UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

APPRAISAL OF GROUND WATER IN THE VICINITY OF THE LEADVILLE DRAINAGE TUNNEL, LAKE COUNTY, COLORADO

By John T. Turk and O. James Taylor

Open-File Report 79-1538

Prepared in cooperation with the
U.S. Bureau of Reclamation

Lakewood, Colorado

November 1979

For sale by:

Open-File Services Section
Branch of Distribution
U.S. Geological Survey, MS 306
Box 25425, Denver Federal Center
Lakewood, CO 80225
Open-File Report 79-1538

CONTENTS

ILLUSTRATIONS

TABLES

METRIC CONVERSION TABLE

Multiply inch-pound unit	*By*	*To obtain metric unit*
inch (in.)	25.40	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot per day (ft/d)	0.3048	meter per day
foot squared per day (ft^2/d)	0.0929	meter squared per day

APPRAISAL OF GROUND WATER IN THE VICINITY OF THE LEADVILLE DRAINAGE TUNNEL, LAKE COUNTY, COLORADO

By John T. Turk and O. James Taylor

ABSTRACT

Ground water in the Leadville mining district occurs in granite, quartzite, limestone, sandstone, porphyry dikes, and unconsolidated material. These rocks form a single aquifer system because the formations are hydraulically connected through contact, mine workings, faulting, and fracturing. The aquifer is recharged by precipitation and water moves toward California Gulch and probably toward Evans Gulch, in the drainage basin of the Arkansas River. The Leadville drainage tunnel was constructed from 1943 to 1945 and later extended during 1950 to 1952, in order to drain the mine workings. Discharge from the tunnel lowered water levels 30 to 96 feet in mine shafts from 1944 to 1951. Installation of an impervious plug in the tunnel has been proposed in order to reduce the discharge of water containing objectionable concentrations of trace metals into the East Fork Arkansas River. The proposed plug would reduce the discharge from the tunnel, cause water levels east of the town of Leadville to rise, flood some mine workings, and increase ground-water discharge to California Gulch. However, the proposed plug is not expected to cause water levels in Leadville to rise substantially, but more current and detailed data are needed to verify this.

Discharge from the Leadville drainage tunnel is probably a mixture of water in equilibrium with carbonate aquifer materials from the mineralized zone, water acidified by the localized oxidation of pyrite from the mineralized zone, and water nearly saturated with calcite from the glacial mantle. Based on limited data, water from the carbonate mineral deposits has a pH of about 7.0 and concentrations of manganese of about 1,800 micrograms per liter and zinc concentrations of about 13,000 micrograms per liter.

INTRODUCTION

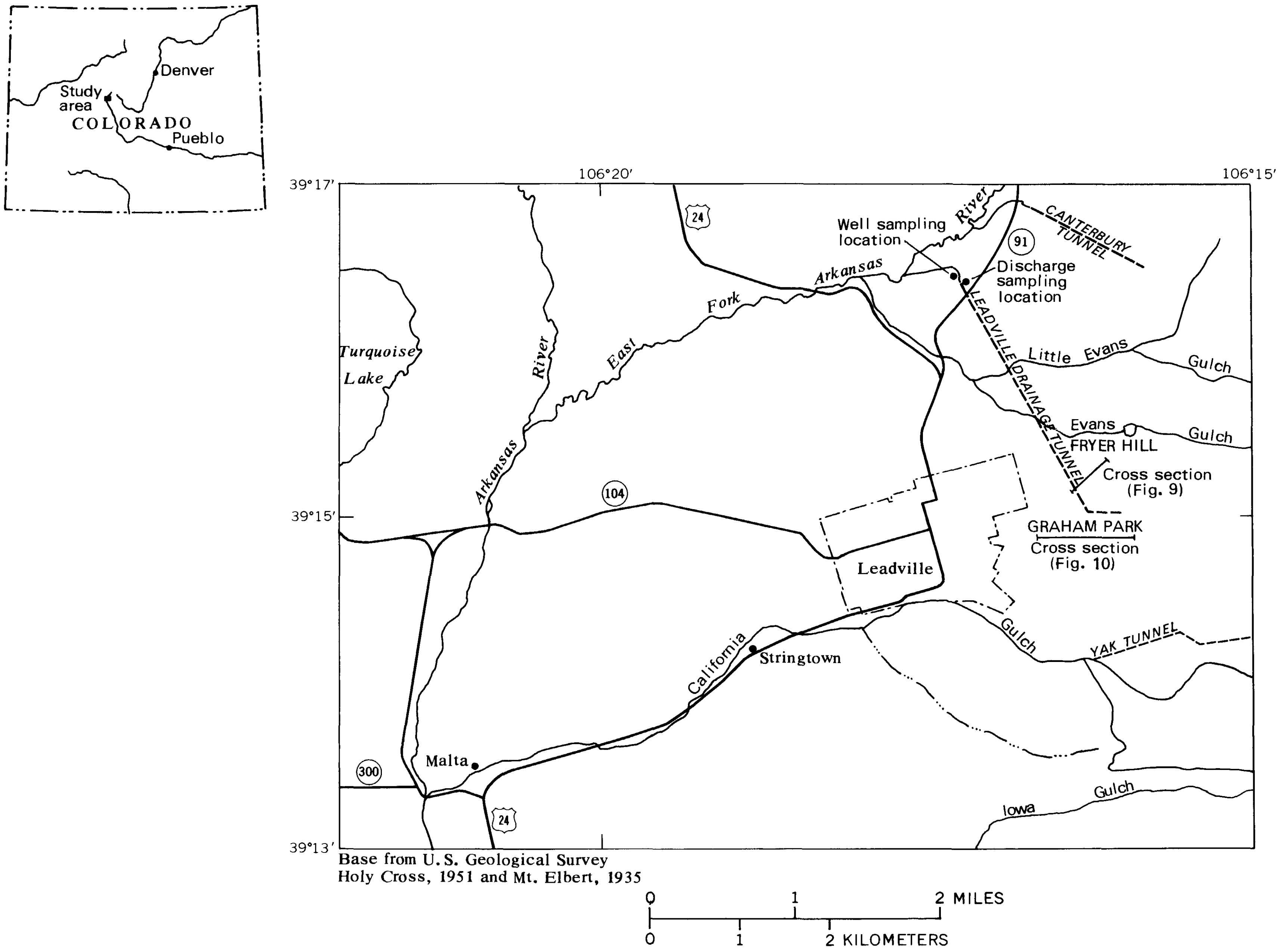
The occurrence of ground water in the Leadville mining district (fig. 1) probably was noted about 1874, when hard-rock mining for lead ores began (Elgin, Volin, and Townsend, 1949). As mine shafts and other mine workings were constructed, mine-flooding problems developed because of the abundance of ground water in most rock types. The Yak tunnel was started in 1895 for drainage purposes. The Canterbury tunnel was started in 1921 for exploration and drainage purposes. Large pumps were installed in various mine shafts from the late 1800's until 1940 and pumping rates ranging from 2.2 to 11.1 ft^3/s are reported. Apparently the pumping was discontinued because of the large expense compared to the value of mined ores. The Leadville drainage tunnel was constructed to drain mine workings from 1943 to 1945 and later extended during 1950 to 1952. The tunnel was constructed with a portal altitude of 9,957 ft and completed at an altitude of 9,986 ft at a distance of 11,299 ft from the portal. Parts of the tunnel have collapsed and the overlying surface has subsided. Currently parts of the tunnel are being reopened in order to stabilize the land surface. Despite the collapse of the tunnel, the tunnel continues to drain the area. In 1978 the average discharge from the tunnel was about 3.23 ft^3/s (U.S. Bureau of Reclamation, 1978).

The Leadville drainage tunnel discharges water to the East Fork Arkansas River. Concentrations of metals, particularly manganese and zinc, in the discharge result in noncompliance of the discharge with the National Pollution Discharge Elimination System (Public Law 92-500, 1972) requirements for this point source. Proposed alternatives to stop the pollution caused by the discharge include construction of a wastewater-treatment plant or plugging of the tunnel approximately 5,000 ft from the portal. An appraisal of the wastewater-treatment plant option has been completed (U.S. Bureau of Reclamation, 1978). This report presents the results of a preliminary appraisal to estimate the effect of the proposed plug on the ground-water flow system and geochemistry adjacent to the Arkansas River.

GEOLOGIC SETTING

Several detailed descriptions of the geology and mineralogy of the Leadville area and the ore deposits within the area have been previously published (Emmons, 1886; Loughlin, 1918; Loughlin, 1926; and Emmons, Irving, and Loughlin, 1927). For the purposes of the discussion in this paper, a much abbreviated summary of the geological and mineralogical characteristics of the area is sufficient. Bedrock consists of Precambrian granite overlain by quartzite, limestone, and sandstone of Paleozoic, Mesozoic, and Cenozoic age. Intrusive porphyritic rocks of Tertiary age form dikes and sills. Deposits of Quaternary age include unconsolidated glacial drift and alluvium. Faulting, fracturing, and folding are common (Tweto, 1974).

Mineralized solutions associated with the igneous activity in the area deposited metals in veins and as blanket replacements of the strata more susceptible to dissolution, particularly the limestone. Although the minerals found within the mineralized zone form a complex assemblage ranging from the native metals (copper, silver, and gold) to sulfides, carbonates, and silicates of individual metals and



Base from U.S. Geological Survey
Holy Cross, 1951 and Mt. Elbert, 1935

Figure 1.--Map showing location of study area.

mixtures of several metals, the initial deposits were primarily sulfides of iron, zinc, and lead. In late Tertiary time, faulting divided the host rock and the mineralized deposits into a number of fault blocks. At this same time, parts of the mineralized deposits were exposed to oxidizing conditions and large amounts of the sulfide deposits were oxidized, subsequently reacting with the host rock to form carbonate minerals and, to a lesser extent, silicate minerals. Oxidation of the original mineral deposits has changed the mineralogy in the oxidized zone from one predominated by pyrite, sphalerite, and galena to one predominated by manganosiderite, smithsonite, and cerussite. Data from the previously mentioned references indicate that at altitudes above the level of the Leadville drainage tunnel, ground water is in contact primarily with carbonate minerals, and to a much lesser extent the corresponding sulfide and silicate minerals.

GROUND WATER

Occurrence

All rock types in the Leadville mining district contain ground water. Construction records for the Leadville drainage tunnel indicate that ground water occurs in fractured granite and quartzite, limestone, sandstone, porphyry dikes, and unconsolidated material. Though available hydrologic data are meager, the various rock types are considered to form a single aquifer system because they are hydraulically connected through contact or mine workings, and because of extensive faulting and fracturing.

Recharge

Aquifers of the Leadville mining district are recharged mainly by direct infiltration of precipitation. Normal annual precipitation for this area is about 20 in.; normal May-September precipitation is about 9 in. (U.S. Department of Commerce, 1956). Wells drilled for observation and exploration purposes in the portal area of the Leadville drainage tunnel are shown in figure 2. The hydrograph of a well near station 6+34 of the Leadville drainage tunnel is shown in figure 3. The effects of natural recharge are apparent on the hydrograph for 1969-71 and 1974. Rises of about 7 to 15 ft in late summer and autumn are due to natural recharge from rainfall and snowmelt. Seasonal increases in tunnel discharge for the same time periods (fig. 4) also are due to the interception and discharge of natural recharge. The general rise in water level shown in figure 3 indicates an increase in storage. This increase is probably due to collapse of parts of the tunnel which was accompanied by a gradually decreasing discharge from the tunnel prior to 1969. The water level and tunnel discharge also were affected by other events, such as tunnel modifications and pumping that are labeled on figures 3 and 4.

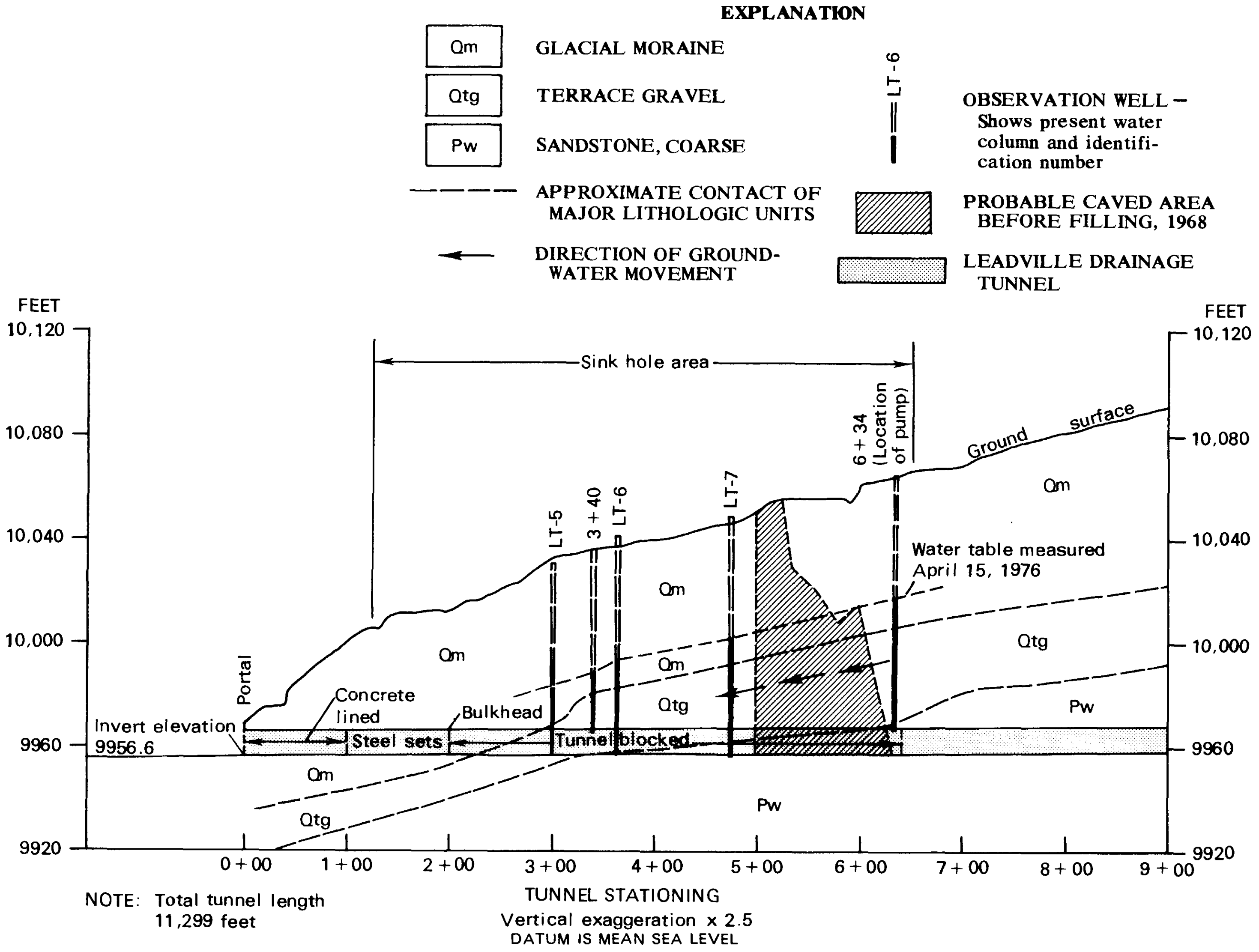


Figure 2.--Geohydrologic section of portal area of Leadville drainage tunnel (modified from unpublished report by U.S. Bureau of Reclamation, 1976).

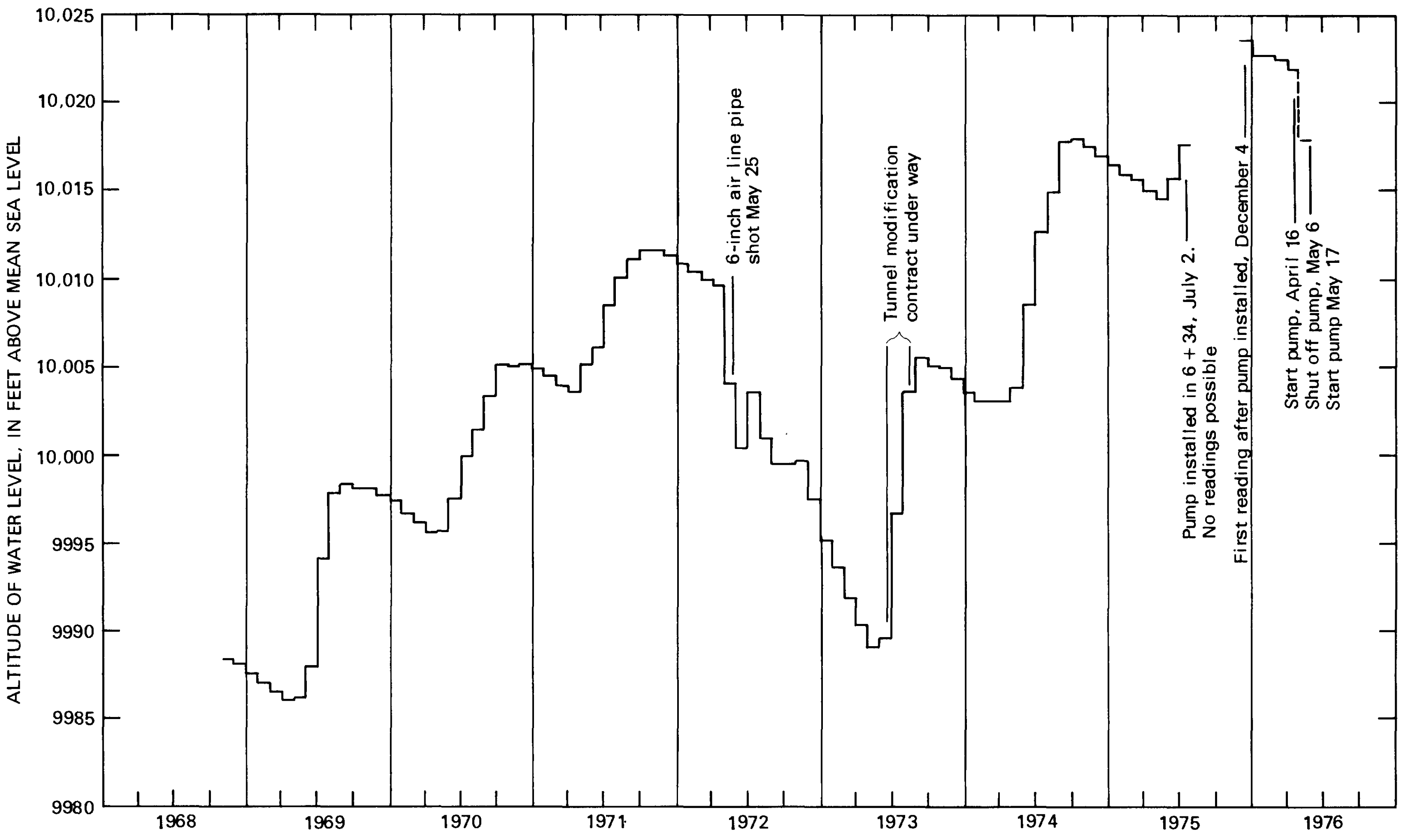


Figure 3.--Water level in well near station 6+34 of Leadville drainage tunnel, 1968-76 (modified from unpublished report by U.S. Bureau of Reclamation, 1976).

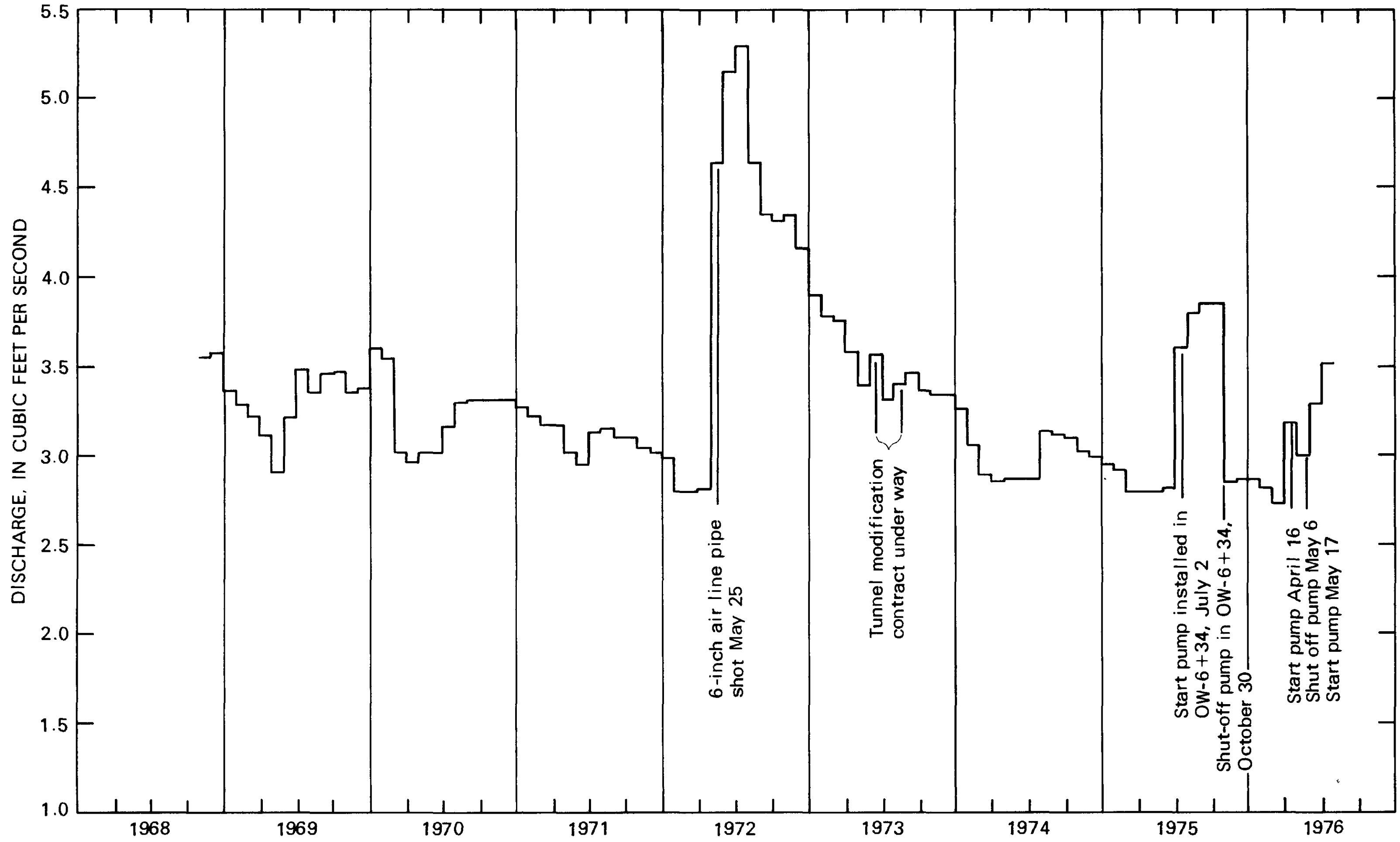


Figure 4.--Discharge from portal of Leadville drainage tunnel, 1968-76 (modified from unpublished report by U.S. Bureau of Reclamation, 1976).

Movement

Ground-water movement was evaluated from a potentiometric map. The recorded altitudes of water levels in mine shafts in 1944 were plotted and contoured to produce the potentiometric map shown in figure 5. The data do not extend over the entire region, but indicate that east of the town of Leadville the general direction of ground-water movement is toward the southwest. The limited extent of the Leadville drainage tunnel in 1944, as shown in figure 5, may not have been sufficient to induce a change in mine drainage east of Leadville. The effect of the Yak tunnel on mine drainage east of Leadville cannot be determined because of the lack of data near the tunnel.

The natural direction of ground-water movement north of the town of Leadville and near the portal of the Leadville drainage tunnel is not known. Ground water probably discharges into the valley of Evans Gulch. In 1976 ground water was moving toward the portal of the tunnel as shown on figure 2. However, the movement has been altered by the combined effects of drainage into the tunnel and ground-water pumping.

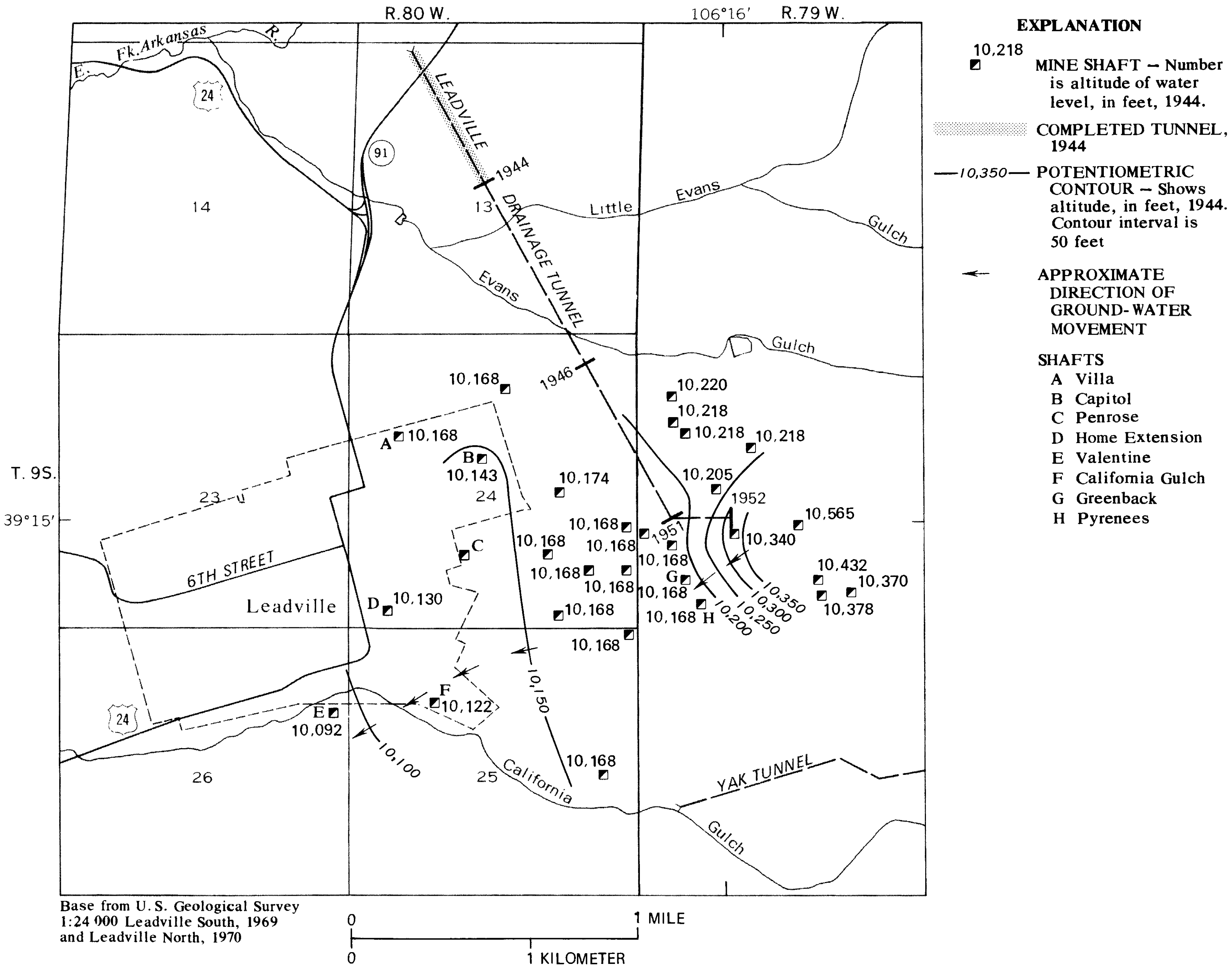
The rate of ground-water movement from the region east of Leadville was estimated using Darcy's law. The transmissivity of the aquifer system was calculated using a simplified version of the Thiem equation:

$$T=1.4\frac{Q}{s}$$

where T is transmissivity, the product of aquifer thickness and hydraulic conductivity, in feet squared per day,
Q is steady discharge from a well or shaft, in cubic feet per day, and
s is drawdown measured at the pumping site, in feet.

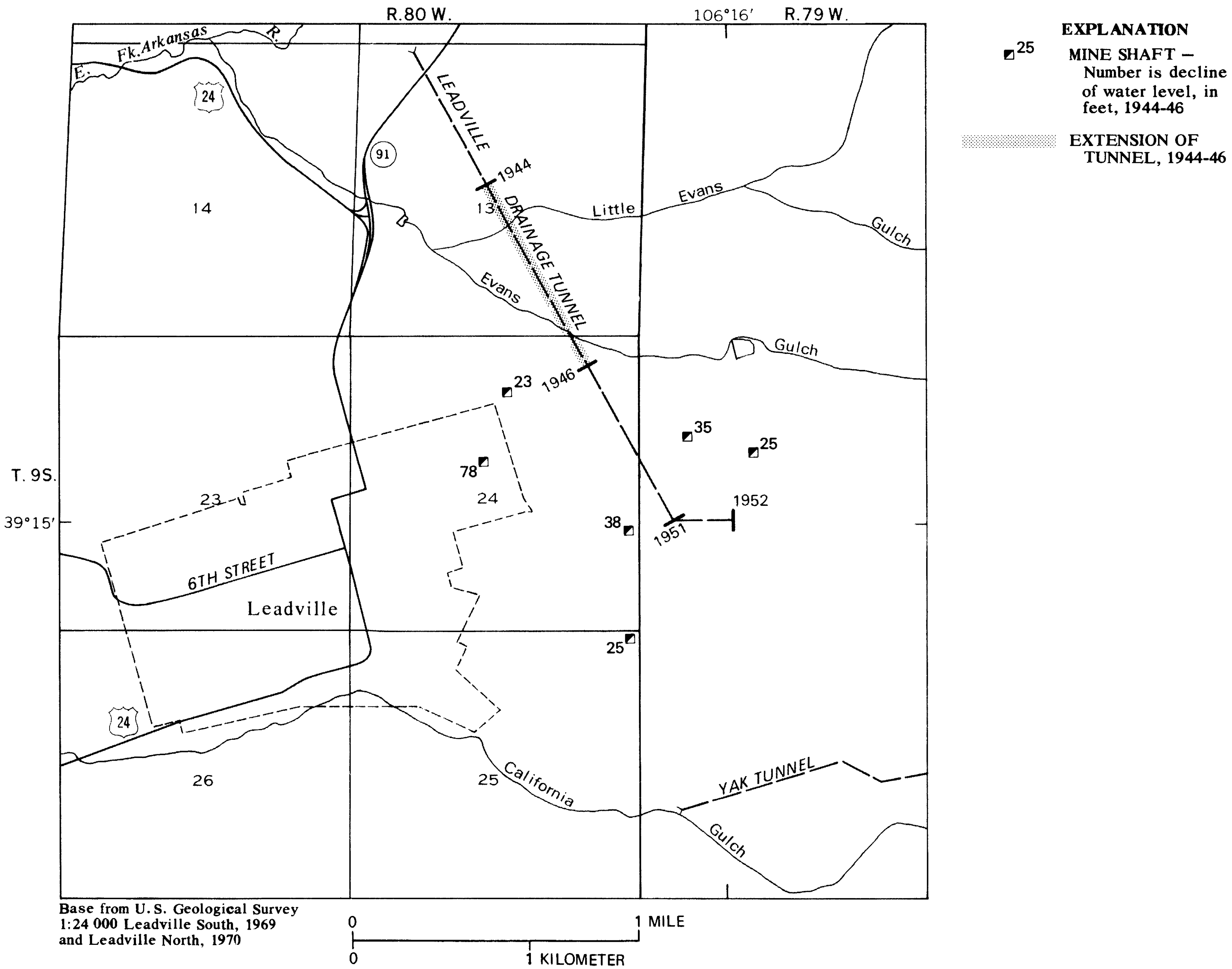
Data for steady pumping in mine shafts (Elgin, Volin, and Townsend, 1949, p. 9-10; Hedges, 1940, p. 20-21) and calculated transmissivity values using the Thiem equation are shown in table 1. The stratigraphic section near the Penrose shaft consists of about 200 ft of granite, 370 ft of sandy, pebbly silt of the Dry Union Formation of Tertiary age, and 60 ft of glacial drift and outwash gravel. Average horizontal hydraulic conductivity was calculated as 1.5 ft/d. The stratigraphic section near the Greenback and Pyrenees shafts consists of about 265 ft of porphyry and about 625 ft of granite. Average horizontal hydraulic conductivity was calculated as 0.4 ft/d. Estimated flow through the aquifer system east of Leadville was calculated using a hydraulic conductivity of 1.5 ft/d, an aquifer thickness of 1,000 ft, and a hydraulic gradient of 1.4×10^{-2} ft/ft, as indicated in figure 5. Calculated flow is 1.3 ft^3/s through the aquifer, across the 10,200-ft potentiometric contour, a section about 1 mi wide and perpendicular to the direction of flow.

Water levels in shafts declined 25 to 78 ft from 1944 to 1946, as shown in figure 6. The limited extent of the tunnel by 1946 is also shown. Water levels declined 30 to 96 feet from 1944 to 1951, as shown in figure 7. By 1951 the tunnel extended east of Leadville and greater drainage was possible. Declines indicate a reduction of ground water in storage during those time intervals.



Base from U.S. Geological Survey
1:24 000 Leadville South, 1969
and Leadville North, 1970

Figure 5.--Altitude of potentiometric surface, 1944.



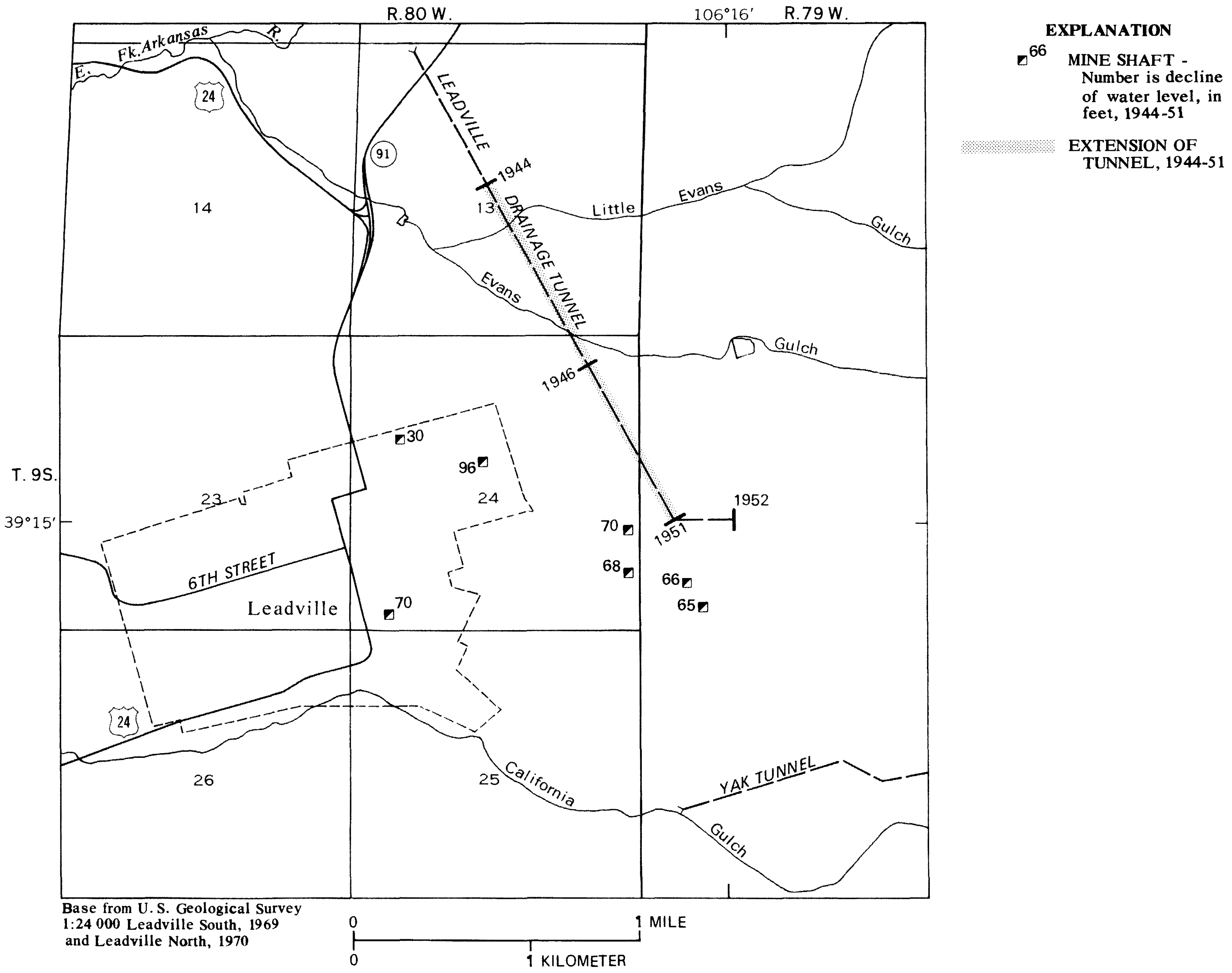
EXPLANATION

■25 MINE SHAFT – Number is decline of water level, in feet, 1944-46

▨ EXTENSION OF TUNNEL, 1944-46

Base from U.S. Geological Survey 1:24 000 Leadville South, 1969 and Leadville North, 1970

Figure 6.--Decline of water levels in selected mines, 1944-46.



Base from U. S. Geological Survey
1:24 000 Leadville South, 1969
and Leadville North, 1970

Figure 7.--Decline of water levels in selected mines, 1944-51.

Table 1.--*Characteristics of pumped shafts*

Shaft	Date	Steady pump rate (cubic feet per day)	Drawdown (feet)	Aquifer transmissivity (feet squared per day)
Penrose---------	July 1916	580,000	733	1,100
Greenback and Pyrenees.	July 1925	270,000	891	400

An indication of the aquifer characteristics of the unconsolidated alluvium near the tunnel portal was obtained by analysis of the drawdown in well LT-7 resulting from the pumping of the well near station 6+34 at a distance of 160 ft (fig. 2). The well was pumped at 1 ft^3/s from April 15 to May 6, 1976. Measurements of water levels in well LT-7 by the U.S. Bureau of Reclamation produced the drawdown curve in the observation well as shown in figure 8. Indicated transmissivity is 2,300 ft^2/d for about 50 ft of glacial and terrace gravel. Average horizontal hydraulic conductivity was calculated as about 50 ft/d, much higher than hydraulic conductivities elsewhere. The test results indicate a specific yield of 0.3, indicative of coarse, well sorted gravel.

Discharge

Ground water in the region east of Leadville naturally discharges to the valley of California Gulch. The water may discharge to the channel and to the valley-fill alluvium beneath the channel. Miscellaneous streamflow measurements near the mouth of California Gulch at Malta were made from 1965 to 1967 by the U.S. Geological Survey (1967). Measurements ranged from 2.2 ft^3/s on September 21, 1965, to 7.7 ft^3/s on July 8, 1965. The minimum measured flow of 2.2 ft^3/s presumably includes about 1.5 ft^3/s of discharge from the portal of the Yak tunnel. The difference, 0.7 ft^3/s, represents a single estimate of the ground-water discharge to the stream channel from both sides of the drainage basin of California Gulch. Evapotranspiration in the gulch is not known. Part of the ground water discharging to California Gulch probably occurs as underflow in the valley-fill alluvium.

Effects of Leadville Drainage Tunnel on Ground-Water Conditions

Water that discharges from the portal of the Leadville drainage tunnel is ground water. The tunnel has reduced ground water in storage and intercepted part of the water that was moving toward California Gulch. If the Leadville drainage tunnel is plugged at some location, the ground-water levels will rise in the vicinity of the tunnel to some undetermined altitude until discharge at other areas equals the natural recharge. The rising ground-water levels will flood some existing mine workings that are presently dry.

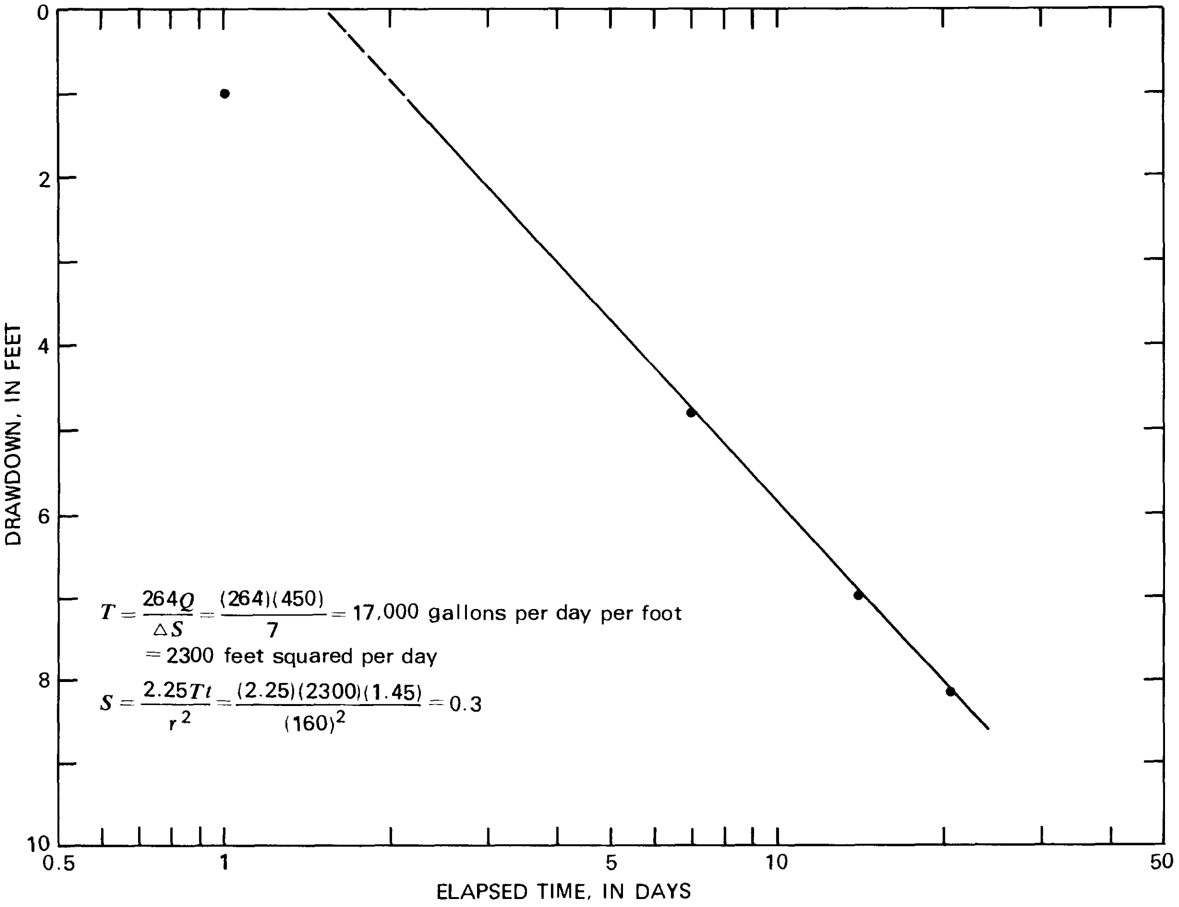


Figure 8.--Results of aquifer test using observation well LT-7.

The effect on water levels cannot be predicted accurately because of the few data on aquifer characteristics and the unknown discharge from the zone east of Leadville into the tunnel. The potentiometric surface within the town of Leadville in 1944 was at an altitude ranging from 10,100 to 10,168 ft, as shown on figure 5. Emmons, Irving, and Loughlin (1927, p. 248) report water levels at an altitude of 9,918 ft in Leadville after the strike of 1896-97. Pumping was stopped in 1896 and in 1897 the mines were flooded by silt-laden surface water. Some mines were abandoned due to voluminous silt deposits and in others the silt was removed and pumping resumed in 1898 (Emmons and others, 1927, p. 120-121). Therefore, the reported water levels of 9,918 ft after the strike do not represent natural conditions. The rise in water levels from 1897 to 1944 was not due to the Leadville drainage tunnel or to natural changes in the flow system. The rise was due to a recovery from the combined effects of pumping, flooding, and sediment deposition. Water levels measured within the town of Leadville in 1940-44 are shown in table 2. Water levels at the land surface were reported only in the valley of California Gulch, the zone of natural discharge.

Table 2.--*Water levels within town of Leadville*

Shaft	Year	Depth to water below land surface (feet)
Villa------------------------	1944	65
Capitol----------------------	1944	150
Penrose----------------------	1940	161
Home Extension---------------	1944	23
California Gulch-------------	1944	0
Valentine--------------------	1944	0

High ground-water levels in the town of Leadville never have been reported as a problem. Although no water levels were measured for this study, it is unlikely that placement of the proposed plug will cause rising water levels because of the proximity of California Gulch, the zone of natural discharge. However, a thorough analysis based on more current and detailed data is necessary to predict the effects on water levels in the town accurately.

WATER-QUALITY DATA

To provide an internally consistent data base, only data for samples collected at the tunnel portal by personnel of the U.S. Geological Survey, and analyzed by the U.S. Geological Survey laboratory in Salt Lake City, Utah, have been used. A total of 31 samples were collected from January 1967 through June 1973. Data for two additional samples collected by the U.S. Bureau of Reclamation from a well completed in glacial till near the tunnel portal also are included. Selected analytical results are presented in table 3.

Table 3.--*Quality of water discharged from the Leadville drainage tunnel and of ground water near the tunnel portal*

[mg/L=milligrams per liter; µg/L-micrograms per liter; °C-degrees Celsius]

Date	Dissolved calcium (mg/L)	Dissolved magnesium (mg/L)	Dissolved sodium (mg/L)	Dissolved potassium (mg/L)	Dissolved chloride (mg/L)	Dissolved sulfate (mg/L)	Bicar-bonate (mg/L)	Dissolved iron (µg/L)	Dissolved manganese (µg/L)	Dissolved zinc (µg/L)	pH	Temper-ature (°C)
					LEADVILLE DRAINAGE TUNNEL							
01/18/67	120	46	4.8	1.7	1.1	395	139	1,600	3,800	6,400	7.0	7.2
06/06/67	120	60	4.7	1.8	2.2	464	130	1,500	5,000	12,000	6.8	7.2
10/05/67	90	43	3.3	1.1	1.7	300	138	10	3,600	5,100	7.5	7.0
11/15/67	94	46	3.6	1.1	1.9	310	140	20	3,700	5,300	7.4	8.0
12/12/67	100	48	4.2	1.4	2.5	329	140	0	3,800	5,700	7.4	6.0
01/11/68	104	52	4.2	1.5	2.7	331	140	40	3,900	6,200	7.3	7.0
02/08/68	109	51	5.0	1.4	2.9	358	144	1,800	4,000	6,100	7.3	7.0
03/04/68	109	51	4.1	1.6	3.5	368	140	1,700	5,900	5,800	7.1	7.0
04/05/68	111	52	4.3	1.6	4.0	375	144	1,600	6,000	6,500	7.0	7.0
05/06/68	116	54	4.4	1.6	3.6	385	140	2,200	6,000	6,000	7.6	7.0
06/06/68	124	63	4.4	1.7	3.7	462	118	1,000	9,000	15,000	7.2	6.0
07/03/68	112	55	4.3	1.5	3.2	405	132	110	7,700	9,900	7.1	7.0
08/09/68	64	42	2.7	1.1	1.9	223	124	20	2,300	7,500	7.6	7.0
09/06/68	55	37	2.4	1.6	1.9	188	131	10	2,000	7,900	7.0	7.0
10/16/68	82	44	3.2	1.3	1.8	270	144	340	2,100	6,400	7.2	7.0
11/06/68	90	40	3.5	1.1	4.0	275	140	410	3,600	10,000	7.3	7.0
12/06/68	91	42	3.6	0.9	3.5	291	142	60	3,400	8,900	7.4	7.0
01/09/69	99	47	3.8	0.9	3.5	327	142	20	4,000	7,000	7.2	7.0
02/10/69	107	48	3.7	0.8	4.0	348	142	1,300	3,900	8,000	7.2	7.0
03/17/69	106	51	4.6	1.7	4.0	322	145	160	3,100	6,000	7.3	7.0
04/14/69	110	50	4.0	1.6	1.2	362	151	100	2,900	5,800	7.5	7.0
05/22/69	114	64	4.2	1.7	0.8	464	118	1,300	7,500	20,000	7.2	7.0
06/16/69	87	45	3.9	1.4	0.1	305	106	310	6,300	9,600	7.6	7.0
11/08/72	110	46	---	---	---	---	168	100	2,000	4,600	6.9	6.5
05/09/73	110	46	---	---	---	---	166	370	2,500	4,600	6.7	7.0
06/21/78	110	47	---	---	---	---	137	130	5,700	13,000	6.5	7.0
					GROUND WATER							
01/11/78	36	14	2.5	1.6	2.1	20	157	<100	<50	<20	7.9	---
01/24/78	34	13	1.8	1.2	2.3	23	148	<100	<50	<20	8.0	---

MINERAL AND WATER INTERACTIONS

The interaction between ore deposits and water depends on the mineralogy of the ore deposits, the initial or pre-interaction composition of the water, the rate of flow through the ore deposits, and the surface area exposed in the deposits. A limiting case for mineral and ground-water interactions is the assumption that the rate of flow is small enough and the surface area large enough for all possible reactions to go to completion during the contact time between a volume of water and the ore deposit. In this case, the equilibrium solubility of minerals is presumed to control the final concentrations of the ions in the water. Lack of data on flow rates and the kinetics of reaction within the ground-water system in the Leadville mining district necessitate the use of such a simplifying assumption.

Sulfide-Mineral and Water Interactions

The large deposits of zinc sulfide mineral in the Leadville area can be a source of some of the zinc in the discharge from the Leadville drainage tunnel. The relative insolubility of the sulfide mineral sphalerite, however, prevents the direct dissolution of this mineral from contributing a significant proportion of the zinc in the discharge. The equilibrium dissolution of the sulfide may be less important to water quality in a natural system than other processes, such as bacterial oxidation of the sulfide or adsorption of the metal ions on particulates in the flow path of the water. Nonetheless, the equilibrium dissolution of minerals known to be present in the system provides a useful minimal estimate of the natural sources of ions.

At any value of pH, the equilibrium solubility of a metal sulfide mineral can be calculated. For example, equation 1 indicates the equilibrium dissolution of the zinc sulfide mineral, sphalerite:

$$ZnS \rightleftharpoons Zn^{++} + S^{=} \tag{1}$$

Using data on the free energy of formation of the reactants and products in equation 1 (Robie and others, 1978), the solubility product of sphalerite can be calculated as equal to $10^{-27.43}$ at 25°C. Equation 2 indicates the solubility product constant for sphalerite, where brackets indicate activities which are essentially equal to concentrations in dilute solution.

$$K_{(\mathrm{sphalerite})} = [Zn^{++}] \times [S^{=}] = 10^{-27.43} \tag{2}$$

In a system composed only of sphalerite and pure H_2O, sphalerite would dissolve to produce zinc and sulfide ions. If neither the zinc nor the sulfide ions reacted further, each would attain a concentration equal to the square root of the solubility product of sphalerite. The sulfide ions, however, react strongly with the hydrogen ions from the dissociation of water as shown in equations 3 and 4.

$$HS^{-} \rightleftharpoons H^{+} + S^{=}; K_{(HS^{-})} = [H^{+}] \times [S^{=}] / [HS^{-}] = 10^{-14} \tag{3}$$

$$H_2S \rightleftharpoons H^{+} + HS^{-}; K_{(H_2S)} = [H^{+}] \times [HS^{-}] / [H_2S] = 10^{-7.1} \tag{4}$$

The effects of reaction between sulfide and hydrogen ion on the solubility of zinc and the other sulfides at any pH can be evaluated by substitution of equations 3 and 4 into equation 5,

$$[Zn^{++}]=[H_2S]+[HS^-]+[S^=] \qquad (5)$$

where $[H_2S]+[HS^-]+[S^+]$ is essentially the molar sum of the reduced sulfur species and is equal to the Zn^{++} concentration. From the above equation and solubility product definition (equation 2), the equilibrium concentration of zinc may be calculated. This value at the median discharge pH of 7.2 is 0.004 micrograms per liter whereas the average measured concentration in the discharge of the tunnel is 8,000 micrograms per liter. In summary, the direct dissolution of the sulfide ore is probably only a minor contributor of the zinc in the tunnel discharge.

Carbonate-Mineral and Water Interactions

As mentioned in the section on the geology of the Leadville ore deposits, natural oxidation of the sulfide deposits occurred in late Tertiary time. Oxidation of metal sulfides generally produces a chemical environment in which the metals are much more soluble than they were as sulfides. Additionally, oxidation of pyrite, a major component of the ore bodies in the Leadville area, acidifies the water by the production of hydrogen ions, as summarized in equation 6.

$$FeS_2+15/4\ O_2+7/2\ H_2O \rightleftharpoons Fe(OH)_3+2\ SO_4^=+4\ H^+ \qquad (6)$$

In general, metals are more soluble at low pH values than at pH values near neutrality. The median pH of discharge samples from the Leadville drainage tunnel, however, is 7.2, or about neutral. The explanation for this near neutrality even in the presence of large amounts of pyrite ore that have undergone oxidation is that the oxidation products have had sufficient time to react with the limestone to be neutralized. This explanation is verified by the fact that the base-metal ores initially mined in the Leadville area were metal carbonates. The carbonate ores could have formed hydrothermally or by the oxidation of the sulfide ores and subsequent reaction with limestone as shown in equations 7 and 8.

$$ZnS+4H_2O \rightleftharpoons Zn^{++}+SO_4^=+8H^++8e^- \qquad (7)$$

$$Zn^{++}+CaCO_3 \rightleftharpoons ZnCo_3+Ca^{++} \qquad (8)$$

The metal carbonates dissolve in water as shown in equation 9, which indicates the dissolution of the zinc carbonate mineral smithsonite.

$$ZnCO_3 \rightleftharpoons Zn^{++}+CO_3^= \qquad (9)$$

As with sulfide ions, carbonate ions react with water to produce bicarbonate and hydroxide ions. Additional reactions with other major dissolved substances result in the formation of ion pairs. To account for the various reactions and their effect on the solubility of the metal carbonates, the water-quality data were processed using the computer program SOLMNEQ (Kharaka and Barnes, 1973) that computed the average carbonate ion activity in the tunnel discharge to be $10^{-6.03}$. By use of this average carbonate ion activity and equations for the solubility product of the metal carbonates, the equilibrium concentration of the metals was calculated as summarized in table 4. In table 4 the mineral rhodochrosite ($MnCO_3$) was used for calculations because thermodynamic data were not available on the impure ore mineral manganosiderite ($(Mn,Fe)(CO_3)$).

Table 4.--*Equilibrium concentration of manganese and zinc carbonates and average concentration of the metal ions in discharge from the Leadville drainage tunnel*

Mineral	Metal equilibrium concentration (micrograms/liter)	Average concentration (micrograms/liter)	Number of samples
Rhodochrosite ($MnCO_3$)------	1,800	4,700	31
Smithsonite ($ZnCO_3$)--------	13,000	9,100	31

The data in table 4 indicate that if the discharge water came entirely from water in contact with the carbonate deposits all of the zinc, as well as a significant proportion of the manganese could be accounted for by the dissolution of these carbonate ores. In summary, the naturally occurring carbonate ores are a likely source of the metals in the discharge from the Leadville drainage tunnel.

EFFECTS OF THE LEADVILLE DRAINAGE TUNNEL ON THE ORE DEPOSITS

In the construction and dewatering of mines by facilities such as the Leadville drainage tunnel, ground water was removed from storage to lower the regional ground-water levels. Lowering of the ground-water levels exposed the sulfide mineral deposits and allowed their oxidation to a more soluble form, thereby resulting in a pronounced change in the ability of the ore deposits to contaminate the ground water with metals. A comparison of historical data on the location of the mineral deposits with data on the elevation of the Leadville drainage tunnel allows an evaluation of the probable effects of the tunnel on the ability of the ore deposits to produce long-term changes in the water quality of the aquifer.

The Leadville drainage tunnel was constructed with a portal elevation of 9,957 ft and completed at an elevation of 9,986 ft at a distance of 11,299 ft from the portal. Investigations during and after the tunnel construction indicated that dewatering was confined primarily to areas shown on figures 6 and 7. The approximate elevation of the top of the sulfide deposits in the dewatered area is shown in figures 9 and 10. In the Graham Park area, the top of the sulfides lies below the elevation of the tunnel; the sulfides lie above tunnel level in the East

Fryer Hill area. Records from the tunnel construction (Salsbury, 1956) also indicate that the tunnel intersected iron, lead, and zinc sulfides between 7,120 to 8,600 ft from the portal. The potential for dewatering of the sulfide deposits by the tunnel, followed by oxidation to a more soluble mineral form existed at least in the East Fryer Hill area. Actually, oxidation will depend on the amount of ground-water flow, dissolved-oxygen content, and sulfide-oxidizing bacteria, as well as exposure to the atmosphere.

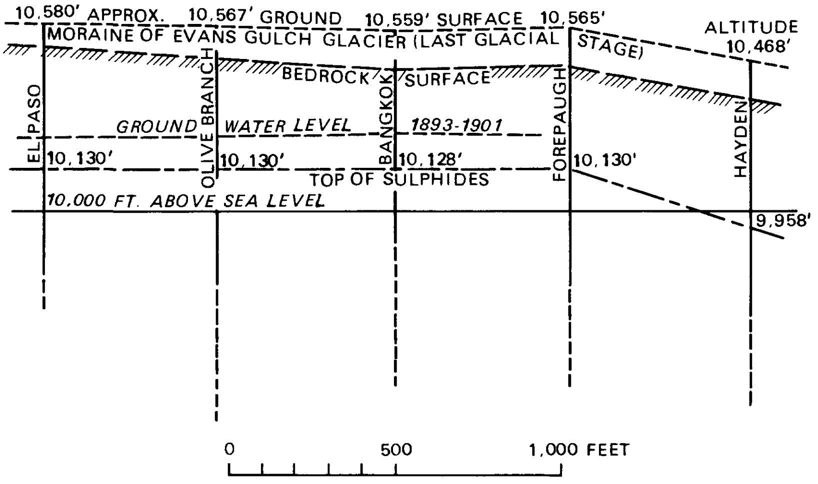
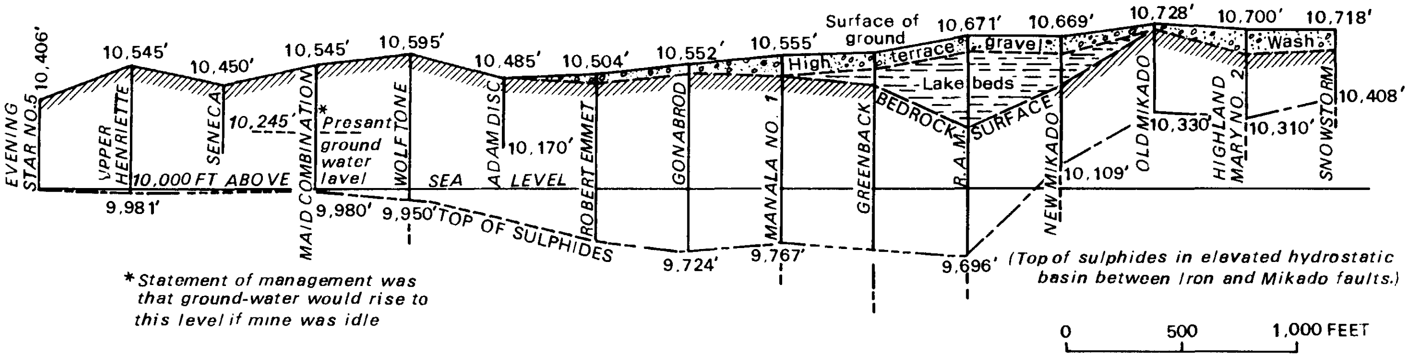


Figure 9.--Top of the sulfides in the East Fryer Hill area (from Emmons and others, 1927).

The data in table 4 indicate that the metal carbonates probably are the source of the metals in the tunnel discharge; however, simple dissolution of the carbonate deposits is not sufficient to explain major-ion data in table 3. At the near neutral pH of the discharge, the dissolution of a metal carbonate such as smithsonite, followed by variable dilution with water from the non-mineralized part of the aquifer, should result in a significant positive correlation of zinc and bicarbonate concentrations, as long as the waters are undersaturated with regard to calcite or any other carbonates. Table 5 indicates that bicarbonate has a significant correlation (Probability=0.05) only with manganese and zinc (highly correlated with each other) and this correlation is negative rather than positive. Thus, one might expect correlation of these metals with sulfate, which can be taken as an indicator of acid which has promoted dissolution of the carbonate ores.



*Statement of management was that ground-water would rise to this level if mine was idle

Figure 10.--Top of the sulfides in the Graham Park area (from Emmons and others, 1927).

Table 5.--*Correlation coefficient and level of significance, in parentheses, among bicarbonate, sulfate, and selected constituents for discharge from the Leadville drainage tunnel*

Ion	Bicarbonate	Sulfate
Ca^{++}	0.17(0.37)	0.32(0.08)
Mg^{++}	-0.17(0.36)	0.54(0.002)
Mn^{++}	-0.44(0.01)	0.44(0.01)
Zn^{++}	-0.43(0.01)	0.30(0.10)
HCO^-	-----------	-0.52(0.03)

Data for the sulfate correlations indicate significant correlation with all constituents except calcium and zinc. Particularly important is the negative correlation with bicarbonate. If sulfate and bicarbonate minerals were dissolving simultaneously, one might expect significant positive correlation as concentrations fluctuate due to changing amounts of dilution. A positive or negative correlation will result depending on whether pyrite oxidation (equation 6) produces acid which subsequently mixes with water from the dissolution of carbonate minerals to produce a neutral pH water, or whether pyrite oxidation occurs at near neutral pH because of bicarbonate buffering. Equation 9 indicates the reactions in an open system, such as the Leadville drainage tunnel.

$$Zn^{++}+HCO_3+H^+ \rightleftharpoons H_2CO_{3(aq)}+Zn^{++} \rightleftharpoons Zn^{++}+H_2O+CO_{2(gas)} \qquad (9)$$

In equation 9, hydrogen ions produced with sulfate as a product of the oxidation of pyrite react with the dissolution products of smithsonite to yield a solution of zinc (and sulfate) ions and liberate carbon dioxide to the atmosphere, thus removing bicarbonate from solution. Such a mechanism is consistent with the data in table 5. It is uncertain, however, whether the pyrite oxidation is the result of dewatering of pyrite by the tunnel because the 1927 data in figure 10 indicate some reduced sulfur deposits above the level of the ground water prior to tunnel construction.

Additional evidence of pyrite oxidation consists of comparative data between the tunnel discharge and ground water from a well completed in the glacial material near the tunnel. Ground water enters the tunnel throughout its length, both in the glacial deposits near the portal of the tunnel and in the mineralized zone near its end. Results from an analysis of the water-quality data using the computer program SOLMNEQ (Kharaka and Barnes, 1973) indicate the ground-water samples to be 65 to 80 percent saturated with $CaCO_3$ (calcite) while the tunnel discharge is only 6 to 42 percent saturated. This indicates that water from the tunnel within the mineralized zone is significantly more undersaturated with respect to calcite than recharged water from the glacial material, as would result from mixing water in equilibrium with the carbonate minerals with acidic water from localized pyrite oxidation. The concentrations of the metals in the discharge are low enough to suggest that mixing probably takes place after the water has left the carbonate mineral deposits, or that the bicarbonate buffering maintains a nearly neutral pH in the vicinity of the pyrite oxidation. Otherwise, the carbonate minerals would be in contact with water at a pH low enough to suggest more dissolution than inferred from the metal concentrations. The concentration of metals also may be kept relatively low by sorption on iron oxyhydroxide formed by sulfide oxidation (see equation 6).

If the tunnel is plugged and water from the ore deposits is affected by a redistribution of ground-water levels within the aquifer, changes in the chemical quality of water in the aquifer discharging to the tunnel probably will be minimal. Significant pyrite oxidation seems to occur only along the ground-water flow path downgradient from the carbonate mineral deposits; increasing ground-water levels throughout the aquifer will not likely have any impact on the relative distribution of ground-water levels, only their absolute magnitudes. If this is the case, then effects upon the hydrologic system will be confined to a redirection of ground water that currently discharges to the tunnel.

A useful approximation of the change in magnitude of zinc and other metals that may move through the aquifer and subsequently discharge to valleys of the Arkansas River can be obtained by multiplying the estimated ground-water concentration by the estimated discharge of mineralized water. The proportion of the tunnel's discharge from the mineralized area can only be approximated.

By assuming that water from the carbonate minerals plus the oxidized pyrite is significantly undersaturated with respect to calcite, the state of saturation can be treated as a conservative quantity for the purposes of the calculation, although this is not necessarily true. Equation 10 calculates the proportion of water from the glacial till (X) and the fraction from the mineralized zone ($1-X$).

$$X(0.72)+(1-X)(0.1 \text{ to } 0.001)=0.25 \qquad (10)$$

The constant 0.72 represents the state of calcite saturation in the glacial till, the 0.1 to 0.001 represents an assumed range of state of saturation of calcite in the mineralized water, and 0.25 represents the state of saturation in the tunnel discharge (mean average). For the assumed range of saturation the value of X is 0.24 to 0.35. Average discharge of the tunnel is 3.23 ft^3/s (U.S. Bureau of Reclamation, 1978), which multiplied by $1-X$ yields 2.10 to 2.45 ft^3/s. Ground water discharging at a rate of 1 ft^3/s would contain a daily load of 4.4 kilograms of manganese and 32 kilograms of zinc (from metal solubility concentrations in table 4).

It should be noted that the discharge of 2.10 to 2.45 ft^3/s represents complete discharge of water from the carbonate ores. Also, if this water ceased to discharge directly into the tunnel, the change would cause the flow to revert to the natural situation. In the pre-tunnel condition, the metals presently diverted from the carbonate ores to the tunnel moved through the aquifer and discharged to the river or mixed with water in the glacial till and alluvium.

SUMMARY AND CONCLUSIONS

A variety of permeable rock types and extensive mine workings form an aquifer system in the Leadville mining district. The aquifer is recharged by precipitation, and ground water moves toward California Gulch and probably toward Evans Gulch. The Leadville drainage tunnel has intercepted ground-water discharge and reduced ground water in storage. The placement of a proposed plug within the tunnel probably will reduce discharge through the portal of the tunnel which will cause rises of the potentiometric surface. The rise in water levels near the tunnel will flood some mine workings. Placement of the proposed plug probably will not cause rising water levels in the town of Leadville because of the proximity of California Gulch. However, a detailed analysis is necessary to accurately ascertain the effects on water levels in the town. In the long term, the net ground-water discharge to the Arkansas River and dissolved-solids concentration will be the same.

Additional hydrologic data are needed to analyze the ground-water system. Information and actions required are:

(1) Inventory of open mine shafts and construction of wells in order to prepare a more detailed and current potentiometric map.

(2) Periodic measurement of water levels in wells and shafts in order to calculate current and future changes in the flow system and in ground water in storage.

(3) Additional aquifer testing using shafts and wells in order to improve information on the transmissivity and specific yield of the aquifer.

(4) Gain-and-loss studies along California and Evans Gulches in order to estimate ground-water discharge and underflow.

(5) Measurement of discharge at various stations of the tunnel so that zones of the aquifer that are being drained may be delineated.

Discharge from the Leadville drainage tunnel is probably a mixture of three different water types: Water equilibrated with carbonate mineral deposits of calcite, cerussite, smithsonite, rhodochrosite, and siderite; water acidified by the localized oxidation of pyrite downgradient from the carbonate deposits; and water nearly in equilibrium with calcite from the glacial deposits in the part of the tunnel near the portal. Oxidation of the pyrite could be the result of dewatering of the deposits by the tunnel or continuing natural oxidation of the deposits which began in late Tertiary time.

Data are not available on the quality of water within the mineral deposits; however, the chemical quality of the tunnel discharge suggests that water in the vicinity of the carbonate minerals probably is a simple product of dissolution of the carbonates at near neutral pH. Carbonate mineral dissolution caused by acid production from the oxidation of sulfides cannot be differentiated. The probable concentrations of manganese and zinc in mineralized ground water tributary to the tunnel would be about 1,800 and 13,000 micrograms per liter, respectively, based on carbonate solubility calculations. The results of this calculation, however, could not be verified because of data limitations, and represent only the most likely of several possible explanations of the available data.

Many of the hypotheses on the nature of interaction between the ore deposits and ground water, as well as the geochemical effects of tunnel plugging, are based on incomplete data. Future geochemical investigations need to include:

(1) Ground-water sampling near the ore deposits and between the tunnel and ore deposits.

(2) Samples of tunnel seepage at discrete points along the tunnel to differentiate ground water from the mineralized zone and ground water from the glacial mantle.

(3) The location and altitude of oxidizing pyrite bodies for future predictions of the effects of plugging.

Collection of these data would not only increase the reliability of the calculations, but would also allow for more effective evaluation of treatment of tunnel discharge or a better basis for deciding the preferred location of a plug.

REFERENCES

Elgin, R. A., Volin, M. E., and Townsend, J. W., 1949, The Leadville drainage tunnel, Lake County, Colorado: U.S. Bureau of Mines Report of Investigations 4493, 37 p.

Emmons, S. F., 1886, Geology and mining industry of Leadville, Colorado (with Atlas): U.S. Geological Survey Monograph 12, 770 p.

Emmons, S. F., Irving, J. D., and Loughlin, G. F., 1927, Geology and ore deposits of the Leadville mining district, Colorado: U.S. Geological Survey Professional Paper 148, 368 p.

Hedges, J. H., 1940, Possibilities of manganese production at Leadville, Colorado: U.S. Bureau of Mines Information Circular 7125, 100 p.

Kharaka, Y. K., and Barnes, Ivan, 1973, SOLMNEQ--Solution-mineral equilibrium computations: Menlo Park, Calif., U.S. Geological Survey Computer Contributions, 81 p.; available only from U.S. Department of Commerce, National Technical Information Service, Springfield, VA 22151 as report PB-215 899.

Loughlin, G. F., 1918, The oxidized zinc ores of Leadville, Colorado: U.S. Geological Survey Bulletin 681, 91 p.

_____1926, Guides to ore in the Leadville district: U.S. Geological Survey Bulletin 779, 36 p.

Robie, R. A., Hemingway, B. S., and Fisher, J. R., 1978, Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures: U.S. Geological Survey Bulletin 1452, 456 p.

Salsbury, M. H., 1956, Leadville drainage tunnel second project--Lake County, Colorado: U.S. Bureau of Mines Report of Investigations 5284, 50 p.

Tweto, Ogden, 1974, Geologic map and sections of the Holy Cross Quadrangle, Eagle, Lake, Pitkin, and Summit Counties, Colorado: U.S. Geological Survey Miscellaneous Investigations Series Map I-830.

U.S. Bureau of Reclamation, 1978, Feasibility study report--Treatment of Leadville tunnel drainage: U.S. Bureau of Reclamation Project Report 78-155, unnumbered.

U.S. Department of Commerce, 1956, Normal annual precipitation, normal May-September precipitation 1931-1960.

U.S. Geological Survey, 1967, Water resources data for Colorado, Part 2, Water quality records: Lakewood, Colo., 101 p.

☆U.S GOVERNMENT PRINTING OFFICE. 1979—682-105/157