The linear regression line for sulfate water has a correlation coefficient of 0.93 and an equation of the form $Y = 0.805x - 45.8$. The linear regression line for bicarbonate water has a correlation coefficient of 0.95 and an equation of the form $Y = 0.606x + 58.4$.

Geochemical Controls on Cation Concentrations

Calcium, magnesium, and sodium, are the dominant cations in the study area; potassium ions occur in concentrations small enough to be disregarded. Two geochemical processes, carbonate dissolution and ion exchange, have an effect on cation concentrations and distribution.

The first geochemical process, carbonate dissolution, is lithology and surface dependent. Dissolution of calcite and dolomite at low temperatures provide calcium and magnesium cations to the aqueous system. Thin discontinuous limy shales, limestones, and dolomitic limestones present in the fine-grained rocks provide a source of calcium and magnesium.

The solubility of the carbonate minerals is controlled by the pH of the local ground water. Water recharging the aquifer carries oxygen and carbon dioxide gasses into the aquifers. These two gasses tend to decrease the pH of the recharge water and thereby increase the solubility of carbonate minerals. Carbon dioxide forms carbonic acid on dissolution in water:



Oxidation of sulfide minerals, such as the iron pyrite that is commonly present in the coal or associated carbonaceous shale, forms sulfuric acid:



The pH of the water in the recharge areas of the basal Williams Fork aquifer averages about 7.5 and is more acidic than the water in deeper parts of the aquifer where the pH averages about 8.5. The carbonic acid and sulfuric acid produced by reactions 3 and 4 may react with calcite to produce calcium, bicarbonate, and sulfate ions:



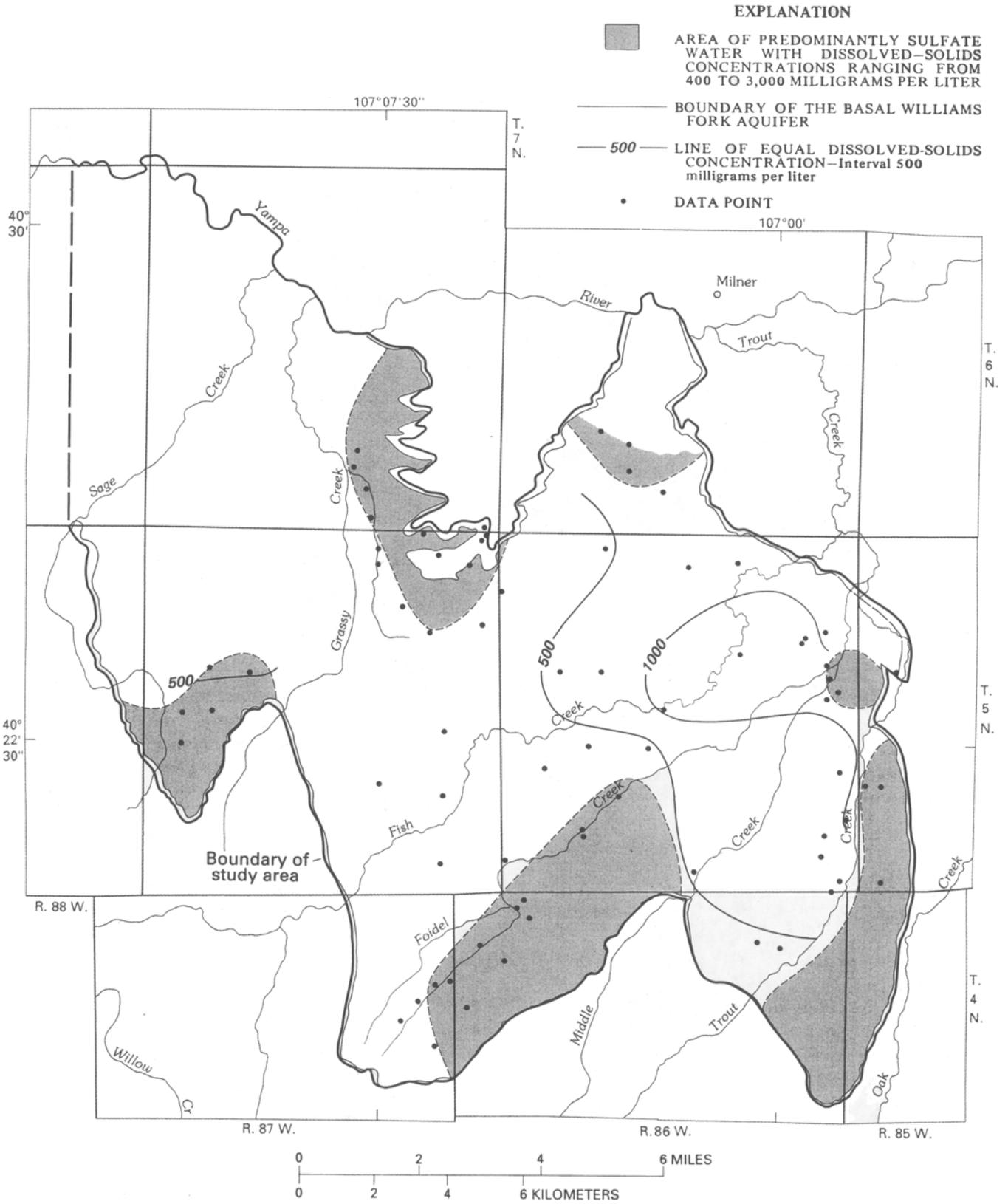


Figure 43.--Dissolved-solids concentrations of water in the basal Williams Fork aquifer in the eastern part of the study are

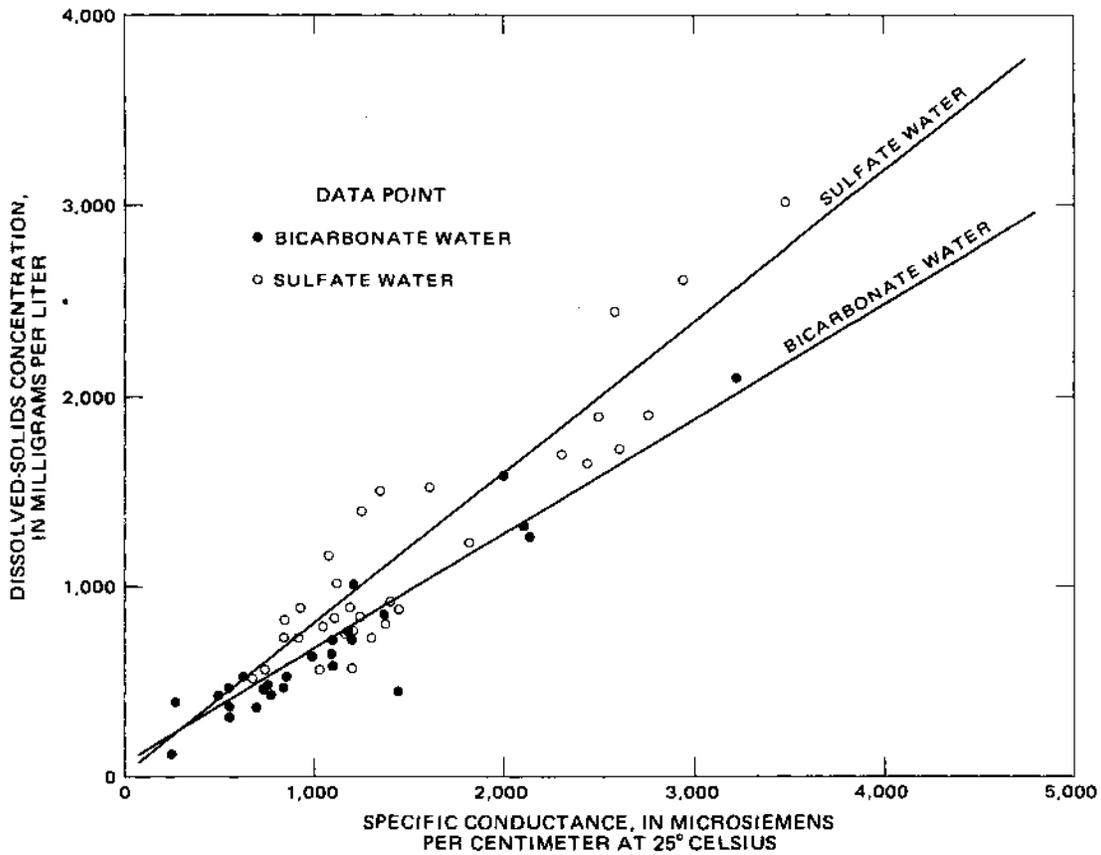
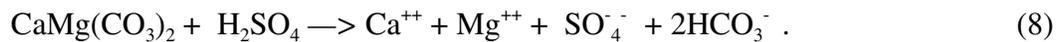
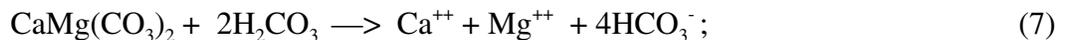


Figure 44.--Relation between specific conductance and dissolved-solids concentrations for sulfate and bicarbonate water in the basal Williams Fork aquifer.

or may react with dolomite to produce calcium, magnesium, bicarbonate, and sulfate ions:



In areas containing marine shales, ion exchange is the predominant geochemical process controlling cation concentration and distribution. The mechanism is an exchange of calcium and magnesium ions in aqueous solution with sodium ions on the clay minerals of the sodium-rich marine shales. This cationic exchange is the principal source of sodium in the ground water. The general equation for monovalent-divalent cation exchange is (Garrels and Christ, 1965):



In this example, A represents sodium, and B represents calcium or magnesium. Sodium is continually replaced at the exchange sites of the clay(X_2), until enough sites are filled with divalent cations to establish a chemical equilibrium with ground water. This process accounts for most of the approximately 200 mg/L decrease in calcium plus magnesium concentrations (and corresponding increase in sodium plus potassium concentrations) that occur as water moves from the recharge areas to the central part of the basal Williams Fork aquifer.

Geochemical Controls on Anion Concentrations

The primary anions in the basal Williams Fork aquifer are bicarbonate and sulfate. Carbonate ions also are present in significant concentrations in local areas that have alkaline water of large pH values. Dissolution of carbonate minerals may yield carbonate or bicarbonate ions. At pH greater than 10.5, a shift from bicarbonate ions to carbonate ions may occur:



Dissolved sulfate anions commonly are derived from two sources—dissolution of authigenic gypsum and oxidation of pyrite and marcasite. Reduction rates for sulfur systems often are slow, resulting in nonequilibrium forms of sulfur being present (Hem, 1970); two forms of sulfur, sulfide ions and hydrogen sulfide gas, can be present in the same sample.

Direct dissolution of gypsum may occur as ground water moves slowly through the gypsum-bearing units. However, larger rates of dissolution occur in the weathered zone or in spoils because weathering and crushing create secondary permeability that allows increased ground-water movement through the materials and increased contact of the water with newly exposed soluble minerals such as gypsum.

Oxidation of reduced sulfur, which primarily occurs in pyrite and marcasite in the bedrock organic shales and coals, produces sulfate. As these beds are exposed to oxygenated water, sulfur is oxidized to produce the sulfate ion, as indicated in equations 4 and 6. Pyritic materials are very common in drill samples from the *area*, and large concentrations of sulfate in wells completed in coalbeds indicate that coal and carbonaceous shale are sources of sulfur.

In a semiarid climate, precipitation may be insufficient to leach all geochemical weathering products out of the soil zone. In areas of finegrained rocks, production of sulfate by weathering and inflow of sulfate in runoff and precipitation may exceed the rate that the sulfate is removed by runoff and subsurface flow. This can cause large concentrations of sulfate to form near the land surface (Hem, 1970). This process may explain the large sulfate concentrations associated with some wells that are completed in alluvial aquifers and also may account for the alkali deposits present along some poorly drained valley bottoms.