Effects of Uranium-Mining Releases on Ground-Water Quality in the Puerco River Basin, Arizona and New Mexico

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Prepared in cooperation with the Office of Navajo and Hopi Indian Relocation, the Bureau of Indian Affairs, the Arizona Department of Environmental Quality, the Arizona Department of Water Resources, The Navajo Nation, and The New Mexico Environment Department

U.S. DEPARTMENT OF THE INTERIOR
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By P.C. Van Metre, Laurie Wirt, T.J. Lopes, and S.A. Ferguson

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Multiply	By	To obtain
millimeter (mm)	25.4	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
square meter (m^2)	10.76	square foot
square kilometer (km^2)	0.3861	square mile
liter (L)	0.2642	gallon
cubic meter per second (m^3/s)	35.31	cubic foot per second
gram (g)	0.002205	pound
kilogram (kg)	2.205	pound
megagram (Mg)	1.102	ton, short

In this report, temperature is reported in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by using the following equation:

$$°F = 1.8(°C) + 32$$

VERTICAL DATUM

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

ABBREVIATED WATER-QUALITY UNITS

Chemical concentration and water temperature are given only in metric units. Chemical concentration in water is given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the solute mass per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 mg/L. For concentrations of less than 7,000 mg/L, the numerical value is about the same as for concentrations in parts per million. Specific conductance is given in microsiemens per centimeter (µS/cm) at 25°C, and oxidation-reduction potential (Eh) is measured in millivolts (mV). Radioactivity is expressed in curies, which is the amount of radioactive decay that would produce 3.7×10^{10} disintegrations per second or as picocuries per liter (pCi/L) or picocuries per gram (pCi/g), which is the amount of radioactive decay that would produce 2.2 disintegrations per minute in a unit volume (liter) of water or mass (gram) of sediment. Chemical concentration in bottom sediment is given in grams per kilogram (g/kg) or micrograms per gram (µg/g). Grams per kilogram is equal to parts per thousands (ppt). Milligrams per kilogram and micrograms per gram are equal to parts per million (ppm). Micrograms per kilogram are equal to parts per billion (ppb).

Effects of Uranium-Mining Releases on Ground-Water Quality in the Puerco River Basin, Arizona and New Mexico

By P.C. Van Metre, Laurie Wirt, T.J. Lopes, *and* S.A. Ferguson

Abstract

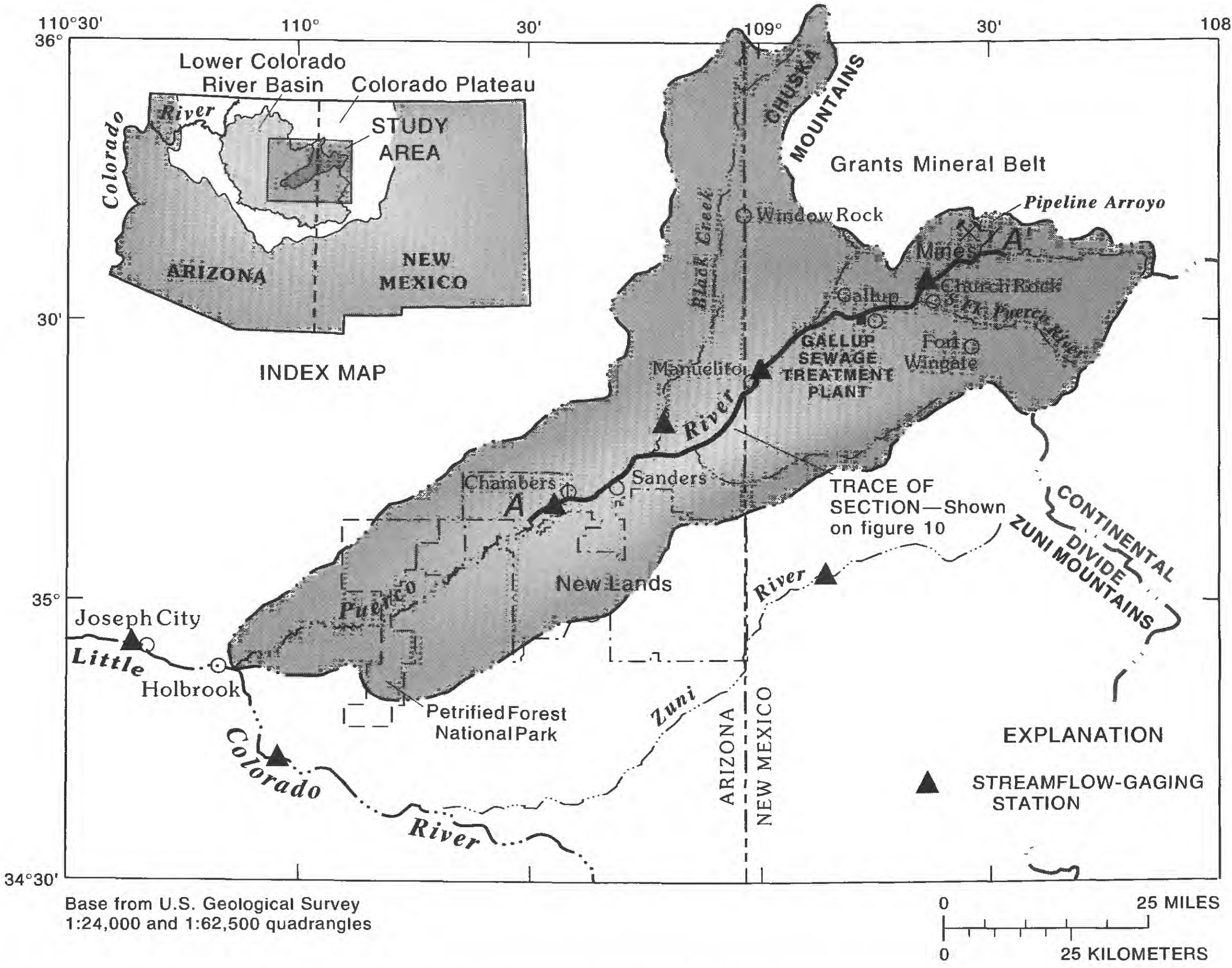
Shallow ground water underlying the Puerco River of Arizona and New Mexico was studied from 1988–91 to determine the effects of uranium mining on water quality. The Puerco River is an ephemeral stream that received effluent from uranium-mine dewatering operations from 1960 until 1961 and from 1967 until mining ceased in February 1986. Activities of dissolved gross alpha, gross beta, uranium, and radium and concentrations of dissolved molybdenum and selenium were elevated in streamflow as far as 140 kilometers downstream from the mines. Mine dewatering released an estimated 560 metric tons of uranium and 260 curies of gross alpha activity to the river. Additionally, on July 16, 1979, a tailings-pond dike failed and released an estimated 1.5 metric tons of uranium and 46 curies of gross alpha activity to the Puerco River. These mining related releases of radionuclides caused concern about the quality of water resources in the basin.

Ground-water analyses indicate that in 1989 a zone of larger concentrations of dissolved uranium in ground water extended about 65 kilometers downstream from where mine effluent entered the Puerco River to near the Arizona–New Mexico State line. Ground-water samples collected in 1990 and 1991 from immediately below the streambed had smaller concentrations of dissolved uranium than in 1989. Uranium-isotope ratios, which distinguish the source of uranium in mine-dewatering effluent from uranium that occurs naturally in the alluvial aquifer, indicate that larger concentrations of uranium in the alluvial aquifer are caused principally by mine-dewatering releases. Except for selected locations near the streambed, all ground-water samples collected from the alluvial aquifer downstream from Gallup, New Mexico, met the U.S. Environmental Protection Agency's maximum contaminant levels for gross alpha, gross beta, and radium and the proposed maximum contaminant level for uranium. Alluvial ground water, however, has commonly exceeded the U.S. Environmental Protection Agency's secondary maximum contaminant levels for dissolved solids, iron, and manganese.

Mass-balance calculations indicate that most of the uranium released by mining-related activities was not in solution in ground water in 1989. Geochemical modeling indicates that most alluvial ground water is undersaturated with respect to uranium minerals and that mine-dewatering effluent, when it flowed in the Puerco River channel, was probably undersaturated with respect to uranium minerals. Sorption of uranium on sediments is a likely fate of some of the uranium. Radionuclide concentrations and uranium-thorium isotope ratios in streambed and well-core sediments indicate that there are larger concentrations of radionuclides and excess uranium on near-channel sediments than on sediments away from the channel.

INTRODUCTION

The Puerco River, in the southeastern part of the Colorado Plateau (fig. 1), drains about 7,800 km^2 over



Base from U.S. Geological Survey
1:24,000 and 1:62,500 quadrangles

Figure 1. Study area of the Puerco River Basin, Arizona and New Mexico.

its 230-km length. The headwaters of the Puerco River are in northwestern New Mexico, west of the Continental Divide, and south of the Chuska Mountains of northeastern Arizona and northwestern New Mexico. Under natural conditions, the Puerco River generally is an ephemeral stream; and most runoff occurs in response to spring snowmelt and to brief, intense summer thunderstorms. Since the 1950's, flow in some reaches of the river changed from ephemeral to perennial as a result of effluent discharged from uranium mines and from the sewage-treatment plant (STP) at Gallup, New Mexico (Perkins and Goad, 1980; Gallaher and Cary, 1986).

From 1960 until 1961 and from 1967 until 1986, mine-dewatering effluent was discharged from uranium mines to Pipeline Arroyo, which is tributary to the Puerco River northeast of Gallup. That effluent contained larger concentrations of dissolved uranium, molybdenum, and selenium, and larger activities of dissolved gross alpha, gross beta, and radium than runoff (Gallaher and Cary, 1986; Van Metre and Gray, 1992). Additionally, on July 16, 1979, a tailings-pond dike failed at a uranium mill northeast of Gallup that released large amounts of thorium, radium, uranium, and sulfate into the Puerco River (Weimer and others, 1981). Contamination of ground water in the alluvial aquifer from mine-related sources of uranium was documented by Gallaher and Cary (1986) in the area between the mouth of Pipeline Arroyo and Gallup.

Because of radionuclide and trace-element releases from uranium mining and milling activities, there was concern that surface water and ground water in the Puerco River Basin may not be safe for human consumption. That concern was enhanced by recent growth of population in the area and the associated development of ground-water resources. In 1980, an amendment to the Relocation Act (Public Law 93–531) permitted the addition of about 1,600 km^2 of land to the Navajo Reservation in Arizona and New Mexico (fig. 1). The land, commonly known as the New Lands, is being used by Navajo people who are relocating from the former Navajo and Hopi Joint Use Area, which is now part of the Hopi Reservation (Paul Tessler, Legal Counsel for the Navajo and Hopi Indian Relocation Commission, oral commun., 1989). As of June 1990, 149 families had relocated to the New Lands area (Christopher Bavasi, Director, Office of Navajo and Hopi Indian Relocation, oral commun., 1990), and the population is expected to increase from a pre-1983 population of approximately 875 to about 3,000 people.

In 1985, the Office of Navajo and Hopi Indian Relocation requested that the U.S. Geological Survey (USGS) study the distribution of radionuclides in the water resources in the basin. Webb and others (1987a, b) made a reconnaissance-level study of the ground-water quality in the Puerco Basin and determined that radionuclide activities in water from 5 of 14 wells were at or above the maximum contaminant level (MCL) for the State of Arizona (McClennan, 1984) and the U.S. Environmental Protection Agency (USEPA; 1986a) of 15 pCi/L of gross alpha minus the sum of uranium and radon activity. A more detailed study began in 1988 to evaluate surface-water and ground-water quality and define the hydrology of the basin. This study was done in cooperation with the Office of Navajo and Hopi Indian Relocation (ONHIR), the Bureau of Indian Affairs (BIA), the Arizona Department of Environmental Quality (ADEQ), the Arizona Department of Water Resources (ADWR), The Navajo Nation, and the New Mexico Environment Department (NMED).

Purpose and Scope

The purpose of this report is to describe: (1) the water quality of the Puerco River alluvial aquifer, (2) the movement of water between the Puerco River and underlying alluvial aquifer, and (3) changes in the water quality of the alluvial and bedrock aquifers related to releases of contaminants by uranium-mining activities. This report focuses on the alluvial aquifer near the reach of the Puerco River that was subjected to continuous flow containing mine-dewatering effluents and to flow from the tailings-pond spill (Gallaher and Cary, 1986; Shuey, 1986; Van Metre and Gray, 1992). That area extends from the mouth of Pipeline Arroyo in New Mexico to about 10 km downstream from Chambers, Arizona (fig. 1). Field measurements were collected from June 1988 to September 1991.

Description of Study Area

Physical Setting

The Puerco River drains about 7,800 km^2 of the Little Colorado River Basin (fig. 2). The headwaters of the Puerco River are in northwestern New Mexico, north of the Zuni Mountains and south of the Chuska Mountains in the southeastern part of the Colorado Plateau. The river flows 170 km southwest through Gallup, New Mexico, and west-southwest to the Little Colorado River near Holbrook, Arizona. The Puerco River is ephemeral along most of its length and is characterized by long periods of no flow. Peak runoff typically occurs in March and April from snowmelt and rainfall or in July and August from rainfall from thunderstorms (U.S. Department of Agriculture, 1981). Streamflow in some reaches of the Puerco River has become perennial as a result of effluent discharge from the municipal sewage-treatment plant at Gallup, New Mexico (Perkins and Goad, 1980; Gallaher and Cary, 1986).

Bedrock formations of the Puerco River Basin consist predominantly of consolidated interbedded clay and sand units that form a multilayered, confined-aquifer system (Cooley and others, 1969; Raymondi and Conrad, 1983). Bedrock formations have been folded into a series of north-northwestward-trending anticlines, synclines, and monoclines (fig. 2; Cooley and others, 1969). The structural geology influences ground-water flow in bedrock and alluvial aquifers (Cooley and others, 1969; Mann, 1977; Raymondi and Conrad, 1983). The Nutria monocline, about 5 km east of Gallup, forms a ground-water divide for the regional-flow systems. Recharge that occurs east of the Nutria monocline flows in a north-northeastward direction toward the San Juan basin (Cooley and others, 1969; Raymondi and Conrad, 1983). Recharge that occurs west of the Nutria monocline flows in a westward direction (Cooley and others, 1969; Mann, 1977). Previous studies indicate that artesian ground-water conditions in bedrock formations exist east of the Defiance monocline and downstream from Chambers, Arizona (Cooley and others, 1969).

Overlying the bedrock formations is a thin layer of alluvium that generally is less than about 50 m thick and was eroded from exposed bedrock and deposited

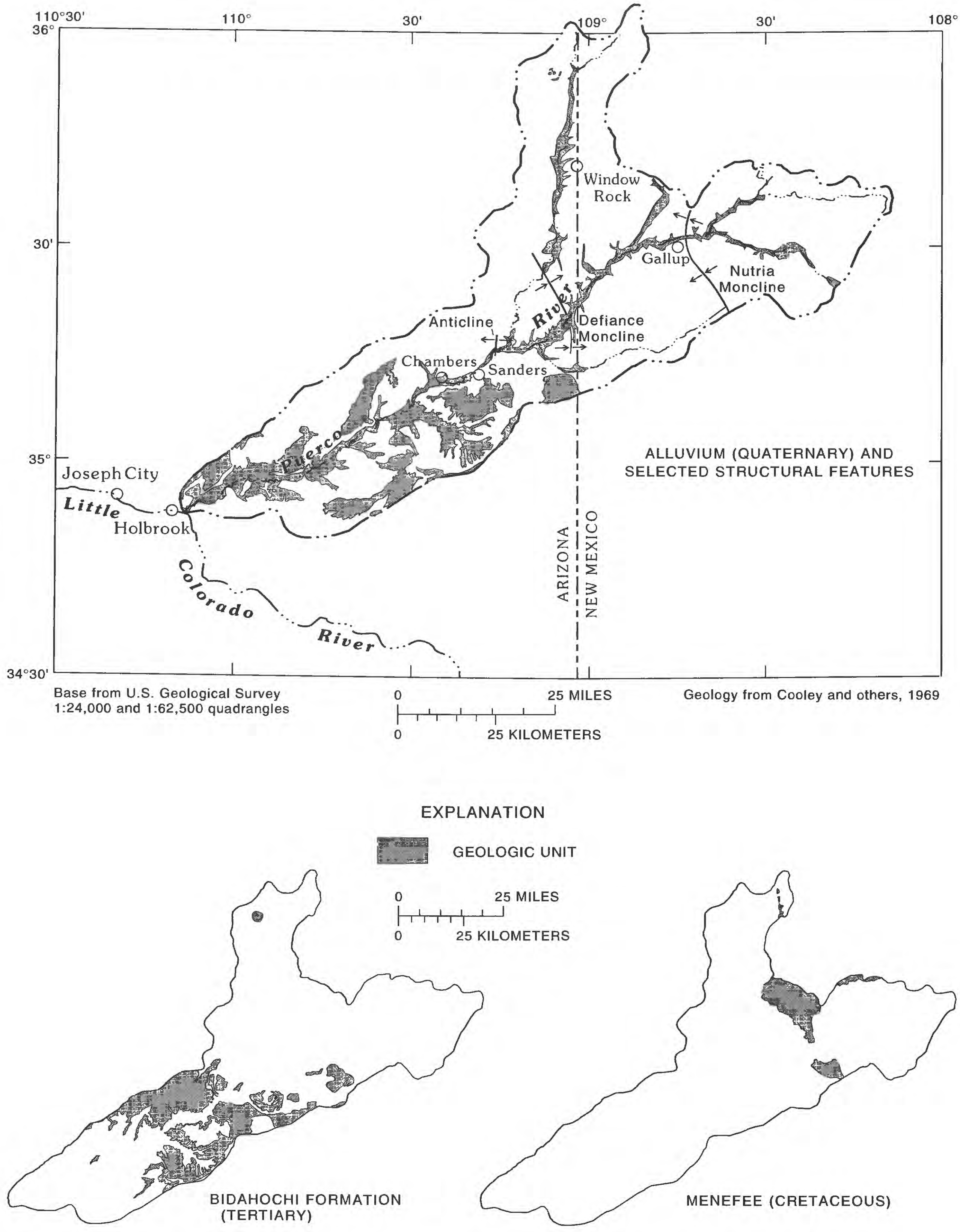
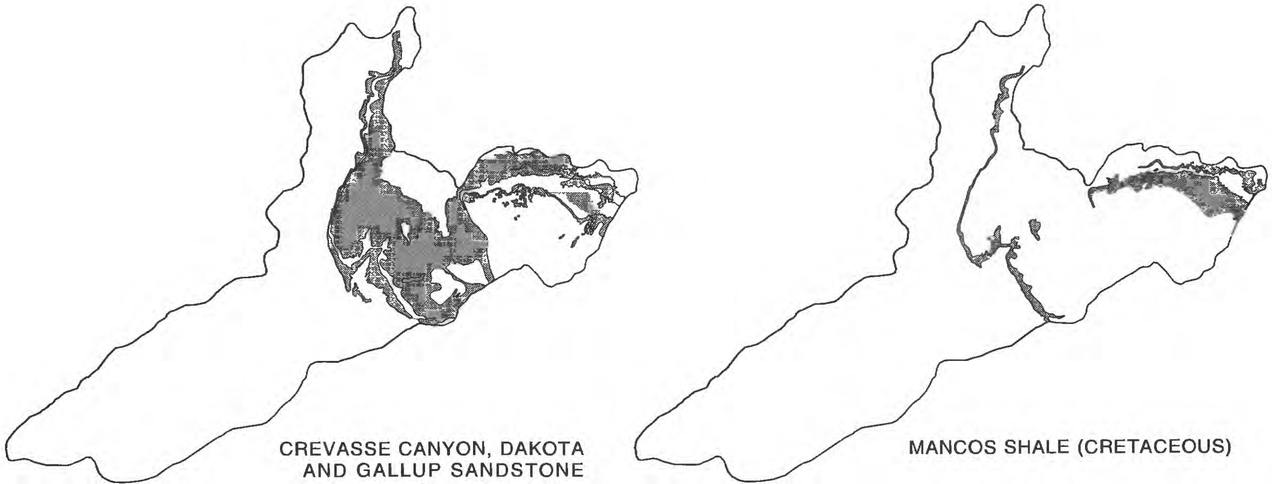
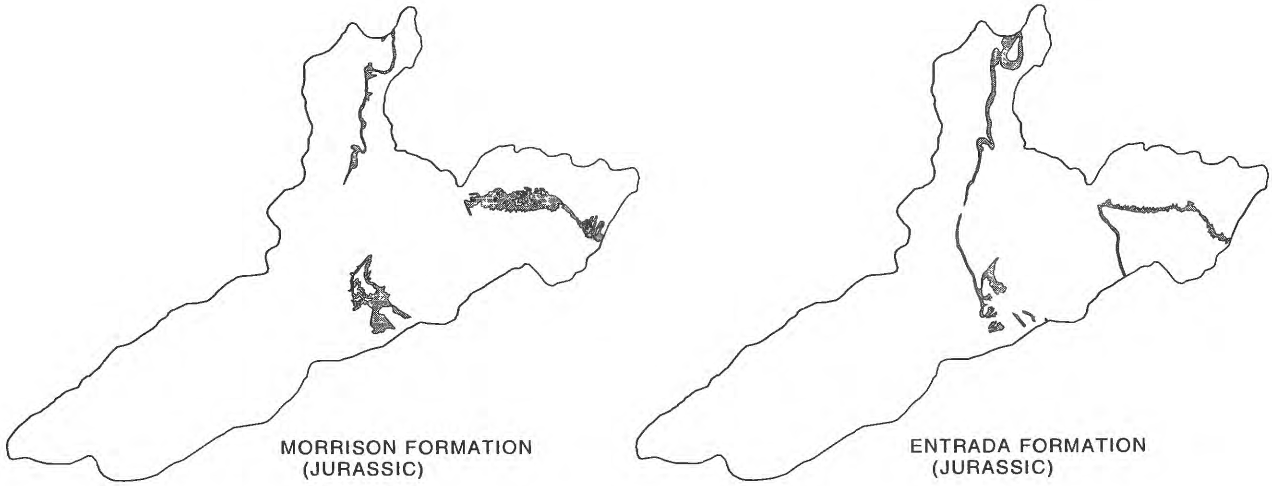


Figure 2. Geology of the Puerco River Basin, Arizona and New Mexico.



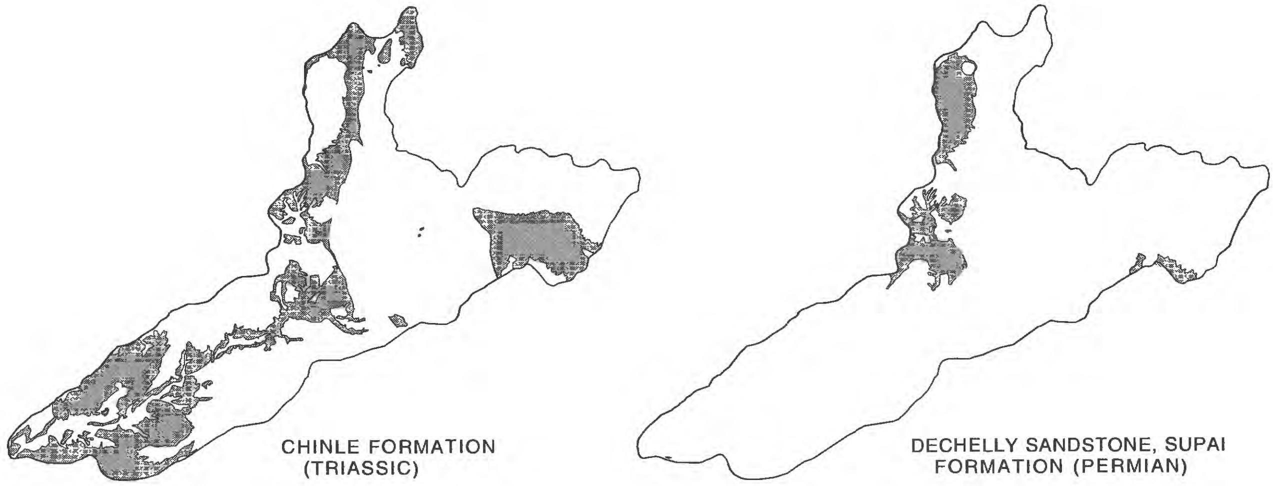
CREVASSE CANYON, DAKOTA AND GALLUP SANDSTONE (CRETACEOUS)

MANCOS SHALE (CRETACEOUS)



MORRISON FORMATION (JURASSIC)

ENTRADA FORMATION (JURASSIC)



CHINLE FORMATION (TRIASSIC)

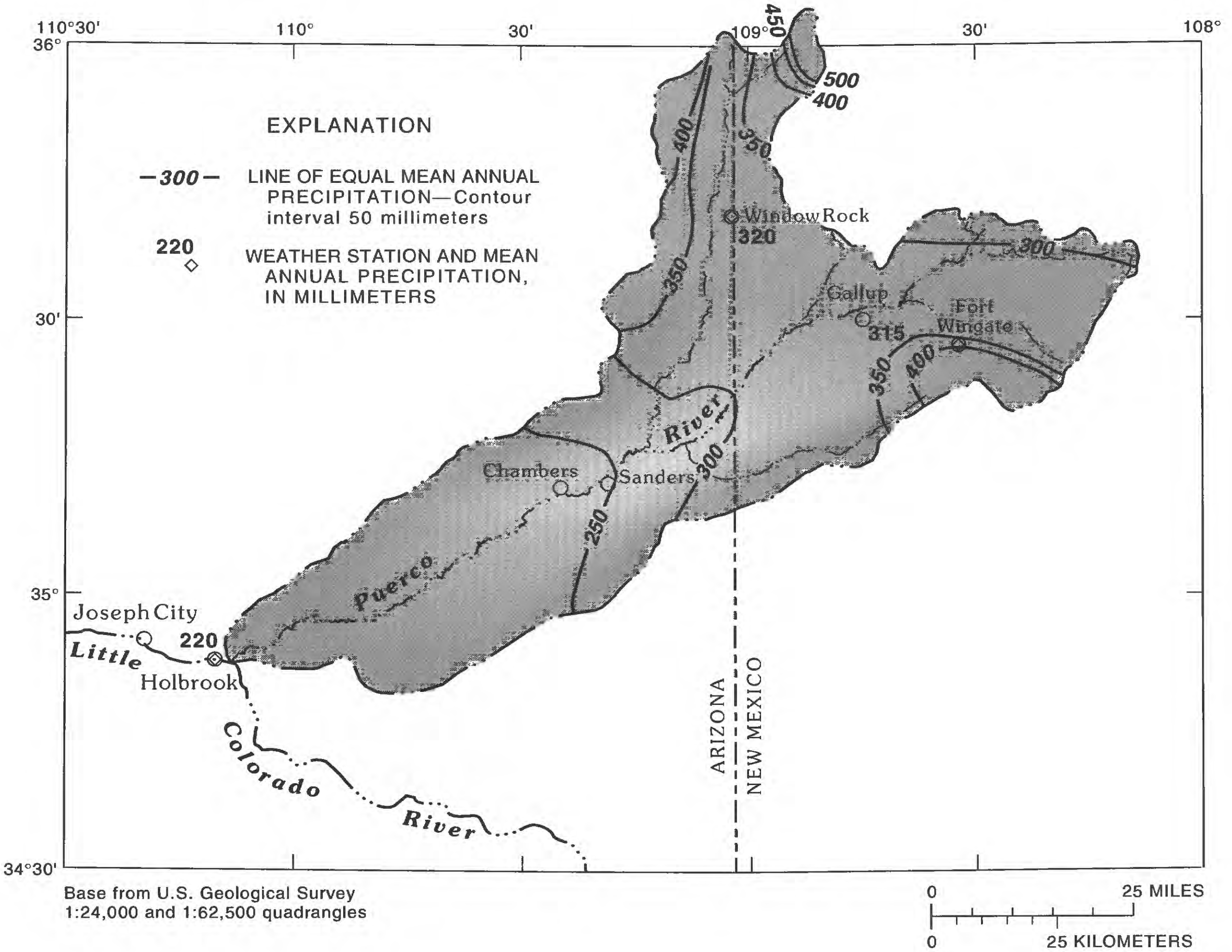
DECHELLY SANDSTONE, SUPAI FORMATION (PERMIAN)

Figure 2. Continued.

along the banks of the Puerco River. That alluvium hereafter is referred to as the Puerco River alluvial aquifer or simply the alluvial aquifer. The alluvial aquifer consists of interbedded clay, silt, sand, and gravel (Mann and Nemecek, 1983). From the mouth of Pipeline Arroyo in New Mexico to Chambers, Arizona, the lateral extent of the alluvial aquifer from the Puerco River varies in width from a few meters at a bedrock anticline about 8 km upstream from Sanders, Arizona, to about 4 km downstream from Sanders. Seven wells drilled along the river from near Church Rock, New Mexico, to near Chambers, Arizona, encountered alluvial thicknesses from 10 to 45 m. A well near Sanders, Arizona, was drilled to a depth of 59 m and did not reach bedrock. Depth to ground water in the alluvial aquifer is less than 1.0 m below the streambed along most of the Puerco River, and flow in the alluvial aquifer is predominantly downvalley.

Mean annual rainfall ranges from 220 mm at Holbrook, Arizona, to 320 mm at Window Rock, New Mexico, and correlates with altitude (fig. 3; Cooley and others, 1969). Mean annual snowfall ranges from 250 mm at Holbrook, Arizona, to 810 mm at Fort Wingate, New Mexico. Precipitation occurs mostly during two periods—July and August and December until February (Haitt, 1953). Summer precipitation is sporadic and usually occurs during high-energy convectional and frontal-convectional storms. Summer precipitation often results in local runoff and flash flooding. Winter precipitation results chiefly from frontal-storm activity and generally is distributed evenly. Intensity of winter storms generally is low, and the precipitation probably contributes substantially to ground-water recharge (Cooley and others, 1969).

Vegetation is divided informally into three rather broad zones—grass and shrub, pinyon and juniper, and montane conifer forest (fig. 4). The grass-and-shrub



Base from U.S. Geological Survey 1:24,000 and 1:62,500 quadrangles

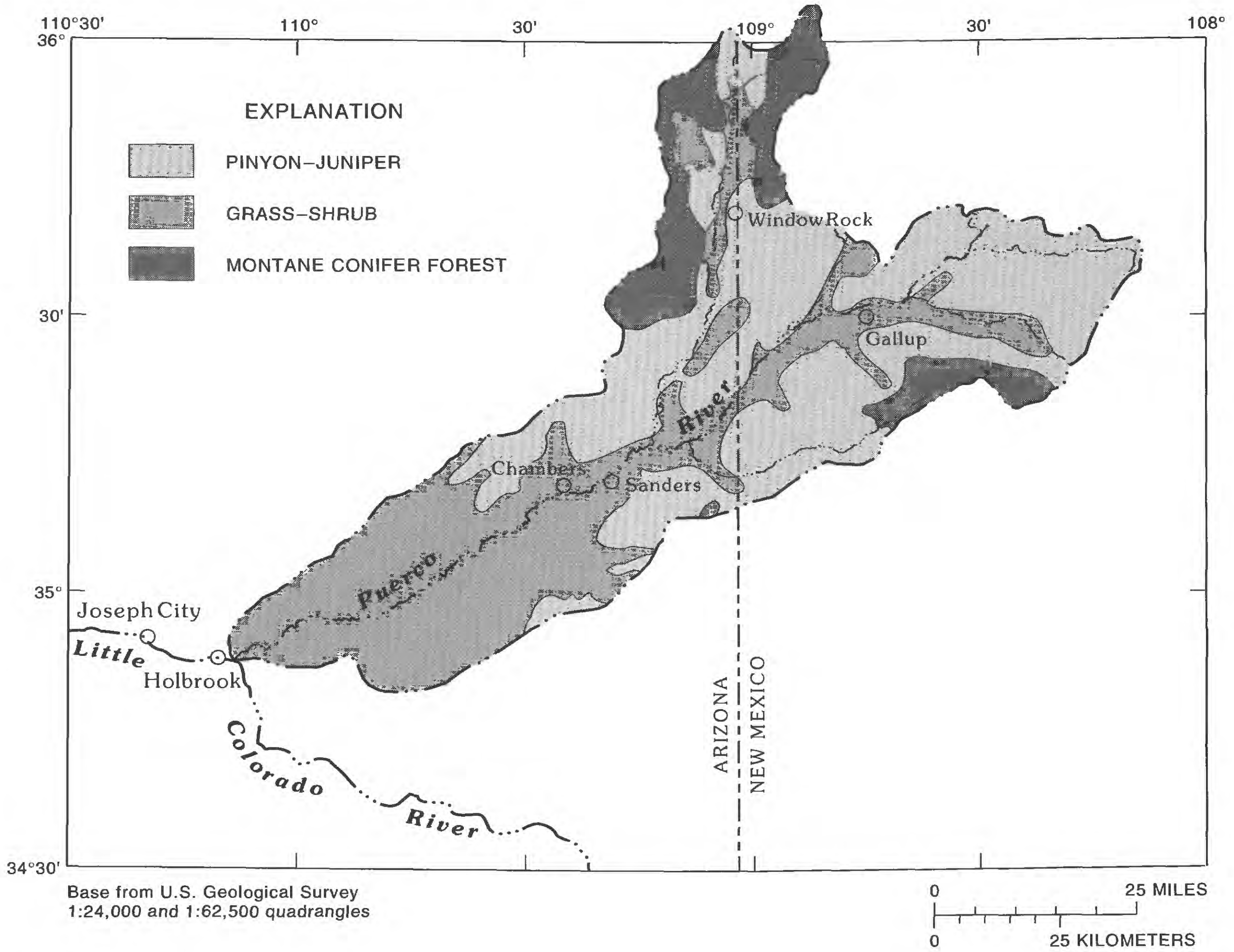
Figure 3. Average annual precipitation, Puerco River Basin, Arizona and New Mexico (Cooley and others, 1969).

zone is below 1,700 m in altitude and consists of sparse grassland-browse types of vegetation. Grass and shrub is characteristic of the lower part of the Puerco River Basin downstream from about the Arizona–New Mexico State line. The pinyon-and-juniper zone ranges in altitude from 1,700 to about 2,300 m and is dominated by woodland-browse species. Good rangelands are in this zone, which is characteristic of most of the upper Puerco River Basin. Small parts of the Puerco River Basin in the Chuska and Zuni Mountains and on the Defiance Plateau contain pine forest (Hicks, 1969).

History of Mining

The headwaters of the Puerco River lie within the Grants Mineral Belt of New Mexico. About 65 percent of all the uranium produced in the United States through 1982 was mined in the Colorado Plateau and more than 40 percent of that production was from the Grants Mineral Belt (Chenoweth and McLemore, 1989). In the Puerco River Basin, uranium deposits occur primarily as elongated, lenticular deposits within poorly sorted and cross-stratified fluvial sandstones (Hilpert, 1969; Wenrich and others, 1989). Uranium ore bodies are in the Westwater Canyon Member of the Morrison Formation and the Dakota Sandstone (Hilpert, 1969).

Beginning in 1960, uranium was mined near Pipeline Arroyo, a small tributary to the Puerco River about 35 km northeast of Gallup, New Mexico (fig. 1). The area is known locally as the Church Rock Mining District. Uranium-mine shafts near Pipeline Arroyo averaged 500 m deep. Because the ore bodies being mined are below the regional water table, water seeping into shafts was pumped to prevent flooding. From 1967 to 1986, the discharge rate from mine dewatering



Base from U.S. Geological Survey
1:24,000 and 1:62,500 quadrangles

Figure 4. Dominant vegetation types, Puerco River Basin, Arizona and New Mexico (Cooley and others, 1969).

averaged about 0.25 m^3/s causing continuous streamflow in the Puerco River from the mouth of Pipeline Arroyo to as far as a few kilometers downstream from Chambers, Arizona (Gallaher and Cary, 1986; Shuey, 1986). Effluent discharged to the Puerco River from the Gallup STP about 37 km downstream from the mines also contributed to continuous flow.

Before the mid-1970's, untreated effluent from dewatering operations discharged directly to Pipeline Arroyo (Gallaher and Cary, 1986). Beginning in the mid-1970's, measures were taken to improve the quality of mine waters discharged to watercourses to comply with limitations specified by the Federal National Pollution Discharge Elimination System (NPDES) permits. Implementation of effluent treatment on each of the three mines near Pipeline Arroyo occurred over several years during the mid-1970's. Effluent was treated by using a flocculent to reduce suspended-solids concentrations and barium-chloride to coprecipitate radium with barium sulfate. Concentrations of dissolved uranium were reduced by using an ion-exchange treatment (Perkins and Goad, 1980). This treatment reduced concentrations of uranium and activities of radium by about 85 percent between 1975 and 1982 (table 1). Uranium mining ceased in 1985, and mine dewatering ceased in February 1986.

On July 16, 1979, a tailings-pond dike failed at the United Nuclear Corporation uranium mill near Pipeline Arroyo (table 2). An estimated 360,000 m^3 of uranium mine-tailings liquid and 1,000 metric tons of tailings were discharged to the Puerco River through Pipeline Arroyo (Weimer and others, 1981). The pH of the tailings liquid was about 1.9, and the total gross alpha activity was estimated as 130,000 pCi/L (U.S. Environmental Protection Agency, 1982).

Radionuclides in Water

Radionuclides undergo spontaneous transformations in their nuclei that cause the emission of alpha and beta particles, and to a lesser extent, gamma rays (Faure, 1977). Three decay series that occur in nature are the uranium–238, uranium–235, and thorium–232 decay series (^{238}U, ^{235}U, and ^{232}Th; Aswathanarayana, 1986). Naturally occurring uranium contains, on average, 99.2830 percent, by weight, ^{238}U; 0.7110 percent ^{235}U; and 0.0054 percent uranium–234 (^{234}U) (Hammond, 1970). Uranium ores commonly mined in the United States contain little ^{232}Th (Haywood and others, 1977). Thus the bulk of the radioactivity in the

Table 1. Comparison of concentration of uranium and activities of radium in mining effluent, Church Rock, New Mexico, 1975 and 1981–82

[Modified from Gallaher and Cary (1986, p. 82)]

	Flow-weighted average			
Constituent	**1975[1]**	**Number of samples**	**1981–82[2]**	**Number of samples**
Total uranium, natural, in milligrams per liter.	7.25	23	1.0	14
Total radium–226, in picocuries per liter.	71.2	23	10.5	15

[1] Calculations made from data from U.S. Environmental Protection Agency (1975).

[2] Calculations made from data from New Mexico Environment Department.

Table 2. Selected water-quality constituents in tailings solution and in contaminated streamflow in the Puerco River, July 16, 1979

	Concentrations, in milligrams per liter, except as noted	
Constituent	**Tailings pond[1]**	**Contaminated streamflow, Puerco River[2]**
Uranium	4.1	6.5
Radium–226, in picocuries per liter.	210	[3]100
Thorium–230, in picocuries per liter.	10,200	8,100
Arsenic	.07	.008
Sulfate	4,800	27,000
Sodium	520	7,700
Chloride	50	5,500
Chromium	.15	1.6
Iron	160	2,210
Manganese	14	73
pH (standard units)	1.9	1.4

[1] Sampled February 5, 1979, from tailings pond (Weimer and others, 1981).

[2] Sample collected by United Nuclear Corporation at Puerco River at Pinedale Bridge, New Mexico, July 16, 1979 (Wirt and others, 1991).

[3] Dissolved.

ore is associated with ^{238}U and its daughter products (Landa, 1980; fig. 5). Other natural radionuclides occur, for example potassium–40, which can be an important source of beta activity in some waters (Thomas and others, 1993).

The relation between the concentration of the radionuclide, in micrograms per liter (μg/L), and the activity of the radionuclide, in picocuries per liter, for any radionuclide is calculated from:

$$C = k(WTD)$$

where

C = concentration, in micrograms per liter;
W = atomic weight;
T = half-life, in seconds;
D = radioactivity, in picocuries per liter; and
k = conversion constant given by the following relation:

$$k = \frac{1}{(ln2)\,(6.0225 \times 10^{23})} \times 10^{-12} \times 10^{6} = 8.865 \times 10^{-20},$$

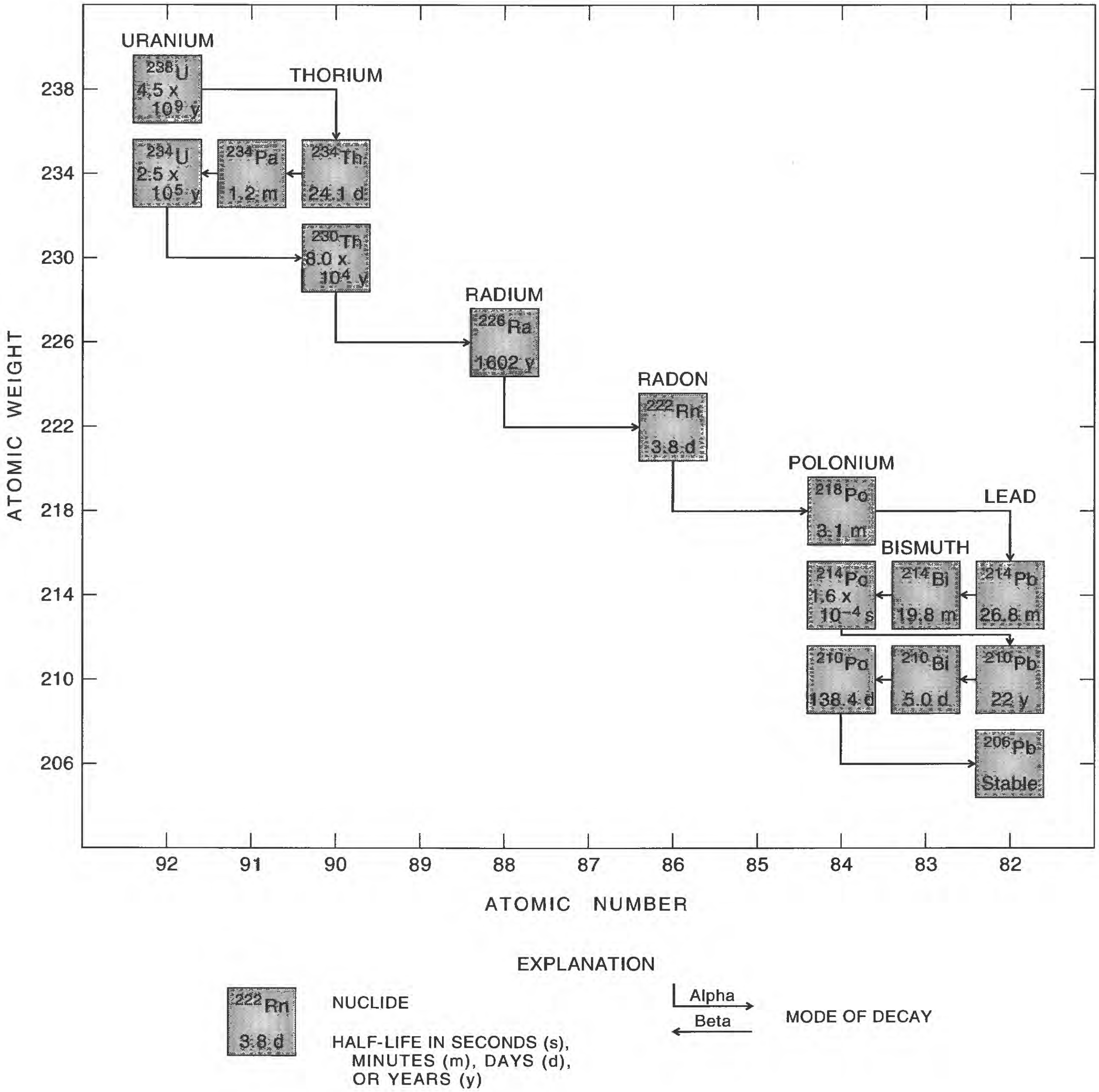


Figure 5. Radioactive-decay scheme of the uranium–238 series (modified from Landa, 1980).

where

6.0225×10^{23} = number of atoms in a gram-molecular weight,
10^{-12} = conversion factor to convert from curies to picocuries,
10^{6} = conversion factor to convert from grams to micrograms.

In summary, radionuclides with short half-lives produce greater amounts of radioactivity than radionuclides with long half-lives for the same atomic abundance.

Radionuclides in the ^{238}U decay series can be harmful to human health because of a combination of radiotoxicity and chemical toxicity. Different radionuclides exhibit varying degrees of both radiotoxicity and chemical toxicity. Radiotoxicity is the damaging effect of ionizing radiation on tissues. Although uranium is a radioactive element, its radiotoxic effects are insignificant compared with its chemical toxicity because of the long half-lives of its isotopes and subsequent low activity. Uranium toxicity primarily is due to the chemical effects of its aqueous hexavalent ions on the kidneys (Wrenn and others, 1987).

The MCL's for radionuclides applicable to the Puerco River Basin in Arizona and New Mexico are based on regulations of the States of Arizona and New Mexico and the USEPA (table 3). Because of its high radiotoxicity, radium in water forms a basis for monitoring natural radionuclides in drinking-water supplies in the United States. The USEPA primary MCL for total ^{226}Ra plus ^{228}Ra is 5.0 pCi/L. The MCL for gross alpha activity minus the sum of uranium and radon activities is 15 pCi/L. The USEPA limit for gross beta from man-made sources is 4 millirem/yr; however, it is given in an annual dose exposure and not easily applied to water samples. A value of 50 pCi/L is considered a presumptive screen for compliance (Diana Marsh, Arizona Department of Environmental Quality, written commun., July 25, 1994). An MCL has not been set for uranium in drinking water. The USEPA has proposed MCL's for uranium and radon in drinking water of 20 μg/L and 300 pCi/L, respectively (U.S. Environmental Protection Agency, 1991).

Acknowledgments

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APPROACH

This study had three objectives related to ground water—(1) to describe the occurrence of radionuclides and other trace elements in the Puerco River alluvial aquifer, (2) to evaluate the movement of contaminants between the stream and alluvial aquifer, and (3) to evaluate the movement of contaminants between the alluvial aquifer and adjacent geologic units. The occurrence of radionuclides and other trace elements was evaluated by sampling a network of wells completed at various depths and distances from the stream. The network was capable of providing water-quality data in three dimensions along the part of the Puerco River subjected to uranium mining-related discharges. Several wells and surface-water tributaries also were sampled in areas where no mining had occurred to evaluate background water quality. The network included monitor wells drilled by the State of New Mexico (Gallaher and Cary, 1986), temporary hand-

Table 3. Federal and State regulatory standards that apply to selected constituents in drinking water and surface water, Puerco and Little Colorado Rivers, Arizona and New Mexico

[Values, in milligrams per liter, as total recoverable fraction unless noted otherwise; pCi/L, picocuries per liter; D, value for dissolved fraction; ---, no established limit]

Constituent	U.S. Environmental Protection Agency[1]	State of New Mexico[2]	State of Arizona						
			Drinking water[3]		Surface water[4]				
		Public water-supply system	Community water system	Non-community water system	Domestic water source	Full body contact	Aquatic and wildlife (warm water fishery)	Agricultural livestock watering	Agricultural irrigation
Arsenic	0.05	0.05	0.05	0.10	0.05	0.50	0.360 D	0.2	2.0
Barium	2	1	1	2	1.0 D	1.0	---	---	---
Beryllium	.001	---	---	---	.000006	.00033	.0065	---	---
Boron	---	---	---	---	---	---	---	---	1.0
Cadmium	.005	.010	.010	.020	.005	.07	(5)	.050	.050
Chloride	(250)	---	(6)	(6)	250	---	---	---	---
Chromium	.1	.05	.05	.5	.1	---	(5)	1.0	1.0
Copper	(1.0)	---	(6)	(6)	---	---	(5)	.50	5.0
Fluoride	(2)	4.0	4.0	6.0	4.0	---	---	---	---
Gross alpha, in pCi/L. Includes radium–226 but excludes radon and uranium.	[7]15	[7]15	[7]15	[7]15	[7]15	---	---	---	---
Gross beta, in pCi/L. Manmade sources only.	---	---	[8]50	[8]50	---	---	---	---	---
Iron	(.3)	---	(6)	(6)	---	---	---	---	---
Lead	.005	.05	.05	.1	.050	---	(5)	.10	10
Manganese	(.05)	---	(6)	(6)	---	---	---	---	10
Mercury	.002	.002	.002	.004	.0021	.0006	.0024D	.01	---
Nickel	---	---	---	---	.14	2.8	(5)	---	---
pH (standard units)	(6.5–8.5)	---	(6)	(6)	5.0–9.0	6.5–9.0	6.5–9.0	6.5–9.0	4.5–9.0
Radium–226, in pCi/L	[9]20	---	---	---	---	---	---	---	---
Radium–228, in pCi/L.	[9]20	---	---	---	---	---	---	---	---
Radium–226 plus radium–228, in pCi/L.	5	5	5	5	5	---	---	---	---

Table 3. Federal and State regulatory standards that apply to selected constituents in drinking water and surface water, Puerco and Little Colorado Rivers, Arizona and New Mexico—Continued

		State of New Mexico[2]	State of Arizona						
			Drinking water[3]		Surface water[4]				
Constituent	U.S. Environmental Protection Agency[1]	Public water-supply system	Community water system	Non-community water system	Domestic water source	Full body contact	Aquatic and wildlife (warm water fishery)	Agricultural livestock watering	Agricultural irrigation
Radon, in pCi/L	[9]300	---	---	---	---	---	---	---	---
Selenium	.05	0.01	0.01	0.02	0.050	0.420	0.02	0.05	0.02
Silver	(.10)	.05	.05	.10	---	---	(5)	---	---
Sulfate	(250)	---	(6)	(6)	250	---	---	---	---
Total dissolved solids	(500)	---	(6)	(6)	500	---	---	---	[10]1,000 [11]2,000
Uranium	[9].020	---	---	---	.035 D	---	---	---	---
Zinc	(5)	---	(6)	(6)	5.0	28	(5)	25	10

[1] U.S. Environmental Protection Agency (1992). Values in this column are primary maximum contaminant levels, except those enclosed by parentheses, which are secondary maximum contaminant levels. These values are maximum limits for water delivered for public drinking-water consumption and are not applicable to surface water.

[2] State of New Mexico Environment Department (1991). Regulations governing water supplies, as amended through April 16, 1991, effective May 16, 1991.

[3] State of Arizona (1992). Designated for domestic water use according to Rule A.A.C. R18–11–104. These values are maximum limits for public drinking-water consumption and are not applicable to water-quality regulations for streamflow.

[4] State of Arizona (1992). Designated for protection of "aquatic and wildlife (warm water fishery)" use according to Rule A.A.C.R18–11–104 for the Puerco and Little Colorado Rivers.

[5] State of Arizona (1992). Regulations designated for protection of "aquatic and wildlife (warm water fishery)" use per Rule A.A.C.R18–11–104 for the Puerco and Little Colorado Rivers. The most restrictive dissolved constituent levels for cadmium, copper, lead, nickel, and zinc are based on chronic toxicity criteria. The most restrictive regulation for silver is based on an acute toxicity criterion because no chronic standard has been established. The standard for the dissolved fraction for each constituent is related to hardness (H, as $CaCO_3$) in milligrams per liter according to the relations:

Cadmium: $e^{0.7852\ln H-3.490}$ Lead: $e^{1.2730\ln H-4.705}$ Silver: $e^{1.72\ln H-6.52}$
Copper: $e^{0.8545\ln H-1.465}$ Nickel: $e^{0.8460\ln H+1.1644}$ Zinc: $e^{0.8473\ln H+0.761}$

Hardness ranged from 110 to 400 milligrams per liter (mg/L) with an average of 273 mg/L for nine samples in the Puerco River near Chambers and ranged from 11 to 100 mg/L with an average of 37 mg/L for six samples in the Little Colorado River near Joseph City. MACL's for data in this study were calculated for an assumed hardness of 150 mg/L.

[6] No regulatory maximum contaminant level. Constituent to be monitored and reported to regulatory agency.

[7] In cases where no data are available for individual radionuclides (radium–226, radon, and uranium), if value is less than or equal to 15 picocuries per liter (pCi/L), compliance is presumed.

[8] If the average annual concentration of manmade beta activity released from a regulated facility exceeds 50 pCi/L, additional analysis is required according to State of Arizona, Department of Environmental Quality, Public and semipublic water-supply system rules: August 8, 1991, Section R18–4–245, p. 33–35.

[9] Maximum contaminant levels for radium–226, radium–228, and uranium are proposed standards under consideration (U.S. Environmental Protection Agency, 1991a, b).

[10] Partial support.

[11] Nonsupport.

driven wells, and monitor wells installed for this study. Temporary hand-driven wells are shallow, small-diameter wells that provided information on flow directions between the stream and alluvial aquifer and on ground-water quality near the streambed. Several private wells also were sampled.

Contaminant migration was evaluated by considering aspects of flow, water quality, sediment chemistry, and geochemistry. Each of these factors could affect the movement of contaminants or may indicate processes that could affect contaminants. Advective flow governs the direction of contaminant migration. If net flow in the alluvial aquifer or bedrock aquifer is toward the Puerco River, contaminants in the river are less likely to move into the ground-water system than if net flow is away from the river. Water-quality studies were used to interpret the results of complex geochemical processes. For example, a lack of contaminants in a water sample indicates either that they have been removed from solution by some process or that the water is not from a contaminant-source area. In addition to ground water, water-quality samples included collection and analysis of surface water and wastewater in order to characterize possible sources of recharge to the shallow alluvial aquifer underlying the Puerco River. Uranium isotope ratios and stable isotopes of hydrogen and oxygen were used to distinguish among various sources of water. Sediment chemistry was studied to determine the fate of contaminants if, for example, significant amounts of the contaminant were removed from solution by sorption of solutes on sediments or precipitation of minerals. Geochemical models were used to calculate the degree of saturation of minerals containing contaminants and to predict the results of mixing of waters from different sources. Ground-water flow modeling was used to determine directions of flow, advective transport, and the degree of connection between units.

Design of Ground-Water Monitoring Network

Ground-water quality studies were done at two scales—the entire Puerco River Basin and in local reaches. The stream was assumed to be a 140-km-long source of contaminants. The placement of monitor wells was designed to encompass that 140-km reach, yet allow the description of flow and water quality on a scale of from meters to tens of meters normal to the streambed. The monitor well network consisted of clusters of closely spaced wells near the stream. Each well cluster was spaced from 2 to 35 km along the stream.

Between September 1988 and May 1990, 31 monitor wells were installed at 6 sites from near Manuelito, New Mexico, to near Chambers, Arizona (fig. 6; table 4). Wells were constructed to obtain "point" measurements of hydraulic head and water-quality samples at short screened intervals (generally 2.5–3.0 m for wells open to the water table and 1.6 m for wells below the water table). Each well cluster consisted of three to nine wells. Two or three vertically separated wells were positioned about 5 to 10 m from the bank of the stream. One to three wells were positioned normal to the stream and farther from the bank. These wells were generally 30 to 120 m from the stream. At four of six clusters, one to three or more wells were positioned from about 30 to 120 m upstream and adjacent to the bank of the stream in order to provide three-dimensional coverage at the local scale. One well at the Chambers well cluster and three wells at the Cedar Point well cluster in the Sanders area were completed in the underlying Petrified Forest Member of the Chinle Formation. At the Cedar Point well cluster, a well was screened at the water table about 240 m from the stream and provided a third sampling point normal to the stream.

The design of a well cluster is illustrated by the well cluster near Chambers (fig. 7). Wells are arranged in a triangular pattern with three wells at each corner. Each group of three wells consists of a well screened at the water table, a well screened at the bottom of the alluvial aquifer, and a well screened about halfway between those points. One of the deep wells, identified as CW–1, is screened in the underlying Petrified Forest Member of the Chinle Formation. Two temporary hand-driven wells were installed below the streambed at the site. One hand-driven well was open to the water table (about 0.8 m below land surface), and the other was open about 4.5 m below land surface.

Lithology was similar at all 31 monitor wells and consisted of interbedded clay and sand layers. Clay layers typically are more abundant near the surface and near the contact with the underlying formation. During drilling, fine to medium-fine silty sand flowed into the boreholes and up the inside of the augers at most locations. These flowing sands collapsed around the well casings during installations from the bottom of the hole to approximately the water table. In the water-table wells, silica sand was installed from the top of the

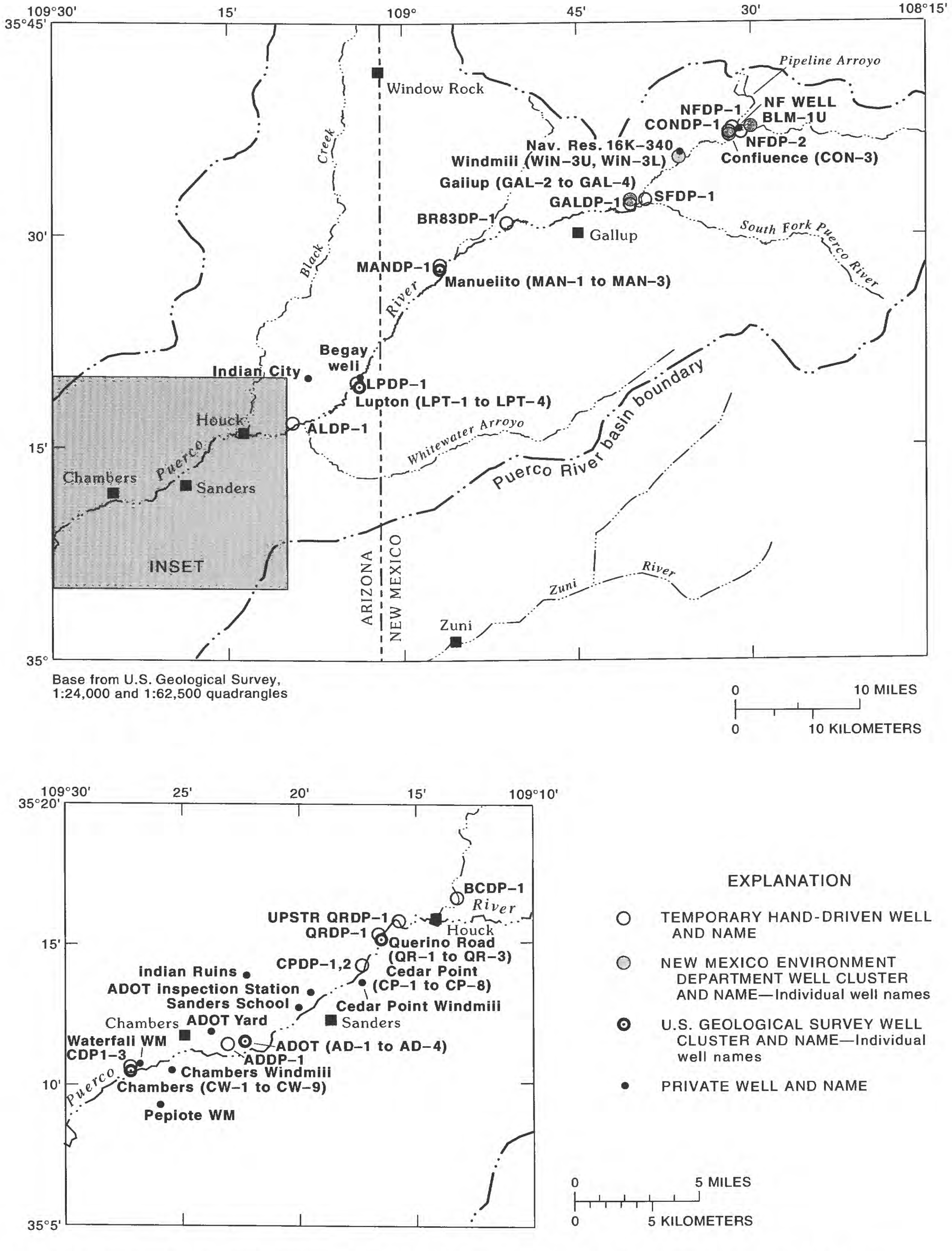


Figure 6. Locations of wells and temporary hand-driven wells, Puerco River Basin, Arizona and New Mexico.

Table 4. Summary of well-completion data for selected wells and temporary hand-driven wells, Puerco River Basin, Arizona and New Mexico

[---, no data]

Well name	Site identification	Altitude above sea level, in meters	Depth of hole, in meters	Casing depth, in meters	Screened interval, in meters		Formation	Water level below land surface, in meters	Date measured
					From	To			
CW–1	351043109270301	1,744.22	32.0	32.0	27.4	29.0	Chinle	4.7	09–27–88
CW–2	351043109270302	1,743.85	25.0	25.0	14.3	15.8	Alluvium	3.6	09–27–88
CW–3	351043109270303	1,744.31	11.7	11.7	4.6	6.1	...do......	4.2	09–27–88
CW–4	351038109270801	1,743.09	30.5	30.5	27.4	29.0	...do......	3.4	09–27–88
CW–5	351038109270802	1,743.02	19.8	19.8	16.8	18.3	...do......	3.4	09–27–88
CW–6	351038109270803	1,743.14	9.1	9.1	4.6	7.6	...do......	3.6	09–28–88
CW–7	351039109270001	1,748.75	30.0	30.0	24.4	26.0	...do......	8.9	09–30–88
CW–8	351039109270002	1,748.88	21.2	21.2	18.3	19.8	...do......	8.9	09–30–88
CW–9	351039109270003	1,748.81	16.5	16.5	11.6	14.6	...do......	8.8	09–30–88
CDP–1	351044109270501	[1]1,740	---	---	---	---	...do......	.7	01–16–89
CDP–2	351044109270502	[1]1,740	---	---	---	---	...do......	---	---
CDP–3	351044109270503	[1]1,740	4.7	---	---	---	...do......	.3	04–04–89
CDP–4	351045109270601	1,740.87	---	---	---	---	...do......	---	---
AD–1	351140109220901	1,766.01	59.1	57.9	36.6	39.6	...do......	5.3	06–20–89
AD–3	351140109220403	1,765.97	12.2	10.1	5.5	8.5	...do......	6.1	06–22–89
AD–4	351144109220701	1,765.23	12.2	11.6	5.5	8.5	...do......	7.6	06–28–89
AD–5	351139109221301	1,765.44	11.1	9.9	5.3	8.4	...do......	3.8	06–23–89
ADDP–1	351135109225001	[1]1,760	11	---	---	---	...do......	.7	05–15–90
CP–1	351411109170701	1,792.23	41.0	33.2	26.8	28.3	Chinle	6.6	06–15–89
CP–2	351411109170702	1,792.30	18.1	18.1	15.4	16.9	Alluvium	6.1	06–28–89
CP–3	351411109170703	1,792.17	8.1	8.1	6.2	7.8	...do......	6.0	06–28–89
CP–4	351415109170201	1,792.11	8.1	8.1	5.8	7.3	...do......	5.7	06–28–89
CP–5	351410109170201	1,791.71	8.1	8.1	5.3	7.8	...do......	5.4	06–19–89
CP–6	351407109165801	1,791.48	7.9	7.7	4.9	7.6	...do......	6.9	06–19–89
CP–7	351407109165601	[1]1,800	20.4	20.4	15.8	18.9	Chinle	5.8	07–26–90
CP–8	351407109165602	[1]1,800	39.6	39.6	35.1	38.1	Alluvium	5.8	07–26–90
CPDP–1	351419109165901	[1]1,790	17	---	1.3	1.6	...do......	.7	11–17–89
CPDP–2	351419109165901	[1]1,790	13	---	---	---	...do......	.5	05–16–90
QR–1	351519109161501	1,796.55	48.3	34.7	31.7	33.2	...do......	4.0	06–30–89
QR–2	351519109161502	1,796.61	9.1	9.0	4.3	7.5	...do......	3.8	06–27–89
QR–3	351519109161801	1,794.39	9.1	8.8	4.3	7.3	...do......	1.4	06–27–89
QRDP–1	351527109161901	[1]1,790	16	---	---	---	...do......	1.6	06–07–89
UPSTRQRDP–1	351620109152101	[1]1,790	---	---	.8	1.1	...do......	1.9	06–08–89
LPT–1	351928109042601	1,888.52	21.6	21.6	14.0	15.5	...do......	1.1	10–11–90
LPT–2	351928109042602	1,888.76	6.1	6.1	3.0	4.6	...do......	1.4	10–11–90
LPT–3	351929109042401	[1]1,890	8.1	8.1	1.8	5.0	...do......	2.1	10–12–90
LPT–4	351930109042701	[1]1,890	9.1	9.0	2.9	5.9	...do......	2.2	10–11–90

Table 4. Summary of well-completion data for selected wells and temporary hand-driven wells, Puerco River Basin, Arizona and New Mexico—Continued

Well name	Site identification	Altitude above sea level, in meters	Depth of hole, in meters	Casing depth, in meters	Screened interval, in meters		Formation	Water level below land surface, in meters	Date measured
					From	To			
LPDP–1	351942109041401	[1]1,880	---	---	1.1	1.4	...do......	[2]0.6	06–11–90
MAN–1	352742108563301	[1]1,910	24.8	24.8	21.8	23.3	...do......	6.5	10–10–90
MAN–2	352743108563401	[1]1,910	13.7	13.7	7.6	10.7	...do......	7.9	06–06–90
MAN–3	352742108563302	[1]1,910	15.7	15.7	9.6	14.2	...do......	7.9	10–06–90
MANDP–1	352743108563201	[1]1,900	---	---	.7	1.0	...do......	[2].1	10–16–90
GAL–2	353219108400301	[1]2,000	12.2	12.2	9.1	12.2	...do......	4.1	10–24–90
GAL–3	353218108400303	[1]2,000	12.2	12.2	9.1	12.2	...do......	4.2	10–24–90
GAL–4	353218108400304	[1]2,000	24.4	24.4	21.4	24.4	Entrada	4.0	10–24–90
GALDP–1	353215108400401	[1]1,980	3.1	---	---	---	Alluvium	[2].5	05–02–90
WIN–3L	353535108355004	[1]2,040	13.7	13.7	---	---	...do......	6.1	10–24–90
WIN–3U	353535108355003	[1]2,040	11.5	11.5	5.5	8.5	...do......	5.6	10–24–90
CON–3	353710108312803	[1]2,080	13.1	13.1	8.5	11.6	...do......	10.0	01–11–88
CONDP–1	353717108312801	[1]2,070	14	---	.7	1.0	...do......	.6	10–18–90
NF Well	353726108303702	[1]2,085	---	---	---	---	...do......	---	---
NFDP–1	353727108311501	[1]2,090	---	---	---	---	...do......	---	---
NFDP–2	353726108303701	[1]2,085	---	---	---	---	...do......	.5	11–18–89
BLM–1U	353742108293601	[1]2,090	16.8	16.8	10.7	13.7	...do......	8.8	01–10–89
ADOT Yard	351202109233001	[1]1,760	---	---	---	---	---	---	---
Indian Ruins	351400109220001	[1]1,870	---	---	---	---	Bedrock	---	---
Indian City	352000109075001	[1]2,010	---	---	---	---	---	---	---
BRIDGE-83DP (BR83DP–1)	350356108504401	[1]1,930	1.46	---	---	---	---	.061	10–16–90

[1] Elevation measured from topographic map.

[2] Water level measured below the surface of the streambed.

zone of collapse to about 1 m above the top of the well screen. A bentonite plug was then installed and the holes were grouted to the surface. In the deeper wells, a bentonite plug was installed above the zone of natural collapse, and the holes were grouted to the surface.

In addition to the six clusters of wells installed during this study, samples were collected from wells in four clusters installed by the NMED along the Puerco River upstream from the mouth of Pipeline Arroyo to near Gallup (fig. 6; Gallaher and Cary, 1986). At 18 locations, hand-driven wells were installed below the streambed upstream from the mouth of Pipeline Arroyo to below the mouth of the Puerco River on the Little Colorado River near Holbrook, Arizona. Several private wells completed in the alluvial aquifer or in adjacent bedrock formations also were sampled (fig. 6).

Data Collection

Water-Level Measurements and Geophysical Logs

Water levels were measured monthly by using a graduated steel tape at monitor wells in the six well clusters installed by the USGS. Water-level recorders were installed on 10 of those wells. Geophysical logging, including resistivity, natural gamma, and gamma-gamma logs were made at 11 of the wells. All water-level and geophysical data are presented by Fisk and others (1994).

Evapotranspiration Measurements

Evapotranspiration (ET) is the major component of ground-water discharge from the shallow alluvial aquifer. In order to determine the amount of ground-

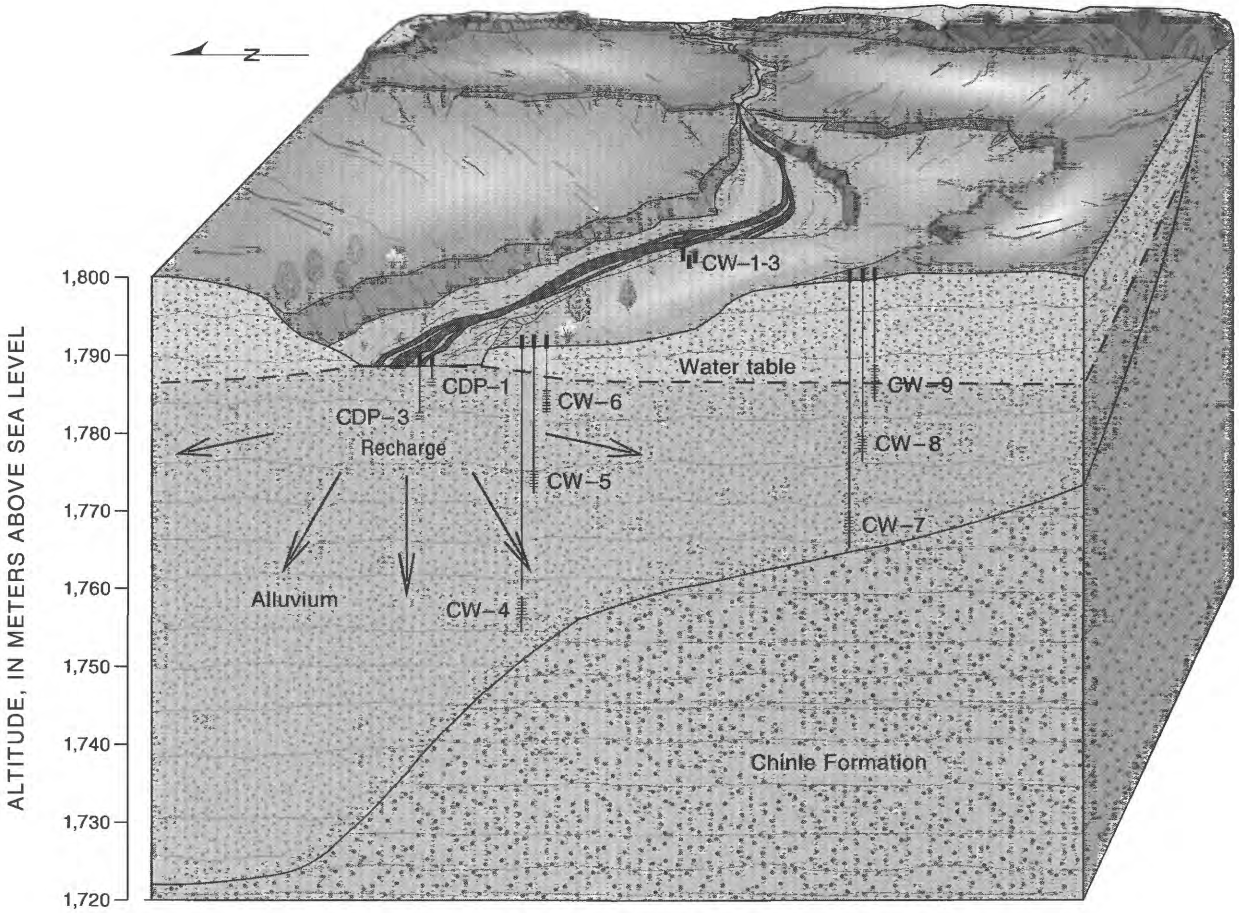


Figure 7. Stylized view of the well cluster at Chambers, Arizona.

water loss, direct measurements of ET were collected from the streambed and from adjacent vegetated terraces on November 1, 1990. Measurements were made to evaluate the relation between ET rate and depth to ground water by using a hemispherical ET measuring chamber (Stannard, 1988). The chamber measures vapor density in a known volume of air above the land surface at rapid time intervals following emplacement. The rate of vapor-density increase inside the chamber soon after emplacement is proportional to ET (Stannard, 1988). Although ET is reported in millimeters per day, it is an instantaneous rate at the time of measurement.

ET measurements were made at 10 sites near the Chambers well cluster. Sites were along a line from near well CW–3 to the low-flow channel in the streambed of the Puerco River. The low-flow channel was near the opposite bank of the Puerco River from well CW–3, contained about 0.02 m^3/s of flow, and intersected the water table. Water levels were measured in three temporary hand-driven wells, two shallow holes dug in the channel, and in well CW–3 to determine the depth to the water table at each of the 10 locations. The depth to the water table ranged from 0 to 3.4 m. Most of the channel cross section was bare sand; therefore, only evaporation and not transpiration was measured at most sites. An exception was two sites on the bank where transpiration from small plants also was measured.

On November 1, 1990, 32 instantaneous measurements of the ET rate were made between 2:20 p.m. and 4:45 p.m. Air temperature decreased from 18 to 15°C during that time, and the weather was windy and partly cloudy. The ET rate decreased during the measuring period, as evidenced by the change in rate for open water (evaporation rate) from 6.0 mm/d at 2:35 p.m. to

2.8 mm/d at 4:20 p.m. The decrease occurred in response to the decrease in air temperature and possibly to changes in sun angle, cloud cover, and wind velocity. Because of the decrease in ET rate, the 32 measurements were divided into three data sets for analysis of the relation between ET rate and depth to ground water (fig. 8).

Measured ET rates ranged from 0.4 mm/d where the land surface was between 1.8 and 3.4 m above the water table to 6.0 mm/d over open water. ET varied with the moisture condition at the land surface (fig. 8). Where the land surface was visibly damp, the ET rate approximated the ET rate (evaporation rate) of open water. The ET rate from a dry surface, however, was about half of the ET rate from a damp surface with a similar depth to water, as indicated by comparison of measurements at adjacent sites. At 2:40 p.m. and 2:48 p.m., the ET rate at a site with a damp surface was 5.7 and 5.6 mm/d, respectively, compared with 3.5 and 2.4 mm/d, respectively, at an adjacent site with a dry surface. Depth to water at the sites was 0.93 m. At the time of these measurements, most of the streambed was visibly damp, and the depth to water was about 0.9 m or less.

Water-Quality Sampling

Water-quality sampling was designed to provide three types of information—(1) descriptive water quality including concentrations of major and trace constituents and radionuclides, (2) information about the ground-water flow system using isotopes and proportions of major ions as tracers of water, and (3) information necessary to perform geochemical modeling to determine speciation and calculate mineral saturation indices for selected uranium minerals.

Water-quality samples were collected by using standard techniques (Wood, 1976). Ground-water samples were collected by using a stainless-steel electric submersible pump at wells and a peristaltic pump at hand-driven wells. Field constituents, which include temperature, pH, specific conductance, dissolved-oxygen concentration, and oxidation-reduction potential (Eh) were monitored continuously during pumping by using a Hydrolab equipped with a flow-through chamber. Samples were collected after several casing volumes of water were removed (usually about 10), and field constituents had remained stable for 5 minutes or more. Surface-water samples were collected manually and by automatic water samplers as described in Fisk and others (1994).

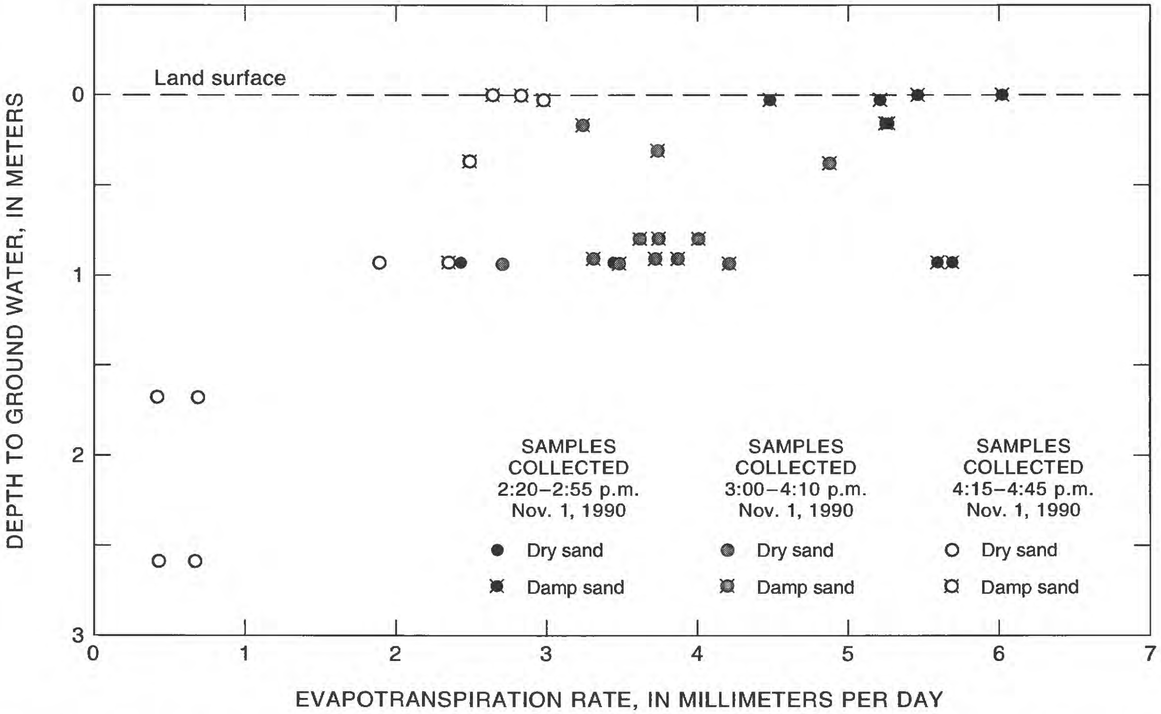


Figure 8. Relation between evapotranspiration and depth to ground water near well cluster at Chambers, Arizona.

Eh was measured by using a platinum electrode and a calomel-reference electrode. The potential of the hydrogen electrode represents the reduction of H^+ ions to H gas and is taken as zero (Hem, 1985). The electrode was calibrated by using Zobell's solution for a range of temperatures before field use. In general, measured Eh values do not correlate with values calculated from concentrations of redox species because of a lack of chemical equilibrium (Lindberg and Runnels, 1983; Welch and others, 1988). In some systems, Eh measurements may yield values that are thermodynamically consistent with a single, dominant redox couple. Examples include systems dominated by iron (Nordstrom and others, 1979), manganese (Bricker, 1965), and sulfur (Berner, 1963). In some systems, Eh measurements also can be a qualitative indicator of redox condition (Champ and others, 1979). Eh was measured in this study because uranium mobility is affected by redox, and even qualitative information on redox was deemed useful.

Each ground-water sample was split into subsamples on site. Samples for analyses of dissolved constituents were filtered at the site through a 140-mm-diameter membrane with a 0.45-µm effective-diameter pore size. The filter was connected in line with the pump to minimize the exposure of the water to the atmosphere before filtering. All analytical results for filtered samples are operationally defined as representing the dissolved concentration of the constituent. Subsamples for analyses of major anions, cations, and trace elements were filtered and acidified with nitric acid to a pH of less than 2. Subsamples for analysis of dissolved organic carbon were filtered through a 0.45-µm silver filter, placed in amber glass bottles, and chilled to 4°C. Subsamples for nutrients including nitrogen and phosphorus were filtered, treated with mercuric chloride, and chilled to 4°C.

Subsamples for selected radionuclides, including isotopes of uranium, thorium, and radium were filtered and acidified with hydrochloric acid to a pH of less than 2. Duplicate subsamples for radon–222 (^{222}Rn) were collected by using a syringe at the outlet tube and immediately transferred to scintillation vials containing mineral oil. Subsamples for gross alpha and gross beta determinations collected in 1988 and 1989 were neither filtered nor acidified in the field, but were resuspended and filtered in the laboratory about a month after the date of collection and analyzed for both dissolved and suspended gross alpha and gross beta activities. Subsamples for dissolved gross alpha and gross beta determinations collected in 1990 and 1991 were filtered at the site and acidified with hydrochloric acid to a pH of less than 2.

Radionuclide analyses other than ^{222}Rn were done by U.S. Testing, Richland, Washington, in 1988; by International Technology Corporation Laboratories (ITC Labs), Oak Ridge, Tennessee, in 1989; and by ITC Labs, Richland, Washington, in 1990 and 1991. Analyses of isotopes of oxygen and hydrogen were done by the USGS in Reston, Virginia, and analyses of isotopes of sulfur were done by the USGS in Denver, Colorado. All other analyses were done by the USGS National Water-Quality Laboratory, Arvada, Colorado.

Approximately 10 percent of the radiochemical samples were collected in duplicate. Results of duplicate analyses of gross alpha and gross beta generally compared within about 25 percent at activities greater than about 5 pCi/L (fig. 9). Duplicate analyses of uranium, uranium–238 (^{238}U), and uranium–234 (^{234}U) compared within about 20 percent at activities greater than about 1.0 pCi/L. The USGS National Water-Quality Laboratory has a three-part quality-assurance program for radiochemical analyses done by contract laboratories (Ann Mullin, hydrologist, USGS, written commun., 1991).

1. Monitor the contract laboratory's results for the USEPA cross-check/drinking-water program to check that the laboratory is maintaining USEPA certification.
2. Prepare samples for all constituents in a wide range of values by using standards received from EPA. Submit those samples to the contract laboratory to check accuracy and determine that stated detection limits can be achieved.
3. Submit duplicate samples sent in by field personnel to check precision in analyzing actual field samples.

The duplicate samples collected in this study helped fulfill the third part of the quality-assurance program.

Solid-Phase Sampling

Solid-phase samples were collected from the streambed during sampling of hand-driven wells and from well cores during drilling. Samples from the streambed were collected by digging approximately 1 m below the land surface at the hand-driven well location following aqueous-phase sampling. Material then was scooped from the sides of the hole by using a

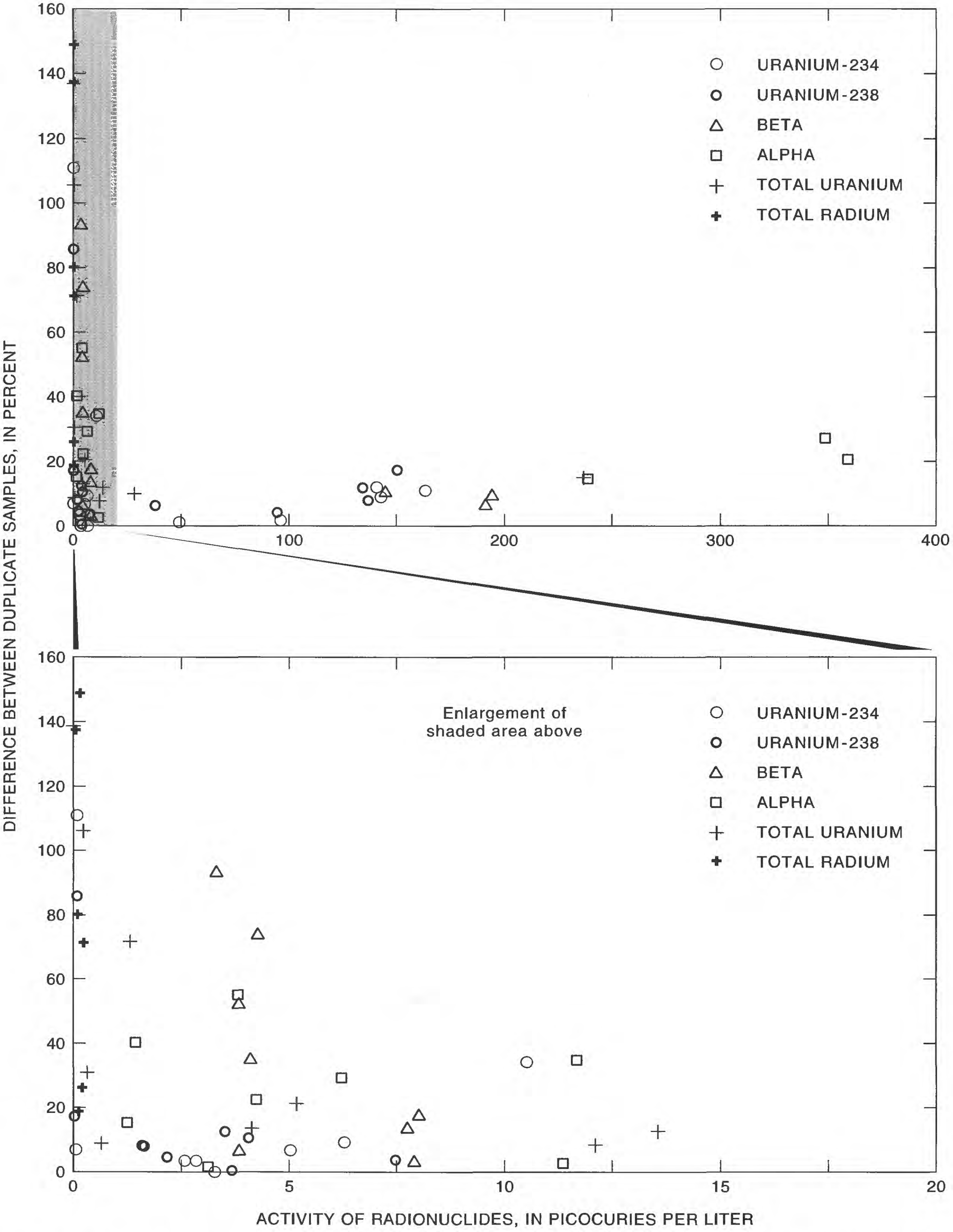


Figure 9. Comparison of analyses of duplicate radiochemical samples from the Puerco River Basin, Arizona and New Mexico.

plastic container. Samples collected during drilling were taken either from cores in a hollow-stem auger or from the outside of the bit after the augers were pulled out of the hole. In each case where samples were taken from the outside of the bit, the sample was of clay or clayey sand from near the bottom of the hole.

In September 1988, 25 samples were collected at the Chambers well cluster during drilling and were individually mixed and split. Subsamples were analyzed for grain-size distribution by using a wet-sieve method. An additional 21 samples were collected in 1989 and 1990 from the streambed upstream from the mouth of Pipeline Arroyo to near the Cedar Point well cluster and during drilling at the Manuelito, Lupton, and Cedar Point well clusters. Those samples were wet sieved by using small amounts of distilled water. The fraction passing a 0.062-mm sieve, which included the distilled water used in sieving, then was oven dried and analyzed for selected radionuclides.

Methods of Flow Analysis

The potential for movement of water containing radionuclides from the stream into the alluvial aquifer was of primary interest in this study. Because the stream is ephemeral in some reaches, and water levels in the alluvial aquifer typically are less than 1 m below the streambed, it was assumed that ground-water flow directions could vary depending on flow conditions in the stream. Water levels, water budgets, and geochemical and isotopic methods for tracing the movement of water were used in the analysis of ground-water flow.

Water-Level and Water-Budget Methods

Water-level measurements were used to determine gradients in hydraulic head, which indicate direction of flow. Because of the distribution of the wells and the positioning of the well screens, hydraulic gradients were determined in three dimensions. Water levels also were measured in hand-driven wells screened from about 0.5 to 5.0 m below the streambed and in the adjacent stream when there was flow.

Water budgets were used in some areas to evaluate recharge to and discharge from the streambed over time. Potential ET was calculated as a function of daily incident solar radiation and average daily temperature by using the Jensen-Haise radiation method as presented by Bauer and Vaccaro (1986). Daily values of potential ET then were summed for periods of varying length for use in the numerical model of ground-water flow and were summed for 1 year to yield an estimated annual ET rate for use in water-budget calculations. Historical data were used to estimate mine-dewatering discharge to the stream and seepage losses between the mines and the USGS streamflow-gaging station at Gallup. Additionally, instantaneous measurements of ET, made at various locations in the streambed adjacent to the Chambers well cluster on November 1, 1990, were used to evaluate the relation between ET rate and depth to ground water.

A numerical model of ground-water flow was developed for a cross section at the Chambers well cluster. The model simulated transient flow between the stream and aquifer. The objective in developing the model was to test the conceptual model of flow for that part of the basin and in particular relations between ET rate, water levels, and ground-water flow directions in relation to the stream.

Geochemical and Isotopic Methods

Four geochemical and isotopic characteristics were evaluated to distinguish sources of water to the alluvial aquifer—(1) proportions of major ions, (2) stable-isotope ratios of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$), (3) stable-isotope ratios of sulfur ($^{34}S/^{32}S$), and (4) tritium (^{3}H). Additionally, isotope ratios of uranium ($^{234}U/^{238}U$) were used to distinguish uranium from mine-dewatering effluent from uranium that occurs naturally in the alluvial aquifer.

Proportions of major ions are determined by the mineralogy of the aquifer material and geochemical processes changing these ratios during evolution of the water chemistry. Proportions of major ions can be displayed on trilinear diagrams (Piper, 1944). A trilinear diagram is a means of expressing water composition in terms of major cation and major anion species. A water sample can be typified according to the area of each trilinear plot in which it falls. Water samples from various locations in the basin were plotted on trilinear diagrams and compared to evaluate possible sources and pathways of migration of water in the alluvial aquifer. Sulfate and chloride concentrations in samples of mine water, surface water, and ground water near the Puerco River and Pipeline Arroyo also were compared graphically. These comparisons were used to evaluate sources of recharge and changes in water chemistry in the alluvial aquifer near the well clusters that occurred after the end of mine dewatering.

Stable isotopes of oxygen and hydrogen, the elements that compose water, were measured to determine sources of water to the alluvial aquifer. The isotope ratios are expressed by delta notation (δ) in parts per mil differences relative to standard mean ocean water (SMOW; Freeze and Cherry, 1979). Phase changes, such as evaporation and condensation, fractionate oxygen and hydrogen isotopes because of differences in mass. Lighter isotopes evaporate preferentially resulting in the water being enriched in oxygen–18 (^{18}O) and hydrogen–2, referred to as deuterium (D), and a vapor phase enriched in oxygen–16 (^{16}O) and hydrogen–1. As water evaporates from the oceans, the vapor is depleted in ^{18}O and D in relation to ocean water by about 12–15 per mil and 80–120 per mil, respectively (Freeze and Cherry, 1979). Stable isotopes of oxygen and hydrogen have conservative properties in low-temperature ground-water systems and virtually are unaffected by chemical processes over geologically short periods of time (Muir and Coplen, 1981). These characteristics result in spatial and seasonal variation in $\delta^{18}O$ and δD values in precipitation and conservative properties in ground-water systems not subject to evaporation. $\delta^{18}O$ and δD of water samples were plotted in relation to each other and to the global meteoric water line to determine sources of the water to the alluvial aquifer.

The ratio of the two most abundant isotopes of sulfur, $^{34}S/^{32}S$, is measured in relation to the ratio measured in the troilite standard from the Canyon Diablo meteorite (Krouse, 1980) and, as in $\delta^{18}O$ and δD values, is reported in parts per mil. Sulfur that is enriched in ^{34}S relative to the Canyon Diablo troilite has positive $\delta^{34}S$ values. Conversely, sulfur that is depleted in ^{34}S has negative $\delta^{34}S$ values. The $\delta^{34}S$ of a water is determined by the isotopic composition of sulfur sources and processes that fractionate the sulfur isotopes. The most significant process that fractionates sulfur isotopes is bacterial reduction of sulfate to sulfide (Krouse, 1980). The net amount of fractionation varies from almost 0 to 70 per mil and depends on the rate of reduction, abundance of sulfate, and type of bacteria. Values of $\delta^{34}S$ were plotted spatially to determine sources of water to the alluvial aquifer.

Tritium (^{3}H) is a radioactive isotope of hydrogen consisting of a proton and two neutrons and having a half-life of 12.3 years. Tritium occurs naturally in small concentrations, in the range of about 5 to 20 tritium units (or 1 to 7 pCi/L; Freeze and Cherry, 1979). Tritium also is produced as a byproduct of thermonuclear explosions. Beginning in 1952, atmospheric testing of hydrogen bombs released large quantities of manmade tritium to the hydrologic cycle. Because tritium is an isotope of hydrogen, it will bond with oxygen to form water and, therefore, has been used as a tracer of water movement. A measured concentration of tritium significantly above pre-1952 levels indicates that the water, or at least a fraction of the water, originally entered the ground-water system sometime after 1952. Areas where flow generally was upward from underlying formations (small tritium concentrations) were distinguished from areas where flow generally was downward from the surface (large tritium concentrations). That distinction was the basis for dividing the study area into three areas that corresponded to three reaches of the stream to define flow relations between the stream and aquifer.

Methods of Water-Quality and Geochemical Analyses

Concentrations of selected water-quality constituents including radionuclides and spatial and temporal variations in concentrations were evaluated graphically, statistically, and by comparison to State and Federal water-quality standards. Graphical techniques included plotting of concentrations in cross section under the Puerco River upstream from the mouth of Pipeline Arroyo to downstream from Chambers and plotting of concentrations normal to the stream at well clusters. Statistical analysis included descriptive statistics and correlations between concentrations and environmental factors that may affect concentrations, for example, correlations between concentrations of dissolved iron and dissolved organic carbon.

Geochemical processes involving dissolved uranium and iron were simulated by using the PHREEQE computer program (Parkhusrt and others, 1980). Modeled saturation indices of iron oxyhydroxide were plotted to evaluate the relation between measured Eh and iron concentrations on the assumption of equilibrium. Aqueous speciation of uranium was modeled for the same samples to evaluate saturation of uranium minerals in ground water as a function of dissolved uranium concentration and Eh. Uranium saturation also was modeled in mine-dewatering effluent in the Puerco River by using historical water-quality data. The objective in modeling historical uranium data was to make a qualitative evaluation of the likelihood that precipitation of uranium minerals could occur in mine-dewatering effluent.

Uranium of mine-dewatering origin was distinguished from naturally occurring uranium by using uranium-isotope ratios. Uranium-isotope activity ratios of ^{234}U to ^{238}U are a useful tracer in some hydrologic systems and have been used to obtain information on sources of water, mixing characteristics, and circulation patterns (Osmond and Cowart, 1976; 1982). Uranium-isotope ratios were used in this study to identify uranium from different sources.

Sorption and (or) precipitation of uranium on sediments in the streambed and alluvial aquifer was evaluated by comparisons of concentrations and ratios of ^{238}U, ^{234}U, and thorium–230 (^{230}Th) in sediments. Uranium to thorium ratios (U/Th) were calculated by dividing the mean of ^{238}U and ^{234}U by ^{230}Th. Over geologic time in a chemically stable environment, radionuclides in the same decay series will reach secular equilibrium, which is a ratio of 1.0. At secular equilibrium, all nuclides in the series have the same activity. Different radionuclides, however, have different chemical and physical properties. For example, in oxidized water at near-normal pH, uranium is more mobile than thorium (Landa, 1980). If significant amounts of uranium either have been leached or have sorbed on sediment, the U/Th ratio will deviate from secular equilibrium. A hypothesis was made that near-channel sediments downstream from the mines would have U/Th ratios significantly greater than secular equilibrium, and sediments in areas not affected by mine-related releases of radionuclides would have U/Th ratios near secular equilibrium.

GROUND-WATER FLOW AND STREAM-AQUIFER RELATIONS

Water levels in the alluvial aquifer varied from near the level of the streambed to about 1.0 m below the streambed in most reaches of the Puerco River from August 1988 until June 1991. The gradient in hydraulic head was approximately equal to the slope of the streambed, as evidenced by a small variance in depth to water in hand-driven wells in the streambed upstream from the mouth of Pipeline Arroyo to downstream from Chambers. Flow in the alluvial aquifer generally was downvalley. The position of the water table relative to the elevation of the streambed reflects a balance between recharge to and discharge from the aquifer. Recharge occurs by infiltration of streamflow, direct infiltration of precipitation through the streambed and adjacent exposures of alluvium, and interformational flow from adjacent aquifers. Sources of streamflow included runoff, wastewater from the Gallup STP, and effluent from uranium-mining discharges from 1960 to 1961 and 1967 to 1986. Discharge from the alluvial aquifer occurs by ET, base flow, interformational flow, and pumpage. Pumpage is mostly from windmills for stock watering, and total pumpage was assumed to be small. Phreatophytes along the banks in some reaches indicate that ground water is discharging to the atmosphere through ET. Ground water also is discharging to the atmosphere by evaporation as indicated by white evaporite deposits and damp sand on the streambed during periods of no flow.

From August 1988 until June 1991, base flow was observed in three locations and was estimated to be less than 0.01 m^3/s at each site. At two of those locations, bedrock crops out in the channel and forms waterfalls 2 to 3 m high. The streambed elevation drops abruptly and intersects the water table at those sites causing small seeps. At both sites, flow persists for a few tens of meters to less than 1 km downstream depending on the season and daily weather fluctuations. Both outcrops are at streamflow-gaging stations—Puerco River near Church Rock and Puerco River near Chambers. The third location where base flow was observed is near Manuelito, New Mexico, where several small springs occur in and near the channel of the Puerco River and on tributaries. Continuous flow also was caused by the discharge of treated wastewater from the City of Gallup. Wastewater entered the channel about 5 km downstream from Gallup at a rate of about 0.1 m^3/s. Flow persisted downstream from Chambers during winter and upstream from the Arizona–New Mexico State line during summer.

An estimated 140 million m^3 of mine-dewatering effluent was discharged to Pipeline Arroyo from 1960 to 1961 and 1967 to 1986 (Van Metre and Gray, 1992). Most of that discharge occurred from 1967 until 1986. Continuous flow resulting from mine-dewatering discharge, supplemented by discharge of wastewater from the Gallup STP, extended from the mouth of Pipeline Arroyo to as far as a few kilometers downstream from Chambers before all of the water either infiltrated or evaporated (Gallaher and Cary, 1986; Shuey, 1986). Mining and mine dewatering were primarily in the Westwater Canyon Member of the Morrison Formation (Perkins and Goad, 1980);

however, several water-bearing strata were penetrated by mine shafts (Gallaher and Cary, 1986). The City of Gallup obtains its water supply primarily from the Gallup Sandstone and also from the Westwater Canyon Member (Stone and others, 1983). The chemical and isotopic composition of recharge from mine-dewatering and Gallup STP discharges, therefore, is influenced primarily by the Gallup Sandstone and the Westwater Canyon Member.

The alluvial aquifer was divided into three reaches to describe the ground-water flow system and flow relations between the stream and aquifer on the basis of differences in bedrock geology, water quality, isotopic composition of water in the alluvial aquifer compared with that of surface water, and the regional-flow system (Cooley and others, 1969; Mann, 1977; Raymondi and Conrad, 1983). Those reaches are indicated by differences in tritium activities in ground-water samples (fig. 10) and correspond to three reaches of the stream from: (1) near the mouth of Pipeline Arroyo to the Nutria monocline (Church Rock reach), (2) downstream from Gallup to downstream from the Defiance monocline (Manuelito reach), and (3) an anticline 8 km upstream from Sanders, near the Querino Road well cluster to near the Chambers well cluster (Sanders reach; figs. 2, 6).

Church Rock Reach

Mine-dewatering pumping caused large drawdowns in bedrock formations underlying the alluvial aquifer in the Church Rock reach. The water level in an abandoned mine shaft near Pipeline Arroyo in the Dakota and Morrison Formations was reported to be 35 m below the land surface in 1968 (Hiss, 1977). By 1978, the water level in the shaft was 116 m below the land surface, a decline of 81 m in 10 years (Stone and others, 1983). That drawdown resulted in downward gradients between the alluvial aquifer and underlying formations and may have induced infiltration from the stream (Bruce Gallaher, environmental engineer, NMED, oral commun., 1988).

The amount of infiltration of mine-dewatering effluent that occurred in the Church Rock reach was estimated from the difference between effluent discharge reported by the mines and the sum of estimated evaporation from the channel and daily discharge past the streamflow-gaging station at Gallup. Evaporation of effluent from the stream and adjacent wetted streambed was estimated to be about 0.6 million m^3/yr. The estimate was made by using an area of 0.3 million m^2 estimated from field observations and a digital map of the streambed from 1:24,000 scale maps. The 0.3-million-m^2 area was multiplied by an estimated evaporation rate of 1.9 m/yr calculated by using the Jensen-Haise method (Bauer and Vaccaro, 1986). Streamflow was monitored at Gallup from 1940 to 1946 and from 1977 to 1982. From 1977 to 1982, the average flow that passed the Gallup streamflow-gaging station was 0.11 m^3/s or about 3.5 million m^3/yr excluding periods when runoff caused flow to exceed the average mine-effluent discharge rate. From 1977 to 1982, the mine-effluent discharge rate averaged about 9 million m^3/yr (Van Metre and Gray, 1992). Subtracting flow past the streamflow-gaging station at Gallup and estimated evaporation from mine-effluent discharge yields an estimated 4.9 million m^3/yr of infiltration losses in the 32-km reach or about one-half of the total mine-effluent discharge.

The estimated volume of infiltration was compared with estimated storage volume in the alluvial aquifer in the Church Rock reach. A storage volume of 135 million m^3 was estimated on the basis of an estimated area of 30 million m^2, a thickness of 15 m, and a porosity of 0.3. Because of large uncertainty in estimating infiltration and aquifer volume by these methods, the estimates are considered qualitative. The estimates of aquifer volume and volume of infiltration of mine effluent indicate that mine effluent could account for about half of the water in the alluvial aquifer. Other possible fates of mine effluent include losses by evaporation at the streambed after mine dewatering ceased and interformational flow from the alluvial aquifer to bedrock aquifers.

Mine dewatering ceased in February 1986 before this study began. Historical samples of mine-dewatering effluent were not analyzed for tritium (Wirt and others, 1991). Because the water was from the deep aquifers, mine effluent probably did not contain tritium above pre-1952 levels. This assumption is supported by a sample of mine effluent that was collected in May 1990 pumped from the Westwater Canyon Member of the Morrison Formation near San Mateo, New Mexico. That sample contained 2.5 pCi/L of tritium, which indicates pre-1952 water (Doney and others, 1992). Tritium activities greater than pre-1952 levels were measured in samples from all hand-driven wells and alluvial wells in the Church Rock reach in 1989 and 1990 (fig. 10). Tritium activities indicate that at least part of the water in the alluvial aquifer is from

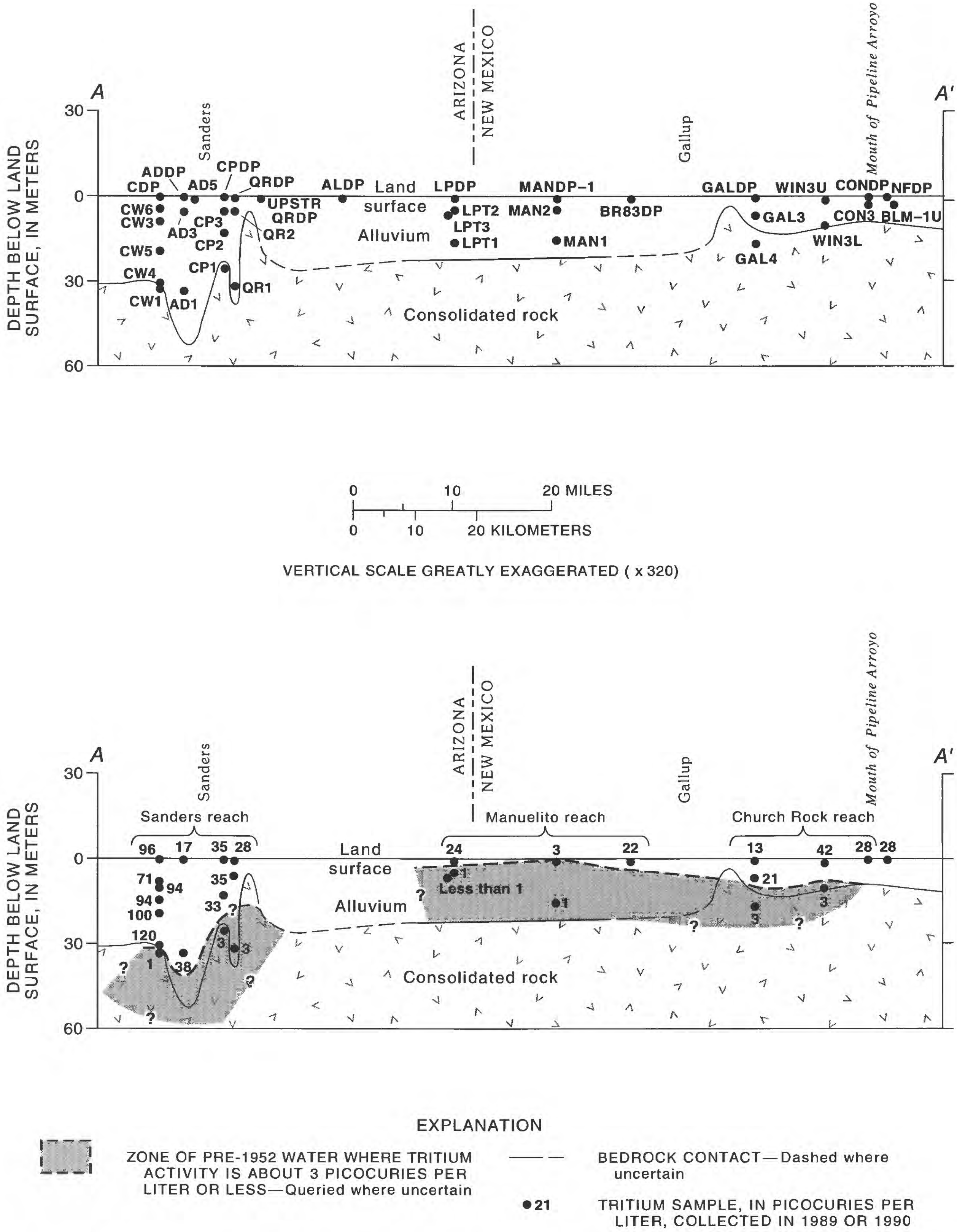


Figure 10. Location of monitor wells and activities of tritium under the Puerco River, 1989. Trace of section, *A—A'*, shown on figure 1.

direct infiltration of precipitation and infiltration of runoff from the stream since 1952.

Two wells (BLM–1U and the NF well) and two hand-driven wells (NFDP–1 and NFDP–2) were sampled near the Puerco River upstream from the mouth of Pipeline Arroyo to determine background water quality in the alluvial aquifer. These samples had a chemistry that was dominated by calcium and sulfate (fig. 11), tritium concentrations above pre-1952 levels (fig. 10), and uranium concentrations of 6 to 13 µg/L. The term *background* is used to refer to an area not subjected to mine-related discharges. The assumption in using these samples to represent background water quality in the alluvial aquifer is that ground water upstream from the mouth of Pipeline Arroyo is chemically similar to ground water downstream from the mouth of Pipeline Arroyo before mining. This assumption probably is not as valid as distance increases downstream from the mouth of Pipeline Arroyo because quality of the ground water also is affected by local differences in geology and climate.

Two wells (CON–3 and WIN–3U) and two hand-driven wells (CONDP–1 and GALDP–1) in the Church Rock reach downstream from Pipeline Arroyo showed geochemical and (or) isotopic evidence of mine-dewatering effluent. Well CON–3 is screened from 1 to 4 m below the water table and is about 10 m from the bank of the Puerco River and about 0.5 km downstream from the mouth of Pipeline Arroyo. Differences in proportions of major ions between samples from well CON–3 and well BLM–1U, 2 km upstream from the mouth of Pipeline Arroyo, indicate different sources of solutes for the two wells (fig. 11). Similarities between ratios of major ions in mine-dewatering effluent and in water from well CON–3 indicate residual mine effluent at well CON–3. The relation of sulfate and chloride concentrations indicate mixing of mine effluent and runoff at CON–3 (fig. 12). The point representing mine

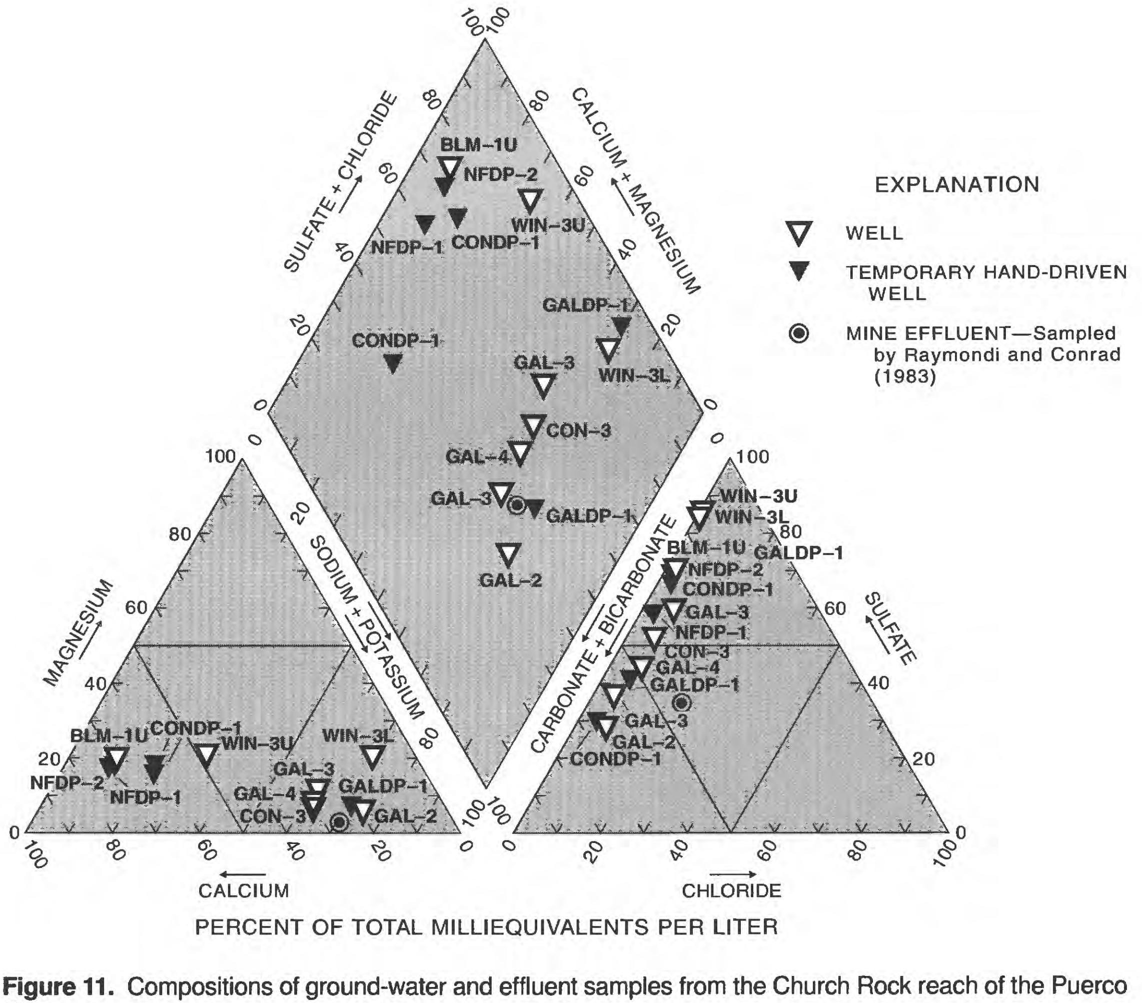


Figure 11. Compositions of ground-water and effluent samples from the Church Rock reach of the Puerco River.

effluent on figure 12 is the median concentration of five samples of mine effluent collected from November 1978 to March 1980, one sample collected in Pipeline Arroyo in November 1980, and five samples collected in the Puerco River between October 1976 and May 1979 (Wirt and others, 1991). The median value of three samples from CON–3 collected between January and December 1982 plots near a line (line A) connecting mine effluent and a sample from BLM–1U collected in 1989 (fig. 12). These relations indicate that a mix of mine effluent and runoff occurs at CON–3 and that the proportion of mine effluent decreased during the 1980's.

Samples from GALDP–1 had proportions of major ions similar to mine effluent (fig. 11), tritium above pre-1952 levels (fig. 10), and uranium concentrations of 140 μg/L in two samples collected in 1990. Samples from CONDP–1 and WIN–3U (fig. 6) screened 0.5 and 1 to 4 m below the water table, respectively, had a chemistry dominated by calcium and sulfate and had tritium activities above pre-1952 levels similar to samples collected upstream from the mouth of Pipeline Arroyo (figs. 10, 11). Sulfate and chloride concentrations for CONDP–1 were similar to Puerco River water (fig. 12); however, concentrations of sulfate in WIN–3U were much larger. CONDP–1 and WIN–3U had uranium concentrations of 130 to 660 μg/L and 40 to 90 μg/L, respectively, compared to 6 to 13 μg/L for background wells.

Manuelito Reach

Flow in the alluvial aquifer is toward the stream in the reach downstream from Gallup to the Defiance monocline near the Arizona–New Mexico State line (figs. 2, 6). Flow toward the stream is caused by interformational flow of water from bedrock aquifers to the alluvial aquifer as indicated by upward water-level gradients between wells MAN–1 and MAN–2 in the Manuelito well cluster (0.14±0.01 in 1990 and 1991), small tritium activities in wells away from the streambed (3.0 pCi/L or less), and differences in $\delta^{34}S$ values between ground water and Gallup STP wastewater (fig. 13). Values of $\delta^{34}S$ in samples from the Manuelito well cluster and hand-driven well BR83DP–1 ranged from 3.3 to 12.5 per mil compared with –2.0 per mil in Gallup STP wastewater. In this report, upward water-level gradients are reported as positive values, and downward gradients are reported as negative values.

During winter, discharge of wastewater from the Gallup STP causes continuous flow in the Puerco River

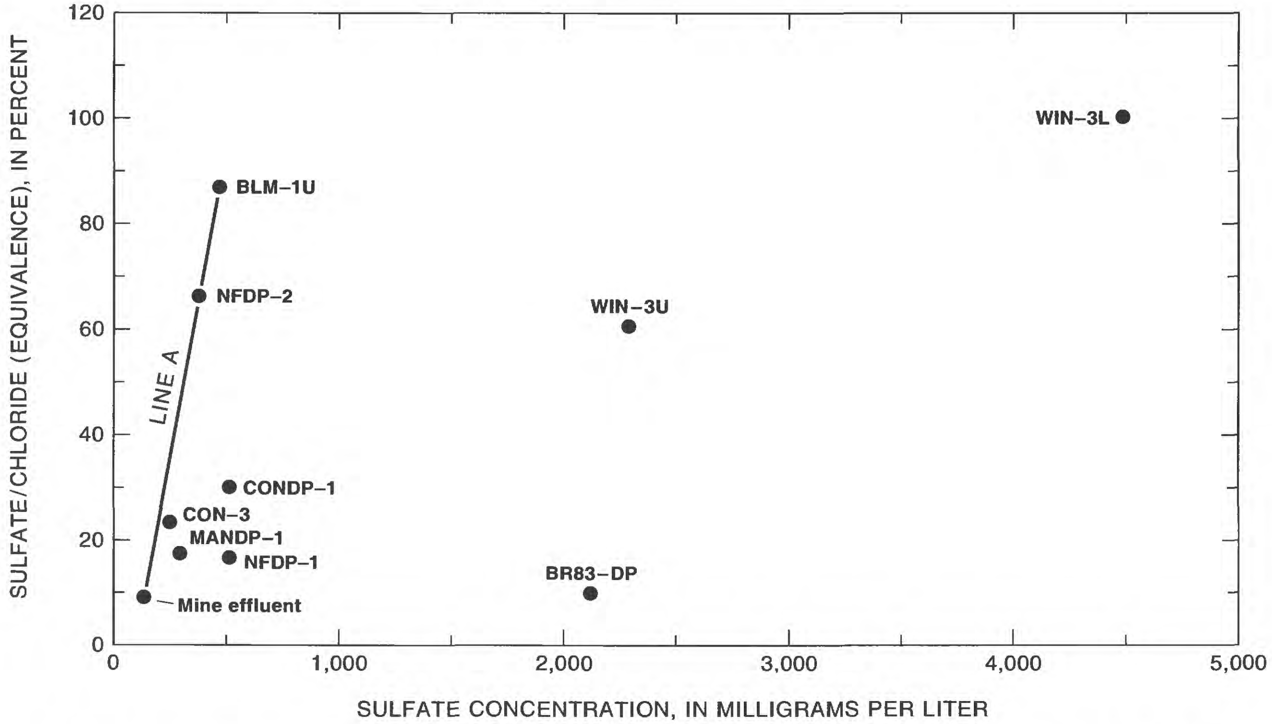
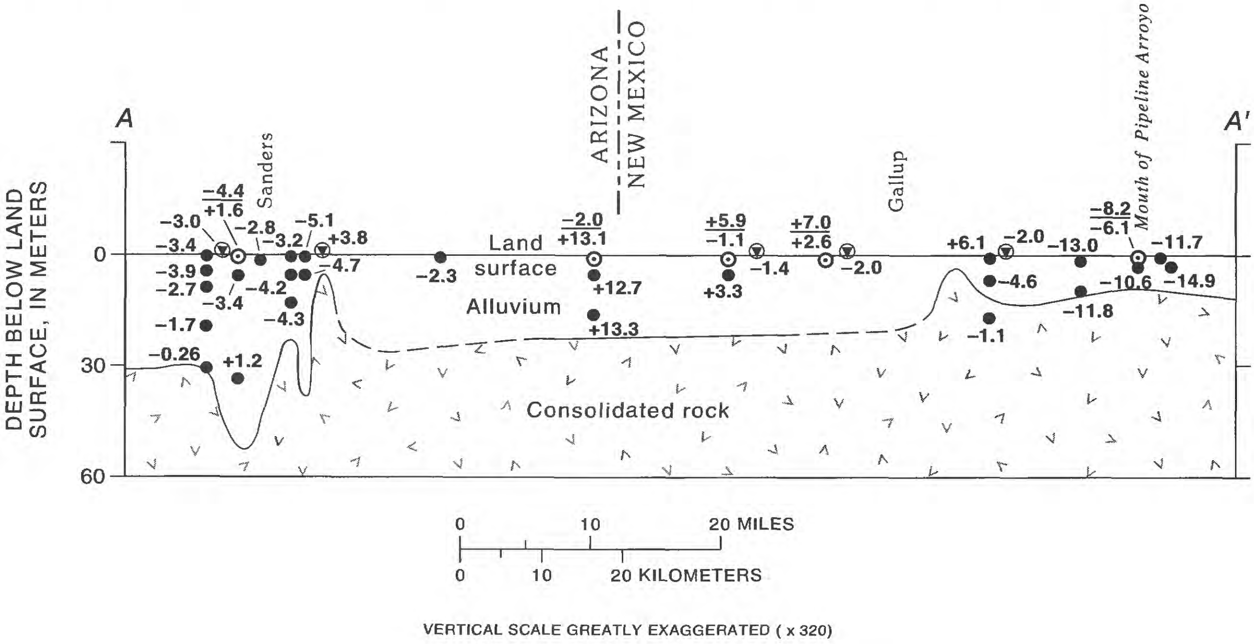


Figure 12. Relation between sulfate-to-chloride ratios and sulfate concentrations in selected samples from the Puerco River basin, New Mexico.

from the outfall, which is about 5 km downstream from Gallup, to about 90 km downstream at Chambers, Arizona. During the summer, continuous flow extends about 20 km downstream from Gallup and either infiltrates the sediments or evaporates before reaching the Arizona–New Mexico State line. Streamflow was sampled below the Gallup STP outfall and at several locations downstream on March 31 and April 5, 1989, when there was no flow in the Puerco River upstream from the outfall (Fisk and others, 1994). At the Gallup STP outfall, a sample had a δ^{34}S value of –2.0 per mil, and δ^{34}S values for streamflow ranged from –1.4 per mil at Manuelito to 3.8 per mil at the Querino Road well cluster (fig. 13). Small seeps occur near the Puerco River channel and on tributaries near the Manuelito well cluster. The shift to more positive δ^{34}S values with distance downstream from the Gallup STP outfall could be the result of wastewater in the Puerco River channel mixing with ground-water discharge that is enriched in ^{34}S.

Interformational flow of water from bedrock aquifers and infiltration of streamflow are indicated at the Lupton well cluster near the downstream end of the Manuelito reach. Water levels in vertically separated wells in the Lupton well cluster (LPT–1 and LPT–2) had a downward gradient of –0.07±0.01 in 1990 and 1991, which indicates a downward flow of water. Tritium was measured at all wells except at the deepest well (LPT–1). Tritium activities, however, were less than 3 pCi/L at three wells in the Lupton cluster. Only hand-driven well LPDP–1 had a tritium activity greater than 3 pCi/L (24 pCi/L), which indicates recent recharge. The δ^{34}S values ranged from 13.3 per mil in the deepest well (LPT–1) to –4.4 per mil in one of the shallow near-channel wells (LPT–3). These data indicate that water from bedrock aquifers occurs in deeper wells and in wells away from the channel at Lupton.



EXPLANATION

—— —	BEDROCK CONTACT—Dashed where uncertain
–1.4	SURFACE-WATER SAMPLE—Number is $^{34}S/^{32}S$
● –4.6	GROUND-WATER SAMPLE COLLECTED IN 1988–90—Number is $^{34}S/^{32}S$
–2.0 +13.1 ⊙	GROUND-WATER SAMPLE COLLECTED IN 1988–90 OR 1991—Numbers are sulfur-isotope ratios (δ^{34}S). Upper number is for 1988–90, lower number, is for 1991

Figure 13. Sulfur-isotope ratios under the Puerco River.

Ground water near the stream is a mixture of water from bedrock aquifers and infiltrated streamflow, which is mostly Gallup STP wastewater.

Large differences in $\delta^{18}O$ and δD occurred between runoff from a summer storm (August 15–19, 1990) and flow primarily from discharge of Gallup STP wastewater (fig. 14). Samples from the August 1990 storm plot on a line parallel and slightly above the global meteoric water line (line A on fig. 14). Samples of flow primarily from discharge of Gallup STP wastewater are increasingly enriched in ^{18}O with distance downstream from the Gallup STP outfall (line B on fig. 14). The trend and slope of line B on fig. 14 results from enrichment of ^{18}O caused by evaporation; the difference in plotting position between lines A and B distinguishes recharge of Gallup STP wastewater from recharge of runoff.

Bedrock is shallow in the Manuelito reach, and $\delta^{18}O$ and δD data (Fisk and others, 1994) support the conclusion that water in the alluvial aquifer is primarily from flow from underlying bedrock aquifer(s). Samples from the alluvial aquifer in the Manuelito reach had $\delta^{18}O$ and δD values that were different from values for summer runoff and flow from the Gallup STP. Samples from the alluvial aquifer are isotopically heavier than summer runoff and plot along a line parallel to and slightly below the meteoric water line (line C on fig. 14). These values are similar to other ground-water values from the southern part of the Colorado Plateau in Arizona about 100 km south of the Puerco River (Robertson, 1989). Samples from the alluvial aquifer beneath the Puerco River probably represent a time composite of precipitation that infiltrated under similar conditions within the region. Differences between the ground-water samples in the Manuelito reach and surface-water samples from the Puerco River indicate ground water is derived mainly from flow from the underlying bedrock aquifers rather than from mine-dewatering or sewage effluent. In addition, these samples do not contain detectable tritium. Samples plotting along line C (fig. 14) are hereafter referred to as native ground water. The term *native* is chosen rather than the term *background* because the term *background* is used differently for the purposes of this report to indicate a site where no mining has occurred upstream.

Sanders Reach

The Sanders reach extends from an anticline about 8 km upstream from Sanders near the Querino Road well cluster to near the Chambers well cluster (figs. 6, 10). The Puerco River is predominantly a losing stream in the Sanders reach as indicated by measured losses of streamflow and a downward water-level gradient of 0.05 between the stream surface and hand-driven well CDP–1 at the Chambers well cluster during 3 days of runoff in August 1988. In most places, the stream is dry except during runoff and during winter months when flow is continuous from the Gallup STP downstream to the Sanders reach. In January 1990, flow was continuous from the Gallup STP to Sanders. In February 1990, flow was continuous from the Gallup STP to downstream from the streamflow-gaging station near Chambers. By late April 1990, with the onset of warmer weather, continuous flow extended only to a few kilometers upstream from the Arizona–New Mexico State line.

In near-channel alluvial wells in the Sanders reach, upward and downward gradients in head were measured from 1989 until 1991. Gradients were small and consistently upward between vertically separated near-channel wells at the Chambers well cluster. From September 1989 until June 1991, 16 of 17 vertical gradients between wells CW–4 and CW–6 ranged from 0.004 to 0.007. The 18 vertical gradients measured during that time period between wells CW–2 and CW–3 ranged from 0.001 to 0.004 and averaged 0.003. Gradients smaller than about 0.001 are less than the error of water-level measurements. Vertical gradients were near zero between vertically separated near-channel wells at the Querino Road and Cedar Point well clusters. Vertical gradients between wells CP–2 and CP–3 ranged from –0.002 to 0.001 from September 1989 to June 1991. Vertical gradients between wells QR–1 and QR–2 were between –0.001 and 0.001. At the ADOT well cluster, the 15 gradients between wells AD–1 and AD–3 that were measured from June 1989 until June 1991 ranged from –0.001 to –0.02, and averaged –0.005. The gradients indicate that flow was away from the stream at the ADOT well cluster.

Ground-water levels at the Chambers, Cedar Point, and Querino Road well clusters gradually rose from October 1989 through March 1990 and were near the streambed elevation in early March (fig. 15). The stream was dry during most of the period of gradual rise from October through January. Ground-water levels began to decline in March and, except for rises during periods of summer runoff, declined through the summer and early fall of 1990. Vertical gradients remained nearly constant throughout this period. Water

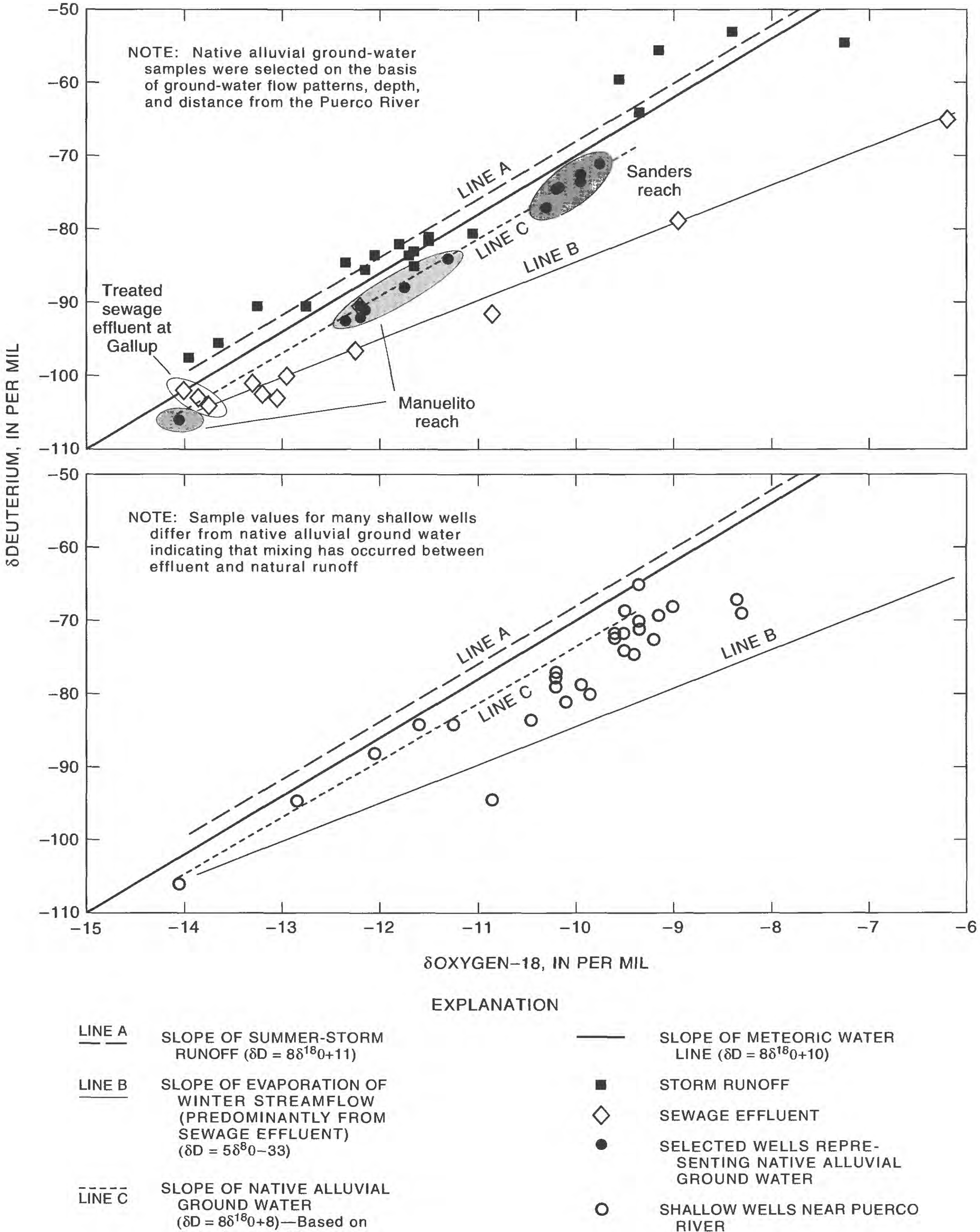


Figure 14. Stable isotopes of oxygen and hydrogen in samples of sewage effluent, surface water, and ground water, the Puerco River Basin, Arizona and New Mexico.

levels rose in the late fall and winter and declined in spring and summer. The annual cycle in water levels was caused by seasonal variation in the ET rate. As the ET rate gradually decreased during fall and winter, water levels rose in response to direct infiltration of precipitation. During late winter, infiltration of Gallup STP wastewater also contributed to the rise in water levels. With the onset of warmer weather in the spring, the ET rate increased, and water levels fell. The downward trend in water levels was partly and episodically offset by infiltration from the stream during periods of runoff in the summer.

A flash flood on July 15, 1990, caused downcutting of about 0.5 m in part of the streambed at Chambers. Because ET at the streambed is a major factor controlling ground-water levels, the lowering of the streambed resulted in a lowering of ground-water levels. Extending the slope of the water-level decline before the July 15 flood indicates that after the flood, water levels declined at a steeper rate and were about 0.2 m lower than the projected decline 2 weeks after the flood (fig. 15). This decline was in spite of almost continuous runoff from July 7 until about July 25. Ground-water levels on November 1, 1990, had established a new equilibrium that was about 0.3 m lower than on November 1, 1989.

Ground-water levels at the Chambers and Querino Road well clusters respond rapidly to changes in stage in the stream (fig. 15). Wells QR–2, CW–3, and CW–6 are about 10 m from the stream channel, and well CW–9 is about 120 m from the channel. The four wells are screened from the water table to about 2 m below the water table, yet the rapid rise and fall of water levels in response to stream-stage variations are responses that would be typical of confined-aquifer systems. Similar water-level response has been measured in other stream-aquifer systems (Loeltz and Leake, 1983) and is commonly referred to as delayed yield (Cooley, 1972). This effect occurs because water cannot drain or fill pore spaces at the water table instantaneously as the head in the aquifer changes. The effect is most pronounced where the water table is in fine-grained sediments. Clay layers were encountered at or near the water table during drilling. During short time intervals after a sudden change in stage in the stream, a confined or poorly confined response occurs in water-bearing zones bounded by those clay layers. A water-table well that is 120 m from the stream and screened in those water-bearing zones will respond to a change in stream stage much more rapidly than would be indicated by theoretical calculations by using typical specific-yield values. This effect also occurs in wells at the Cedar Point well cluster; however, the effect is less pronounced (fig. 15).

Water levels at the ADOT well cluster did not respond to changes in stream stage as rapidly as at the Chambers and Querino Road well clusters and did not show the same pattern of seasonal changes as wells at Chambers, Cedar Point, and Querino Road. Water levels in wells AD–3 and AD–5 declined from October through December 1989 when there was no flow in the stream (fig. 15). In January 1990, water levels began to rise in those wells when flow from the Gallup STP extended as far downstream as the ADOT well cluster. Downward water-level gradients within the alluvial aquifer were measured at the ADOT well cluster, which indicates that the flow in the aquifer was away from the stream. Differences in seasonal changes in water levels and water-level gradients at the ADOT well cluster indicate either less recharge from precipitation away from the stream, more discharge from the aquifer away from the stream, or a combination of both when compared with the other three well clusters in the Sanders reach. Several private wells are in the alluvial aquifer and adjacent Chinle Formation near the ADOT well cluster. Pumping is not substantial but does result in some ground-water discharge away from the stream and possibly accentuates infiltration from the stream.

Four wells in the Sanders reach are completed in the underlying Chinle Formation—CW–1 at the Chambers well cluster and CP–1, CP–7, and CP–8 at the Cedar Point well cluster. From September 1989 until June 1991, downward gradients of –0.03 to –0.04 were measured between wells CW–1 and CW–2. CW–2 is screened about 14 m above CW–1. From June 1989 until June 1991, downward gradients of –0.03 to –0.04 also were measured between wells CP–1 and CP–2. CP–2 is screened 11 m above CP–1. A downward gradient of –0.06 to –0.09 was measured between wells CP–7 and CP–8 from July 1990 until June 1991. CP–7 and CP–8 are vertically separated wells in a single hole in the Chinle at the Cedar Point well cluster. Gradients indicated water flowing downward from the alluvial aquifer into the Chinle in the Sanders reach and downward flow within the Chinle at the Cedar Point well cluster.

In the Sanders reach, tritium activities indicate that recharge from runoff and precipitation has moved to the lower parts of the alluvial aquifer since about 1952 (fig. 10). Tritium activities also indicate that recharge

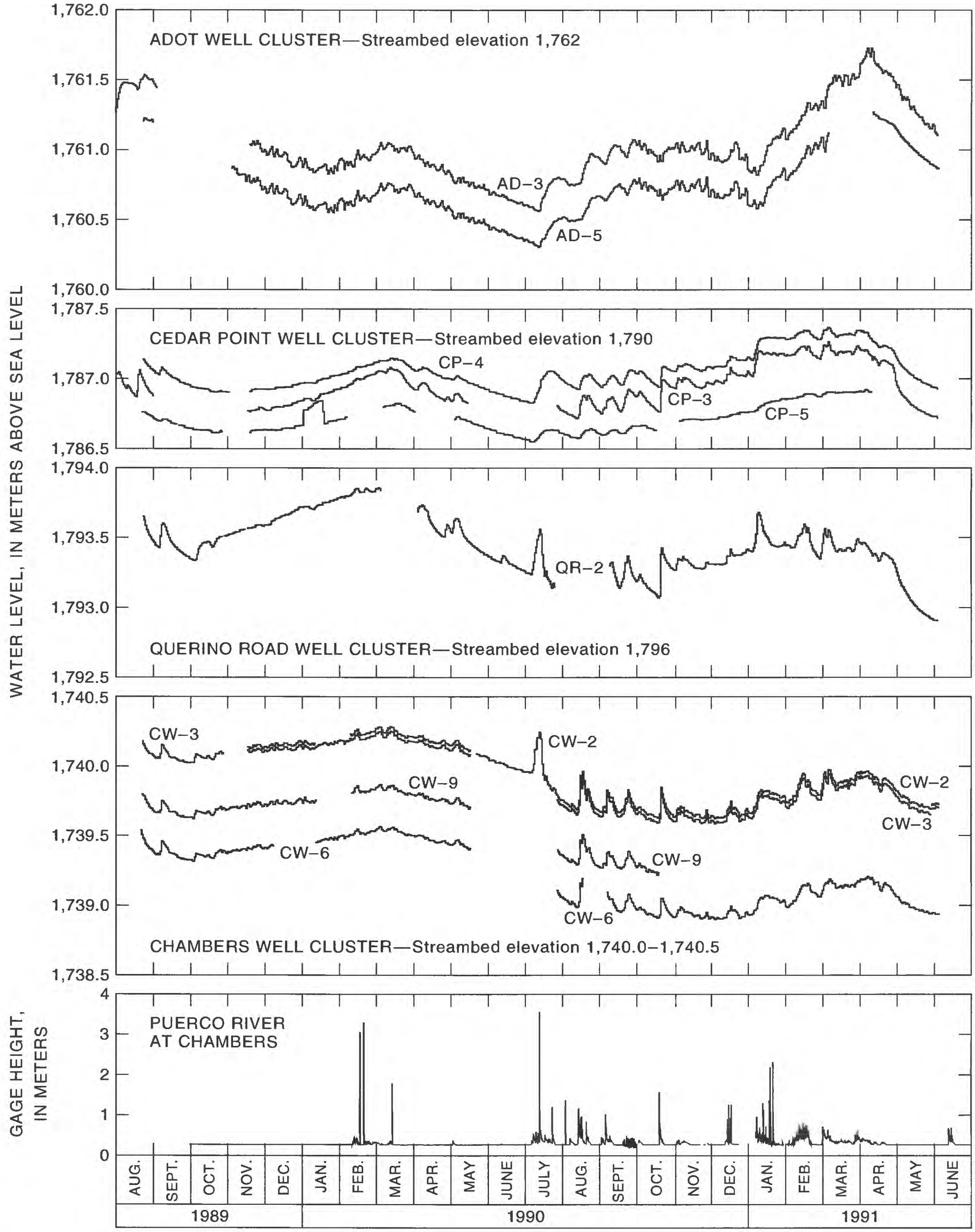


Figure 15. Water levels in selected wells at ADOT, Cedar Point, Querino Road, and Chambers well clusters and gage height of the Puerco River at Chambers, Arizona.

that has occurred since 1952 had not reached the upper Chinle Formation as of 1989. Clay layers probably act as confining units at the contact between the alluvial aquifer and the Chinle Formation. Lack of tritium in the upper Chinle Formation indicates that water from the Puerco River has not reached the bedrock formations through the alluvial aquifer since the advent of uranium mining in 1960.

Values for $\delta^{18}O$ and δD in samples from wells in alluvium containing native water in the Sanders reach plot parallel and slightly below the meteoric water line and are similar to other samples of native alluvial ground water from the Colorado Plateau in Arizona (Robertson, 1990; line C on fig. 14). Other values of $\delta^{18}O$ and δD for wells in the reach plot between line C and the line described by $\delta^{18}O$ and δD values measured in flow from discharge of Gallup STP wastewater (line B). These data indicate that water in the alluvial aquifer is primarily a mix of water from two sources—infiltration of precipitation runoff and infiltration of wastewater from the Gallup STP. The scatter in plotting position reflects variable amounts of mixing from these two sources of water. Seasonal differences in evapotranspiration also could contribute to the variability. The degree of evapotranspiration would be significantly greater for discharges of treated effluent than for natural runoff because of the greater surface area to volume relation for low flows typical of effluent releases.

In summary, a good hydraulic connection exists between the stream and alluvial aquifer, and a poor hydraulic connection exists between the alluvial aquifer and underlying Chinle Formation in the Sanders reach. The elevation of the streambed controls the average elevation of the water table; seasonal and short-term variations in water levels result from seasonal variations in ET rates and runoff in the stream. Vertical gradients in the alluvial aquifer vary between well clusters and shift up and down near the stream. Tritium activities from near-channel wells indicate probable mixing of infiltrated precipitation with recharged treated wastewater and possibly mine-dewatering effluent since about 1952. $\delta^{18}O$ and δD values for samples from near-channel wells (fig. 14) indicate mixing of natural runoff and effluent from one or more sources. The degree to which evapotranspiration causes stable isotopes of oxygen and hydrogen to be enriched in ^{18}O and D is significantly greater for low-flow conditions (effluent) than for high-flow conditions (most natural runoff).

Evaluation of Stream-Aquifer Relations at Chambers by Using a Numerical Model

A numerical model was used to simulate stream-aquifer relations for a hypothetical cross section at the Chambers well cluster in the Sanders reach. The objective in developing the model was to evaluate transient flow and long-term flow directions between the stream and aquifer at Chambers. Transient water levels in the aquifer were simulated by using a three-dimensional finite-difference ground-water flow model (McDonald and Harbaugh, 1988) linked to a geographic information system (Van Metre, 1990).

Description of the Aquifer

The alluvial aquifer at the Chambers well cluster includes fine to medium sands with interbedded layers of clay. Clays occur more frequently near the water table and near the contact with the underlying Chinle Formation. Occurrence of clays at similar altitudes in all wells and clay layers exposed in the vertical banks of the Puerco River at the site indicate that the clays are laterally extensive.

Near the Chambers well cluster, the alluvial aquifer extends about 400 m laterally south from the river where the bedrock crops out as low east-westward-trending hills (fig. 7). The hills are composed of the Petrified Forest Member of the Chinle Formation, which was found below the alluvial aquifer during drilling. Depth to bedrock at each of the well groups was between 29 and 32 m. Surface-seismic mapping of the depth to bedrock at the site indicates the depth to bedrock increases on the north side of the channel to as much as 80 m (Kenneth King, geologist, USGS, written commun., 1989). The stream channel generally is flat, is about 50 m wide, and has a vertical bank about 3 m high on the south side. Two terraces lie between the top of the bank and the hills to the south. The river channel is constrained to the north by exposed bedrock, which forms a waterfall near Chambers.

The water table was about 0.6 m or less below the lowest part of the streambed from August 1988 through June 1991. The water table is approximately horizontal normal to the stream and slopes downvalley at the same slope as the streambed—about 4 m/km. Water levels vary with time in response to changes in ET rate and streamflow and can change in response to changes in streambed elevation as indicated by the decline in water levels following downcutting in the streambed in

July 1990 (fig. 15). The water-level gradient between the alluvial aquifer and the Chinle Formation is downward. Tritium concentrations, however, indicate that water recharged since 1952 occurs in all alluvial wells but does not occur in well CW–1, which is screened from 1 to 2.6 m below the contact with the Chinle. Clay layers at the contact between the alluvial aquifer and the Chinle and clays in the Chinle probably restrict vertical movement of water. The only pumping in the area is from a windmill about 200 m east of the monitor wells. Pumping from that well is assumed to have a negligible effect on water levels at the monitor wells.

Approach to Simulation

The partial-differential equation describing transient three-dimensional ground-water flow in an aquifer can be written as:

$$\frac{\partial}{\partial_x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial_y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial_z}\left(K_{zz}\frac{\partial h}{\partial z}\right)-W = S_s\frac{\partial h}{\partial t}, \qquad (1)$$

where

x, y, and z = mutually orthogonal coordinates oriented parallel to principal axes of the K tensor,
K = hydraulic conductivity,
h = hydraulic head,
W = volumetric flux per unit volume and represents sources and (or) sinks of water,
S_s = specific storage, and
t = time.

Two simplifying assumptions were made in applying equation 1. The first was that head changes in the aquifer could be modeled in a two-dimensional form. If the rate of change of the head gradient on the y axis is small and can be ignored, the second term in equation 1 can be dropped. Equation 1 reduces to:

$$\frac{\partial}{\partial_x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial_z}\left(K_{zz}\frac{\partial h}{\partial_z}\right)-W = S_s\frac{\partial h}{\partial t}, \qquad (2)$$

which was used to simulate transient water levels in the Sanders reach. The validity of applying equation 2 depends on the assumption that the rate of change-of-head gradient parallel to the Puerco River in the Sanders reach is negligible. The head gradient that is parallel to the Puerco River was calculated between each of the four well clusters in the reach. The rate of change of those gradients was determined by using finite differences and was more than five orders of magnitude smaller than the rate of change of head gradients vertically near the stream at the Chambers well cluster. This comparison indicates that flow components parallel to the river can be ignored in the computation of flow components normal to the river. The application of equation 2, however, may result in some errors for a cross section where the course of the river angles sharply relative to the local downvalley flow direction.

The second assumption made in applying equation 2 to a cross section was that the water table could be represented as being horizontal and at a fixed elevation. This assumption was made to simplify the problem numerically by making it linear because the water table is bounded by clay layers. Because the water table lies within the low permeability material, changes in thickness of the saturated zone of the aquifer will not result in significant changes in transmissivity of the aquifer. The horizontal movement of water will occur mostly within the underlying sand layers.

To solve equation 2 for heads and flow components at a cross section, the following information is needed: (1) physical dimensions, (2) distribution of vertical and horizontal hydraulic conductivity (K_z and K_h), (3) distribution of storage coefficients, and (4) flux at all boundaries. Flux, as used in this report, is the volumetric rate of flow per unit area entering or leaving the cross section. Physical dimensions of the cross section were determined from well logs, aerial photographs, and transit-stadia surveys. The model grid consisted of 7 layers, 1 row, and 43 columns (fig. 16). Model layers were designed to approximate the extent and occurrence of sand and clay layers in the alluvial aquifer. Distribution of K_h was estimated on the basis of slug-test results and was modified slightly during model calibration. Distribution of K_z and storage coefficients for some layers were estimated during calibration.

Specified flux-boundary conditions were used and included the special case of no flow (fig. 16). No-flow boundaries were specified for the lower and lateral boundaries of the cross section. The use of no-flow conditions at the lateral boundary under the stream was based on the assumption that the ground-water flow system is symmetric about the stream channel. Specification of the lower boundary and lateral boundary

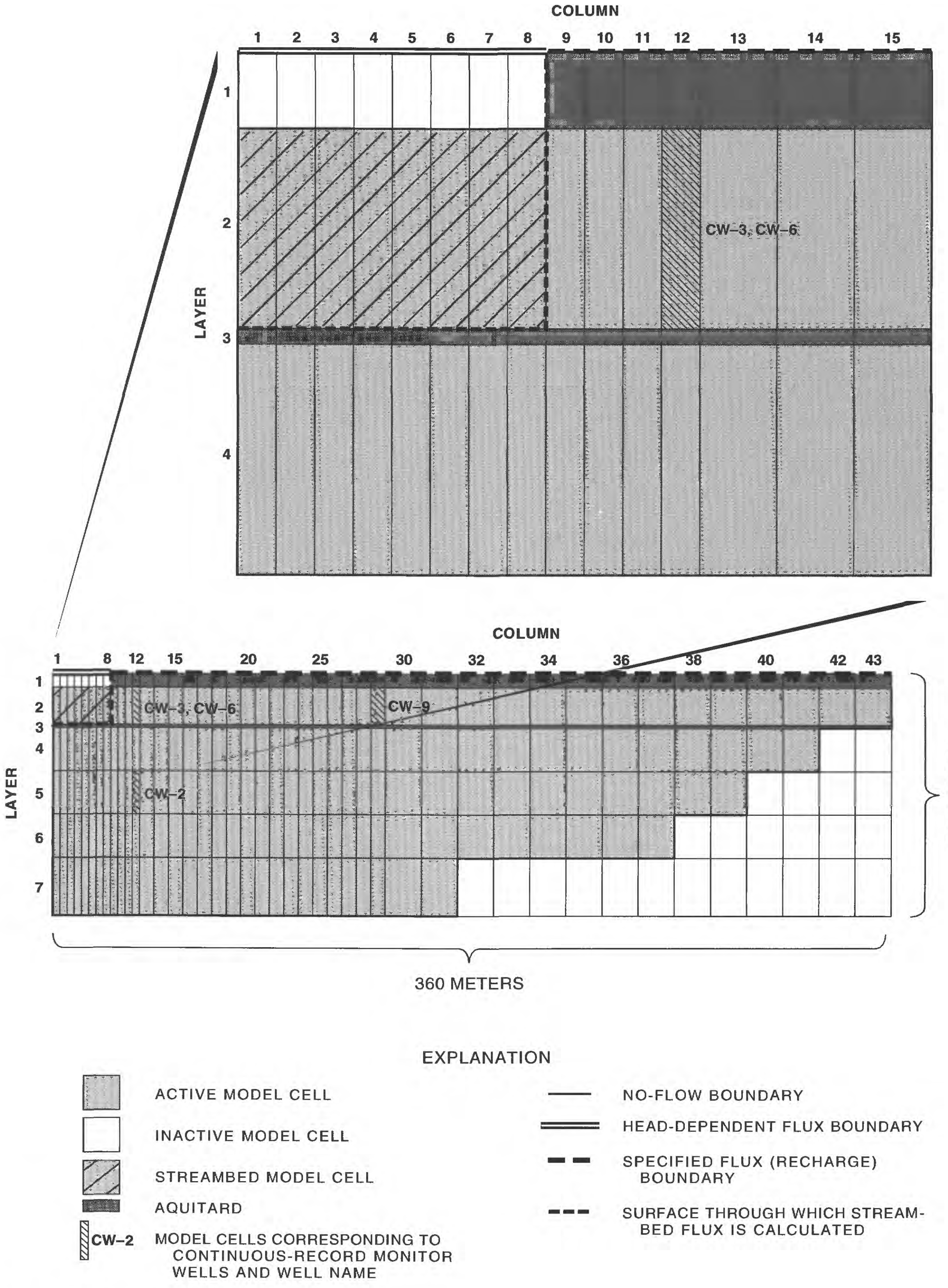


Figure 16. Model geometry and boundary conditions.

away from the stream as no flow assumes that flow between the alluvial aquifer and underlying Chinle Formation is negligible. That assumption is based on the occurrence of clays at the contact with the Chinle and the small concentration of tritium in well CW–1. Flux normal to the water table (areal recharge) initially was estimated by using infiltration rates thought to be typical for the area. Flux was then varied during model calibration. Flux into and out of the model at the streambed was attributed to two processes—infiltration during streamflow and ET. Maximum ET rates and the relation between rate and depth to the water table were estimated by using calculated potential ET (fig. 17) and results obtained with the ET measuring chamber (fig. 8). Infiltration rates from streamflow were estimated during model calibration.

Three functions were used in the model to simulate fluxes at the stream boundary. Infiltration from streamflow was simulated by using specified fluxes that varied as a function of time (McDonald and Harbaugh, 1988; WEL package). ET was simulated by using a function that calculated discharge by ET as a function of a time-varying specified maximum ET rate (fig. 17) and depth to ground water (McDonald and Harbaugh, 1988; EVT package). Areal recharge at the streambed and over the remainder of the upper-model boundary was simulated as specified flux (McDonald and Harbaugh, 1988; RCH package).

Model Calibration and Results

After the model geometry and estimates of model parameters and boundary fluxes are determined, a solution can be generated for heads at each nodal point. Modeled heads then are compared with measured heads at monitor wells to assess the accuracy of the solution. Invariably, differences will exist between modeled and measured heads. Depending on the nature of those differences, model parameters are adjusted (calibrated) to more closely approximate measured heads.

The first step in model calibration was to design a steady-state model to solve for the head distribution. The head distribution was used as the initial condition in a later transient simulation. A steady-state model cannot account for transient stresses on the system such as infiltration from the stream during streamflow. The model, however, can represent the average position of the water table in a system subject to annual cycles but not subject to long-term rises or declines in water levels. In the steady-state model used here, boundary

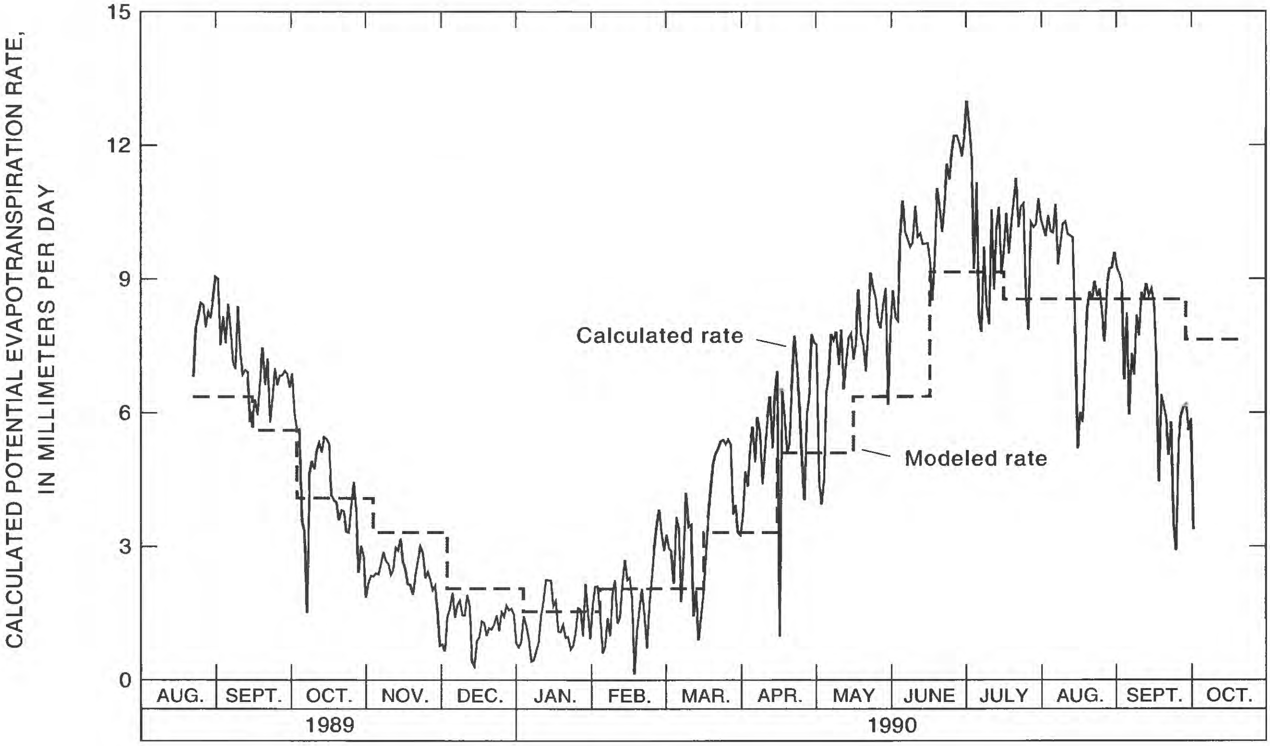


Figure 17. Maximum evapotranspiration rate used in the model and calculated potential evapotranspiration rate.

fluxes were limited to average annual areal recharge and discharge by ET.

In calibration of the steady-state model, the position of the water table under the streambed was of primary interest and depended on the relation between recharge rate and ET rate. Of the two, the ET rate was assumed to be known with greater confidence than the areal-recharge rate. The maximum ET rate was estimated as 1.9 m/yr on the basis of calculated potential ET rate. Actual ET rate is calculated in the model as a linear function of depth to the water table. When the water table is at or above land surface, actual ET rate is equal to the specified maximum ET rate. When the water table drops below a specified extinction depth—1.5 m in this model—ET rate is reduced to zero. The recharge rate was varied to yield modeled heads approximately 0.4 m below the lowest part of the streambed. The recharge rate estimated by this method was 53 mm/yr.

Heads calculated using the steady-state model were used as initial heads for a transient model. The transient model approximates the response of the real system to stress. To calibrate the model, the aquifer was stressed by infiltration from the stream during streamflow and by varying rates of ET discharge at the streambed. The model was used to simulate a 14-month period from August 1989 through September 1990 during which six runoff periods and an annual cycle in ET rate occurred. Additionally, during the runoff period on July 16, 1990, downcutting of approximately 0.5 m occurred in part of the streambed at the site. That downcutting was simulated in the model by lowering the ET surface for model cells representing that part of the streambed. After comparison of the measured and computed responses of ground-water levels, one or more model parameters was changed, and the model was run again. The parameters that were varied during the calibration process were (1) K_h of layer 2, (2) K_z between layers 1 and 2, (3) maximum ET rates, (4) areal-recharge rate, (5) storage coefficient of model layer 2, and (6) infiltration rates from streamflow. This trial-and-error procedure was repeated until the model results satisfactorily approximated measured heads (fig. 18; table 5).

After calibration, areal-recharge and ET rates were varied to determine model sensitivity to those parameters. Small changes in both parameters resulted in significant changes in modeled water levels in relation to the elevation of the streambed (figs. 19, 20), which suggests that parameter values estimated during calibration are reasonable. All combinations of parameters tested that yielded reasonable simulations of measured heads resulted in cumulative flow out of the model at the streambed (fig. 20). The simulation model demonstrates that the conceptual model of flow is reasonable particularly regarding the hypothesis that discharge of water by ET at the streambed can account for the flow out of the alluvial aquifer.

GROUND-WATER QUALITY

Alluvial Aquifer

Water in wells completed in the alluvial aquifer generally was alkaline and had large concentrations of dissolved solids and sulfate. Concentrations and activities of iron, manganese, uranium, radon, gross beta, and gross alpha varied from one to more than three orders of magnitude (figs. 21, 22; Fisk and others, 1994). pH ranged from 6.7 to 8.1. Ground-water temperatures were between 6.5 and 21°C and varied seasonally. Eh ranged from 0 to 400 mV and had a median value of 220 mV.

Alkalinity concentrations as HCO_3 ranged from 130 to 988 mg/L and had a median of 295 mg/L. Concentrations of dissolved solids ranged from 273 to 3,700 mg/L and had a median of 800 mg/L. Only two samples from the alluvial aquifer did not exceed the USEPA secondary maximum contaminant level (SMCL) of 500 mg/L for dissolved solids. Concentrations of dissolved organic carbon (DOC) ranged from 1.1 to 17 mg/L and had a median of 3.2 mg/L.

Concentrations of dissolved iron ranged from 3 to 7,000 μg/L and had a median of 41 μg/L. Thirty-one percent of 112 samples of dissolved iron exceeded the SMCL of the USEPA of 300 μg/L. Concentrations of dissolved manganese ranged from less than 1 to 6,900 μg/L and had a median of 350 μg/L. Seventy-three percent of 113 samples of dissolved manganese exceeded the SMCL of the USEPA of 50 μg/L.

Concentrations of dissolved uranium, measured fluorimetrically, ranged from less than 1 to 220 μg/L and had a median of 7.2 μg/L. Concentrations of dissolved uranium exceeded the proposed MCL of the USEPA of 20 μg/L (U.S. Environmental Protection Agency, 1991) in 15 of 90 samples taken from the alluvial aquifer. In two samples collected in 1989 at CON–3 and CONDP–1, activities of uranium isotopes were measured, and concentrations of dissolved uranium were not measured. Concentrations of dissolved

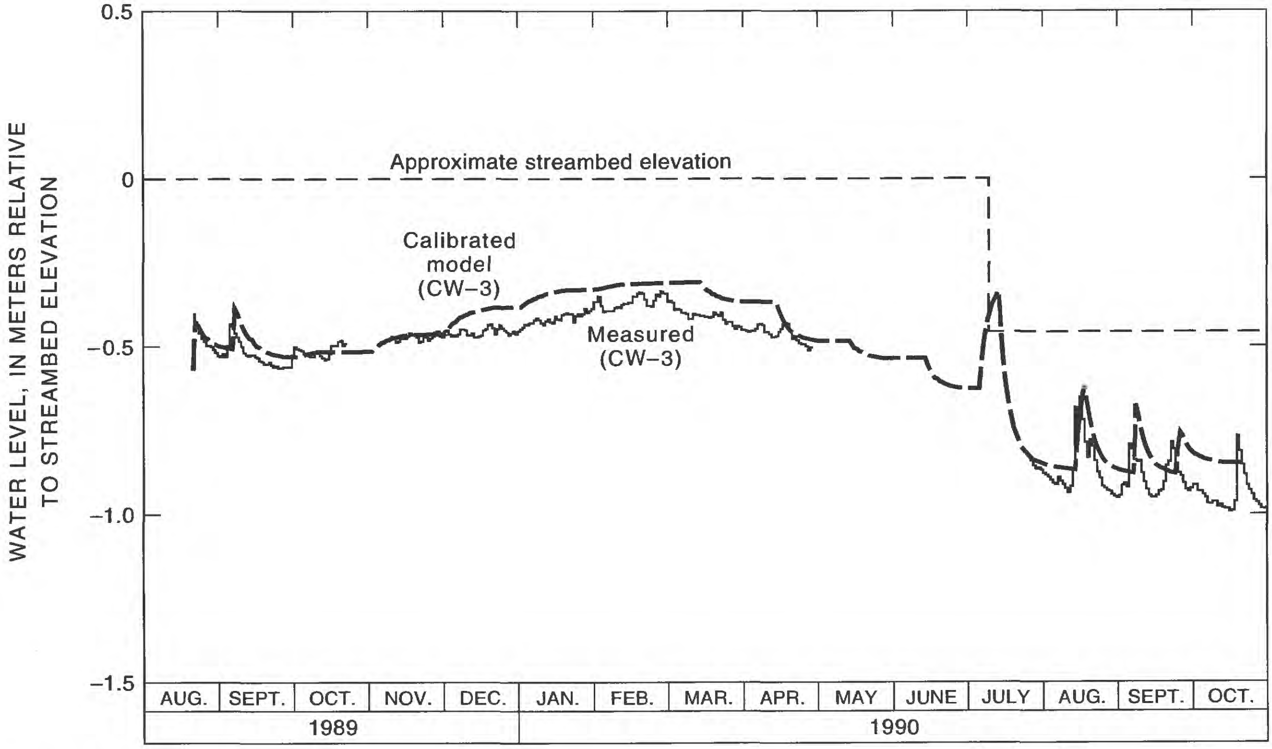


Figure 18. Calibrated model results and measured water levels at well CW–3.

Table 5. Parameter values for calibrated ground-water flow model, Puerco River Basin, Arizona and New Mexico

[---, no data]

		Aquifer and model parameters					
		Conceptualization			Used in model[1]		
Geologic description	Layer	Horizontal conductivity, in meters per day	Vertical conductivity, in meters per day	Layer thickness, in meters	Transmissivity, in meters squared per day	Vertical leakance, time^{-1}	Storage coefficient, dimensionless
Clay, water table	1	0.06	0.0004	1.5	0.09	[2]0.0005	0.25
Sand, partially confined	2	2.3	.23	4.0	[2]9.3	.16	[2,3].00005–0.1
Clay, confined	3	.023	.023	.4	.009	.11	.00005
Sand, confined	4	3.0	1.5	4.6	14	.65	.00005
Do.	5	3.0	1.5	4.6	14	.65	.00005
Do.	6	3.0	1.5	4.6	14	.12	.00005
Sand and clay, confined	7	.35	.35	5.3	1.9	---	.00005

[1] McDonald and Harbaugh (1988F).

[2] Parameter was varied during model calibration.

[3] Value varied from 0.1 in the streambed where layer 1 did not exist to 0.00005 under active rows of layer 1.

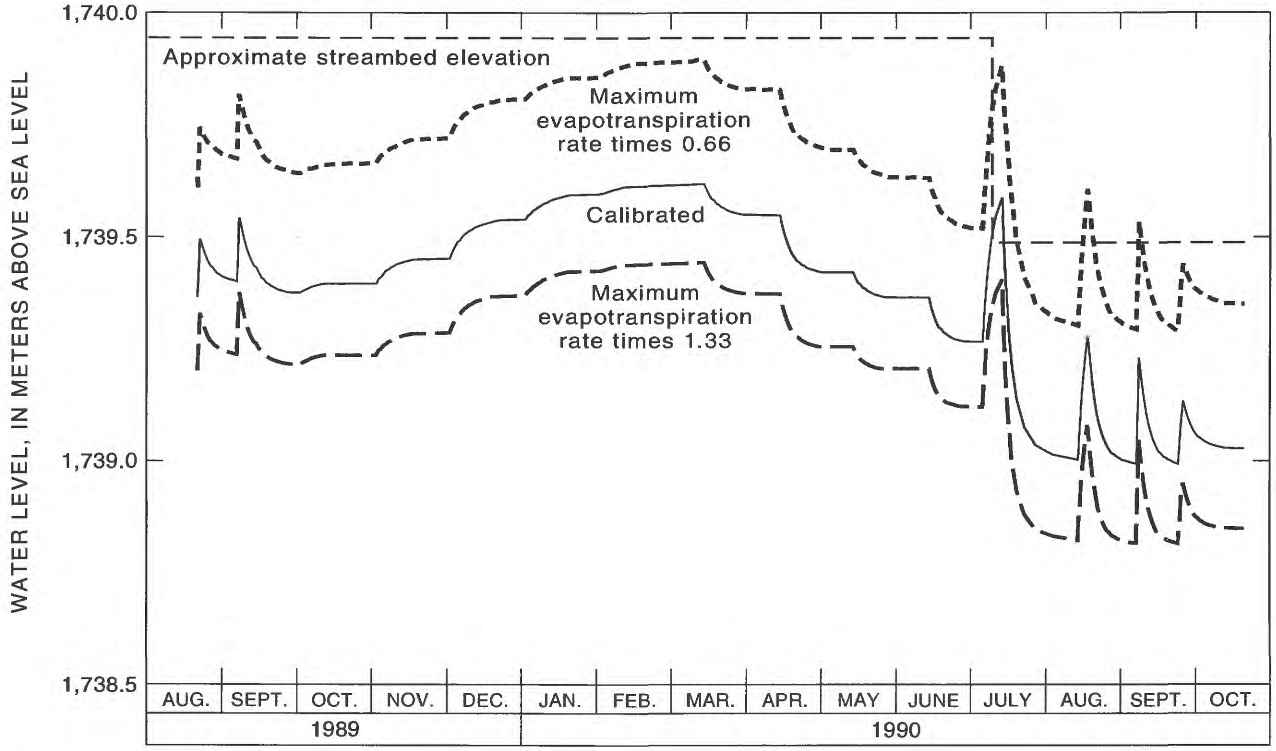


Figure 19. Effect of changes in evapotranspiration rate on model results at well CW–3.

uranium in those samples (870 and 660 µg/L, respectively) were calculated by conversion of uranium activities to concentrations in micrograms per liter. No samples from wells completed in the alluvial aquifer exceeded the MCL of the USEPA of 5 pCi/L for radium (^{226}Ra plus ^{228}Ra). Activities of thorium, lead–210, or polonium–210 in 11 samples did not exceed the laboratory minimum reporting level of about 2 pCi/L.

Activities of dissolved gross beta ranged from less than 1 to 260 pCi/L and had a median of 9.4 pCi/L. Activities of dissolved radon ranged from less than 80 to 1,100 pCi/L and had a median of 360 pCi/L. Thirty-six of 60 samples exceeded the proposed MCL of the USEPA of 300 pCi/L (U.S. Environmental Protection Agency, 1991).

Dissolved gross alpha activities ranged from less than 1 to 720 pCi/L and had a median of 11 pCi/L. All 118 samples from the alluvial aquifer had gross alpha activities minus the sum of uranium and radon activities that were below the MCL of the USEPA of 15 pCi/L. That value is calculated by converting dissolved gross alpha activity reported as an equivalent concentration of uranium in micrograms per liter to picocuries per liter. The conversion factor is 0.68 assuming secular equilibrium of 1.0 for ^{234}U/^{238}U. Total uranium activity, in picocuries per liter, is then subtracted from gross alpha activity and compared to the MCL of 15 pCi/L. Measured radon activity is not subtracted because essentially all the radon in samples analyzed for gross alpha activity is lost before analysis by degassing and radioactive decay (Ann Mullin, hydrologist, USGS, oral commun., 1991).

Trace-element concentrations other than iron and manganese were small (less than the MCL's) in most sampled wells. For example, selenium was detected in only 6 of 68 samples; the detection limit was 1 µg/L. Concentrations of trace elements, however, exceeded MCL's in six samples. Three of 68 samples collected from the alluvial aquifer exceeded the MCL of the USEPA of 50 µg/L for arsenic. One of those samples was collected from well LPT–4 at the Lupton well cluster; the other two samples were collected from MAN–1 at the Manuelito well cluster. Two of 118 samples collected at LPT–2 and MAN–3 in the Lupton and Manuelito well clusters exceeded the MCL of the USEPA of 10 µg/L for cadmium. Cadmium was detected at these two wells only during one sampling trip. One of 116 samples exceeded the MCL of the USEPA of 50 µg/L for lead. The sample was collected from AD–5 in the ADOT well cluster near Sanders and had elevated concentrations of chromium, iron, manganese, molybdenum, and silver. Laboratory error is the

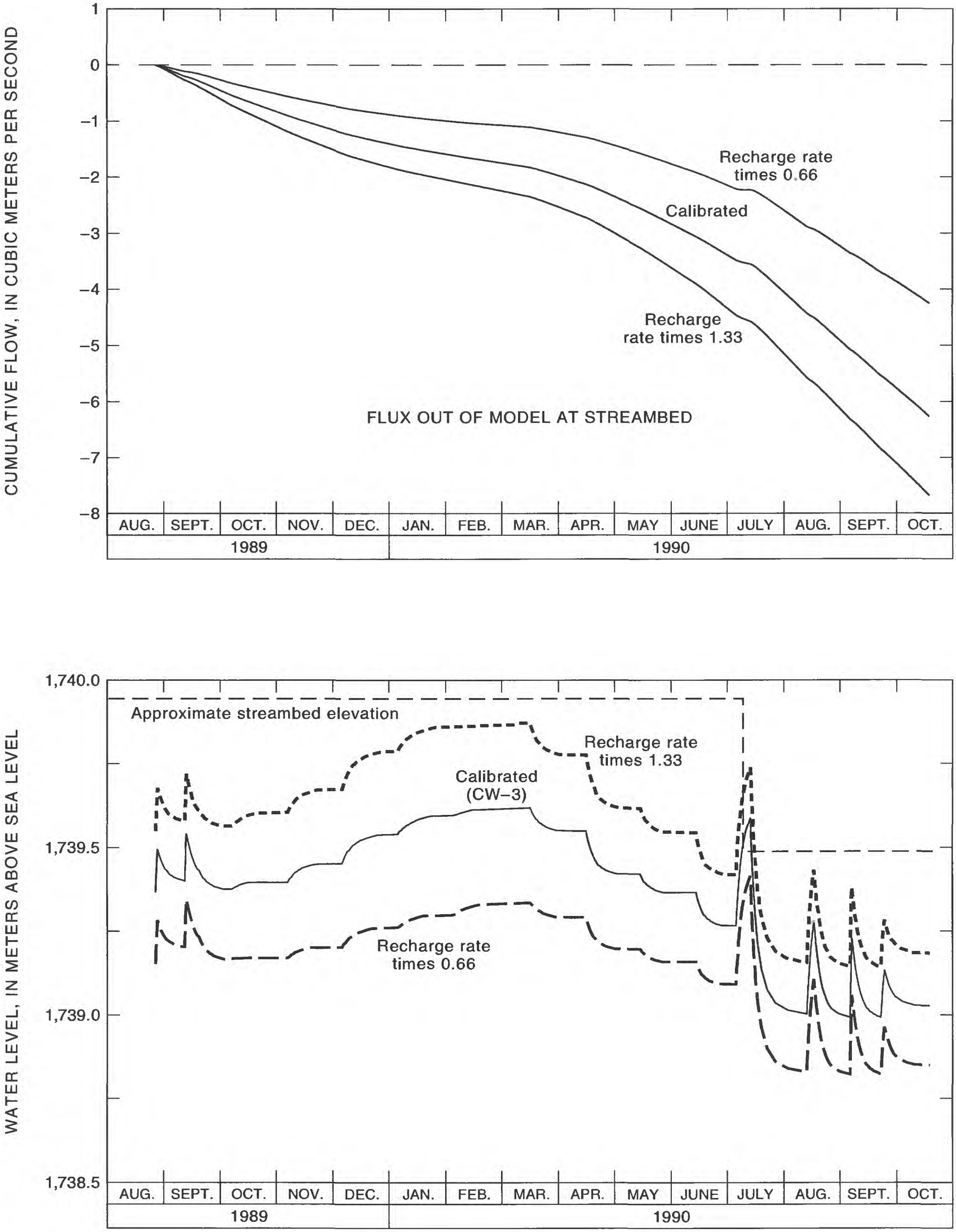


Figure 20. Effect of changes in recharge rate on model results.

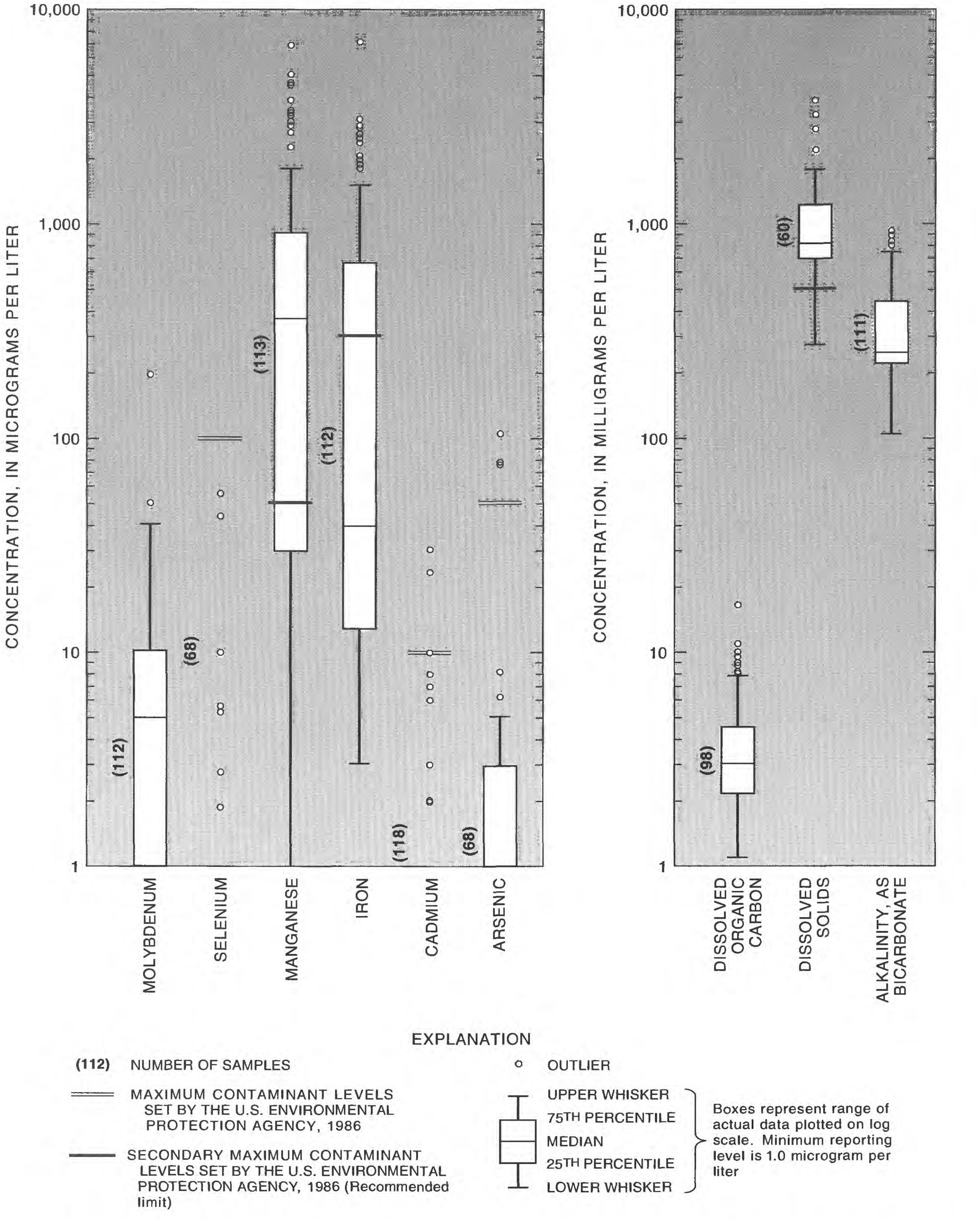


Figure 21. Distribution of dissolved concentrations of selected constituents in alluvial ground water, Puerco River Basin, Arizona and New Mexico.

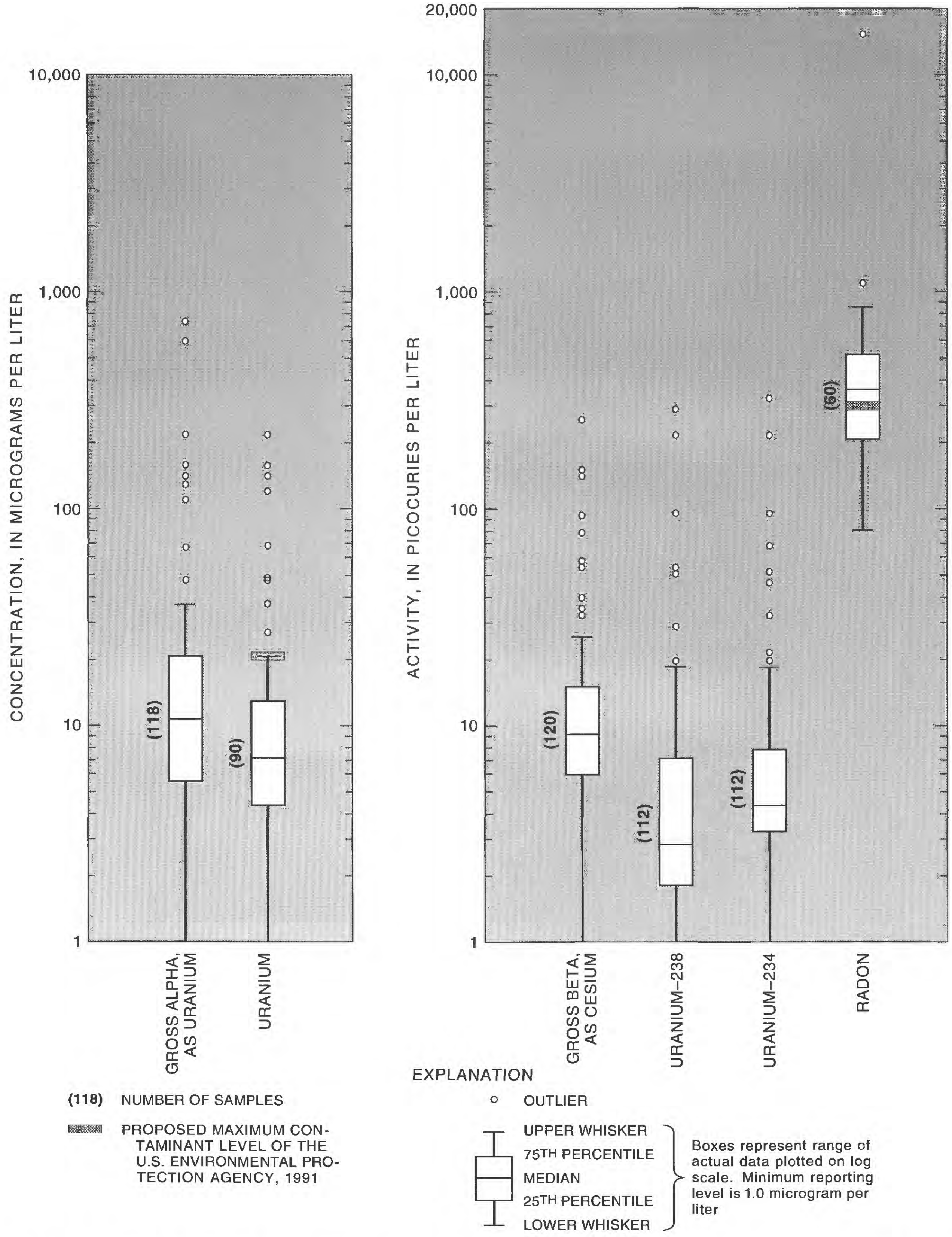


Figure 22. Ranges of dissolved concentrations and activities of selected radionuclides in alluvial ground water, Puerco River Basin, Arizona and New Mexico.

suspected cause of these large concentrations because in four other samples collected at AD–5, dissolved lead was 12 µg/L or less. Concentrations of all other nonradioactive trace elements were less than the MCL's of the USEPA.

Bedrock Formations

Eight wells were sampled that were completed in one of three bedrock formations—Chinle Formation, Entrada Formation, or Mancos Shale. Several other private wells were sampled during this study; however, the formation in which the wells were completed was not known. Six wells were completed in the Chinle Formation; three are monitor wells in the Sanders reach (CW–1, CP–1, and CP–8), and the other three wells are private wells in the Sanders area (ADOT YARD, INDIAN CITY, and INDIAN RUINS). Large variability in radionuclide activities and concentrations of dissolved solids, DOC, iron, and manganese were measured in samples from the wells completed in the Chinle.

Activities of dissolved gross alpha ranged from less than 1 to 380 µg/L as uranium, and gross beta activities ranged from 3.4 to 210 pCi/L. The largest radionuclide activities were measured at well ADOT YARD at the Arizona Department of Transportation facility near Sanders (fig. 6). In addition to the largest gross alpha and gross beta activities listed above, a sample collected from ADOT YARD on January 19, 1989, had a radon activity of 15,000 pCi/L, a dissolved-uranium concentration of 280 µg/L, and an activity of dissolved lead–210 of 6.7 pCi/L. That sample also exceeded the SMCL of the USEPA for dissolved solids. One sample from the Chinle Formation that was collected from the well, INDIAN RUINS, at the Indian Ruins trading post near Sanders had a dissolved radium activity (^{226}Ra plus ^{228}Ra) of 14 pCi/L and exceeded the MCL of the USEPA.

Concentrations of dissolved iron in wells completed in the Chinle Formation ranged from 45 to 1,100 µg/L and exceeded the SMCL for iron in three of five wells sampled for which iron analyses were completed. Concentrations of dissolved manganese ranged from less than 10 to 700 µg/L and exceeded the SMCL for manganese in five of six wells sampled. Other trace-element concentrations for Chinle wells generally were small and did not exceed the MCL's of the USEPA.

Concentrations of dissolved solids in wells completed in the Chinle Formation ranged from 361 to 1,390 mg/L and exceeded the SMCL of the USEPA for dissolved solids in four of six wells sampled. DOC ranged from 0.6 to 32 mg/L. Three samples from well CW–1, collected from December 1988 until May 1990, contained from 27 to 32 mg/L of DOC.

Well GAL–4, about 6 km upstream from Gallup, is completed in the Entrada Formation (David Baker, environmental engineer, NMED, written commun., 1989). Two samples collected at GAL–4 in 1989 and 1990 contained 1,100 mg/L of dissolved solids and small concentrations of trace elements and radionuclides (less than MCL).

Well WIN–3L, about 16 km upstream from Gallup, is completed in the Mancos Shale (David Baker, NMED, written commun., 1989). A sample collected on January 11, 1989, at WIN–3L contained 7,040 mg/L of dissolved solids, 4,500 mg/L of dissolved sulfate, and 9.2 mg/L of DOC. A sample collected on October 24, 1990, contained 1,800 µg/L of dissolved manganese and 2,800 µg/L of dissolved iron. Ratios of major ions were similar in samples from WIN–3L and water from the tailings-pond spill; however, there was less than 3 pCi/L of tritium in a sample from WIN–3L collected in 1989, which indicates water had recharged prior to 1952. The tailings-pond solution may not have contained tritium above pre-1952 levels; however, if the tailings-pond solution from the stream has reached WIN–3L since the spill in 1979, then runoff and infiltration of precipitation also would be expected to occur at the well. Thus, the small tritium activity suggests that the large sulfate concentrations occur naturally and are not the result of the spill.

Spatial and Temporal Variations of Selected Constituents

Concentrations or activities of iron, manganese, uranium, gross alpha, gross beta, and radon had large spatial and, in some cases, temporal variations. Large concentrations or activities of these constituents can affect the usefulness of the water, as evidenced by samples that exceeded the MCL's or SMCL's, or, in the case of uranium and radon, proposed MCL's of the USEPA.

Iron and Manganese

The concentration of dissolved iron in solution depends on the types of iron minerals present, the pH of the solution, and the oxidizing or reducing nature of the ground water. Water containing dissolved oxygen (oxidizing conditions) typically does not contain more than a few micrograms per liter of dissolved iron at equilibrium within the pH range of about 6.5 to 8.5. Hem (1985), however, notes that in that pH range, the maintenance of an Eh below 200 and above −100 mV can permit a considerable dissolved ferrous iron (Fe^{II}) concentration.

Concentrations of dissolved iron and manganese varied spatially (figs. 23, 24) and had statistically significant Spearman rank correlations to measured Eh and to DOC concentrations (table 6). One possible reason for the relation between DOC and iron and manganese concentrations is that the reductive nature of organics in solution leads to reduction of Fe^{III} or Mn^{IV} solids to form Fe^{II} or Mn^{II} in solution. Hem (1985, p. 152) notes that

> ...participation of dissolved organic matter in ground water in metal oxide reduction can help explain increases in manganese and (or) iron in water withdrawn from wells near organic carbon sources.

Iron-mineral saturation was investigated by using PHREEQE, a computer program designed to model geochemical reactions (Parkhurst and others, 1980). PHREEQE was used to calculate the saturation index (SI) for ferric hydroxide for selected ground-water samples that represent a large range in concentrations of dissolved iron (fig. 25). The SI is a measure of the difference between the actual and equilibrium state of a mineral in a given water chemistry. The reaction for the congruent dissolution of ferric hydroxide is:

$$Fe(OH_3) = Fe^{+3} + 3OH^{-}. \qquad (3)$$

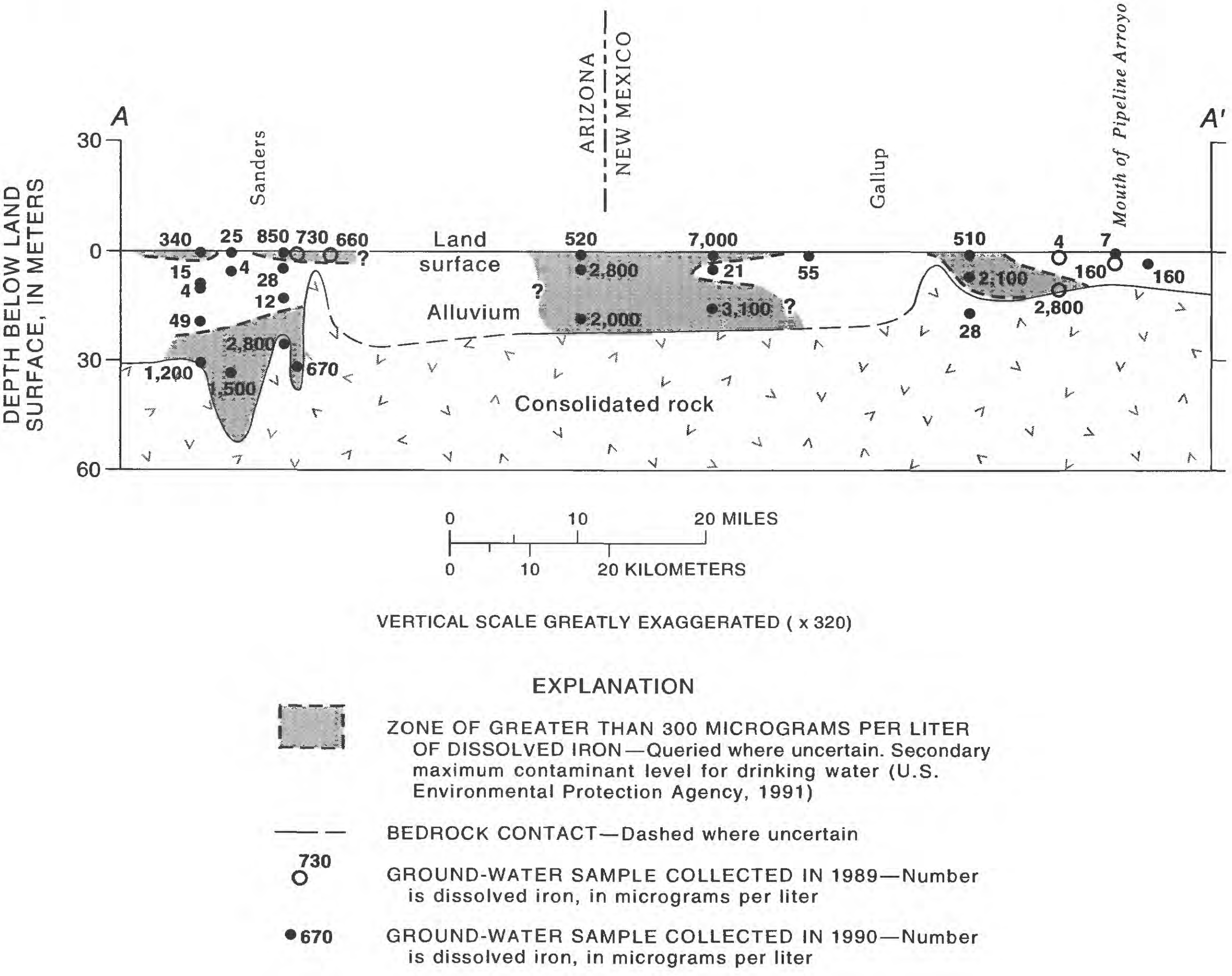
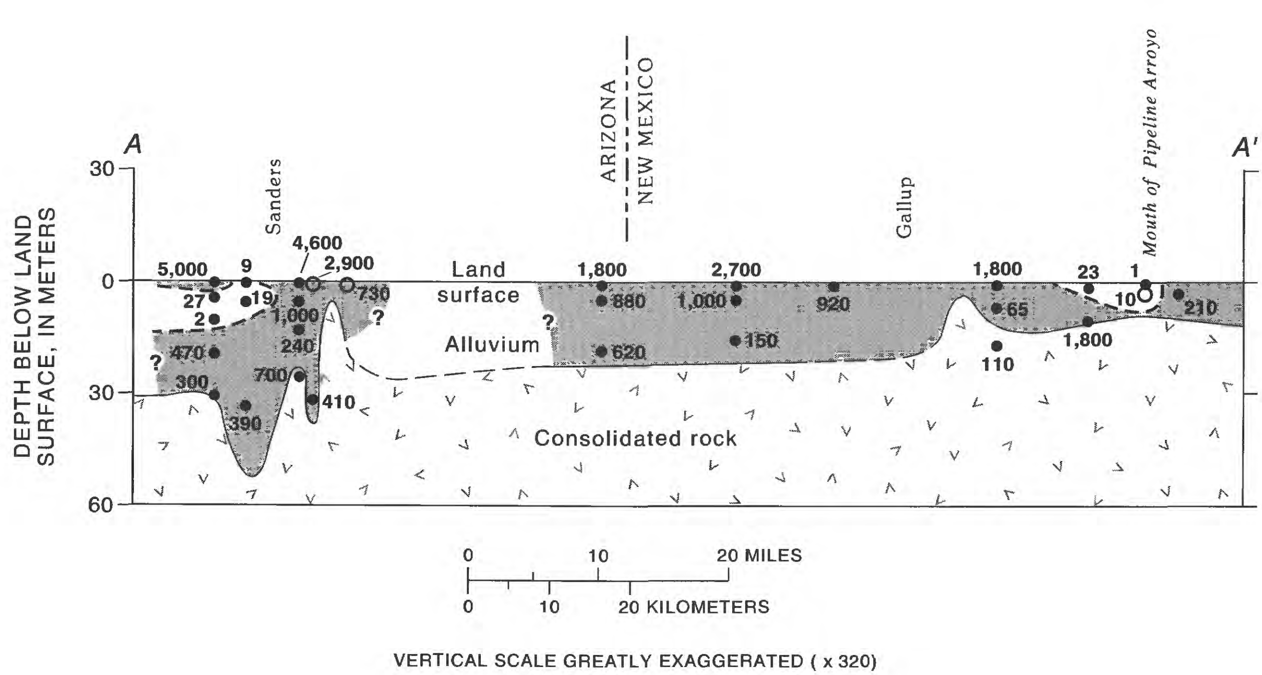


Figure 23. Concentrations of dissolved iron under the Puerco River.



EXPLANATION

▨ ZONE OF GREATER THAN 300 MICROGRAMS PER LITER OF DISSOLVED MANGANESE—Queried where uncertain. Secondary maximum contaminant level for drinking water (U.S. Environmental Protection Agency, 1991)

— — BEDROCK CONTACT—Dashed where uncertain

○ 730 GROUND-WATER SAMPLE COLLECTED IN 1989—Number is manganese, in micrograms per liter

● 670 GROUND-WATER SAMPLE COLLECTED IN 1990—Number is manganese, in micrograms per liter

Figure 24. Concentrations of dissolved manganese under the Puerco River.

Table 6. Spearman rank correlations of dissolved-iron and dissolved-manganese concentrations to dissolved-oxygen concentration and oxidation-reduction potential in ground water, Puerco River Basin, Arizona and New Mexico

Constituent	Number of samples	Probability[1]	Correlation to dissolved-oxygen concentration (coefficient)	Number of samples	Probability[1]	Correlation to oxidation-reduction potential (coefficient)
Iron, dissolved	93	0.000	0.37	86	0.000	–0.66
Manganese, dissolved	93	.000	.48	86	.002	–.33

[1] Probability is that the relation is due to chance and not to group differences.

Near saturation of ferric hydroxide is maintained over a large range in concentrations of dissolved iron and indicates that dissolved iron in ground water is near equilibrium with ferric hydroxide. Correlations between DOC, Eh, and iron indicate that some of the variation in Eh could result from the reduction of iron by dissolved organic matter.

Uranium and Gross Alpha

Uranium has three isotopes of which ^{238}U is predominant. This nuclide is only weakly radioactive, has a half-life of 4.5×10^9 years, and is the parent element of the radioactive-decay series that ends with the stable isotope ^{206}Pb (fig. 5). The uranium oxidation states that are stable in geologic environments are uranous (U^{4+}) and uranyl (U^{6+}); U^{4+} is less soluble than U^{6+} (Landa, 1980).

Concentrations of dissolved uranium correlated strongly with dissolved gross alpha activities (correlation coefficient of 0.978 in 88 samples collected from August 1988 until November 1990). The concentrations of uranium in ground-water samples from this study can be estimated from dissolved gross alpha activity ($r^2 = 0.96$) by using

$$U = (0.984 \times ALPHA) - 2.04\,, \qquad (4)$$

where

U = concentrations of dissolved uranium, in micrograms per liter, and

$ALPHA$ = gross alpha activity, in micrograms per liter, as uranium.

The high correlation between uranium and gross alpha and the regression slope near 1.0 indicate that most of the dissolved gross alpha activity in ground water from the alluvial aquifer is from uranium.

In 1989, concentrations of dissolved uranium in ground water were largest in a zone that extended from the mouth of Pipeline Arroyo to about the Arizona–New Mexico State line (fig. 26). Only in the reach from the mouth of Pipeline Arroyo to the Nutria monocline does the zone extend more than a few meters below the streambed. Concentrations of dissolved uranium decreased with distance downstream from the mouth of Pipeline Arroyo and with distance from the stream at monitor well clusters (fig. 27).

Dissolved gross alpha activities in the Puerco River decreased significantly with the cessation of mine dewatering in 1986 (Van Metre and Gray, 1992). The mean activity for 18 samples in the reach between the mines and Gallup was 1,200 pCi/L during mining

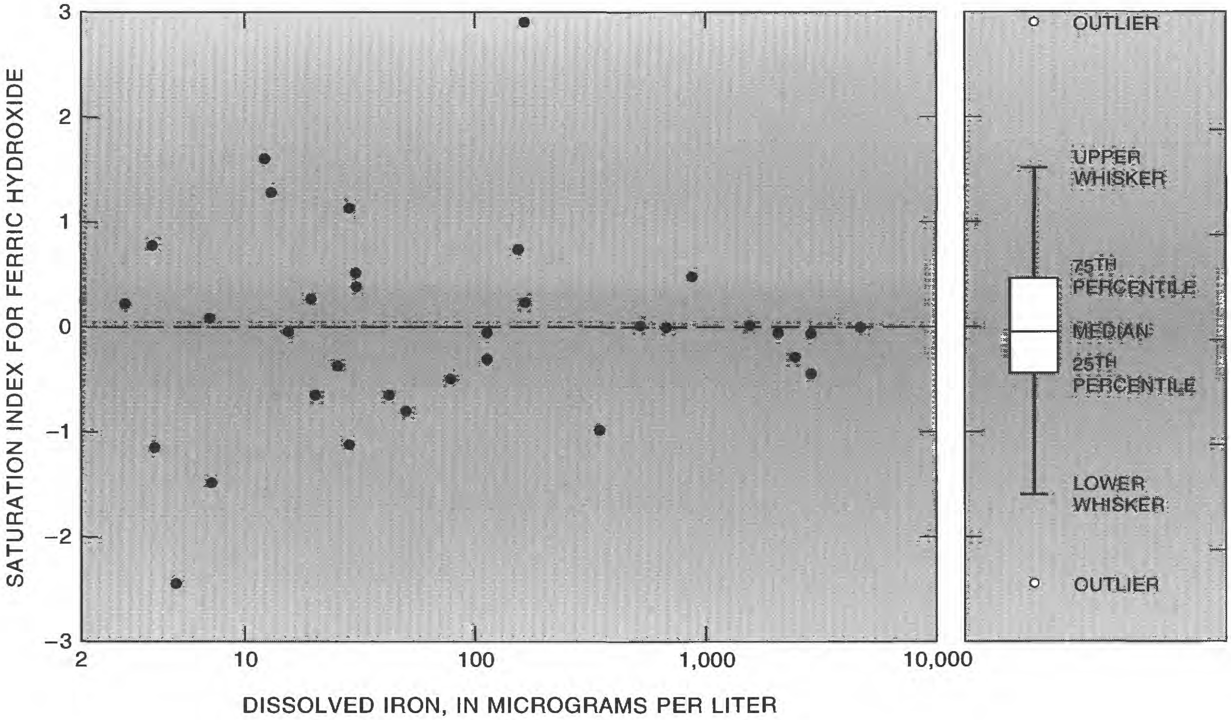


Figure 25. Comparisons of concentrations of dissolved iron and a saturation index for ferric hydroxide (34 samples).

years. In comparison, the mean activity in the Puerco River in 1988 and 1989 was 7.1 pCi/L for 25 samples. Concentrations of dissolved uranium in shallow ground water appear to be decreasing with time as indicated by the decrease in gross alpha activity in samples collected between 1989 (fig. 26) and 1990 (fig. 28). The largest changes in uranium concentration were measured in samples from hand-driven wells, which probably reflect a combination of dilution and chemical reactions including sorption. Concentrations of dissolved uranium at CONDP–1 decreased from 660 µg/L on March 3, 1989 (calculated by conversion of ^{238}U activity to an equivalent concentration of total dissolved uranium) to 220 µg/L on October 18, 1990, and to 130 µg/L on June 10, 1991. Sampling of six hand-driven wells in June 1991, corroborated the smaller uranium concentrations indicated in the 1990 samples.

Gross Beta

Activities of dissolved gross beta had a spatial distribution similar to concentrations of dissolved uranium in 1989 (fig. 29); however, the range in activities was smaller (fig. 22). The only beta-emitting radionuclide measured was ^{210}Pb; concentrations of ^{210}Pb for all samples from the alluvial aquifer were less than 1.0 pCi/L. Most of the gross beta activity can be attributed to delays in laboratory analyses and not to beta-emitting radionuclides in solution in ground water (Thomas and others, 1993; p. 463–468). Samples for analysis of dissolved gross beta were filtered and acidified in the field to a pH of less than 2. They were then shipped to a laboratory and in most cases analyzed several months later (dates of analysis for individual samples are not known). Uranium–238 has two beta-

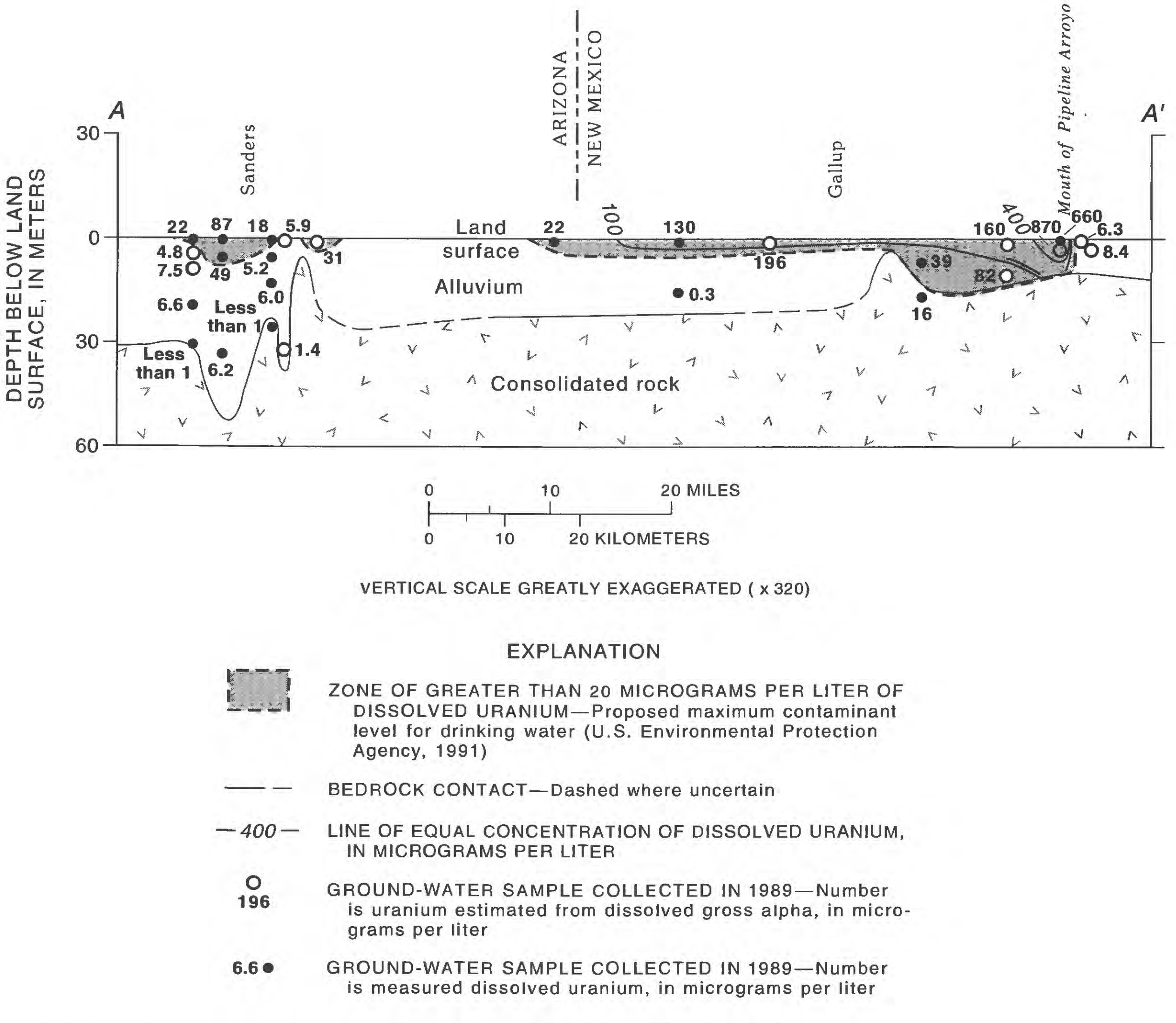
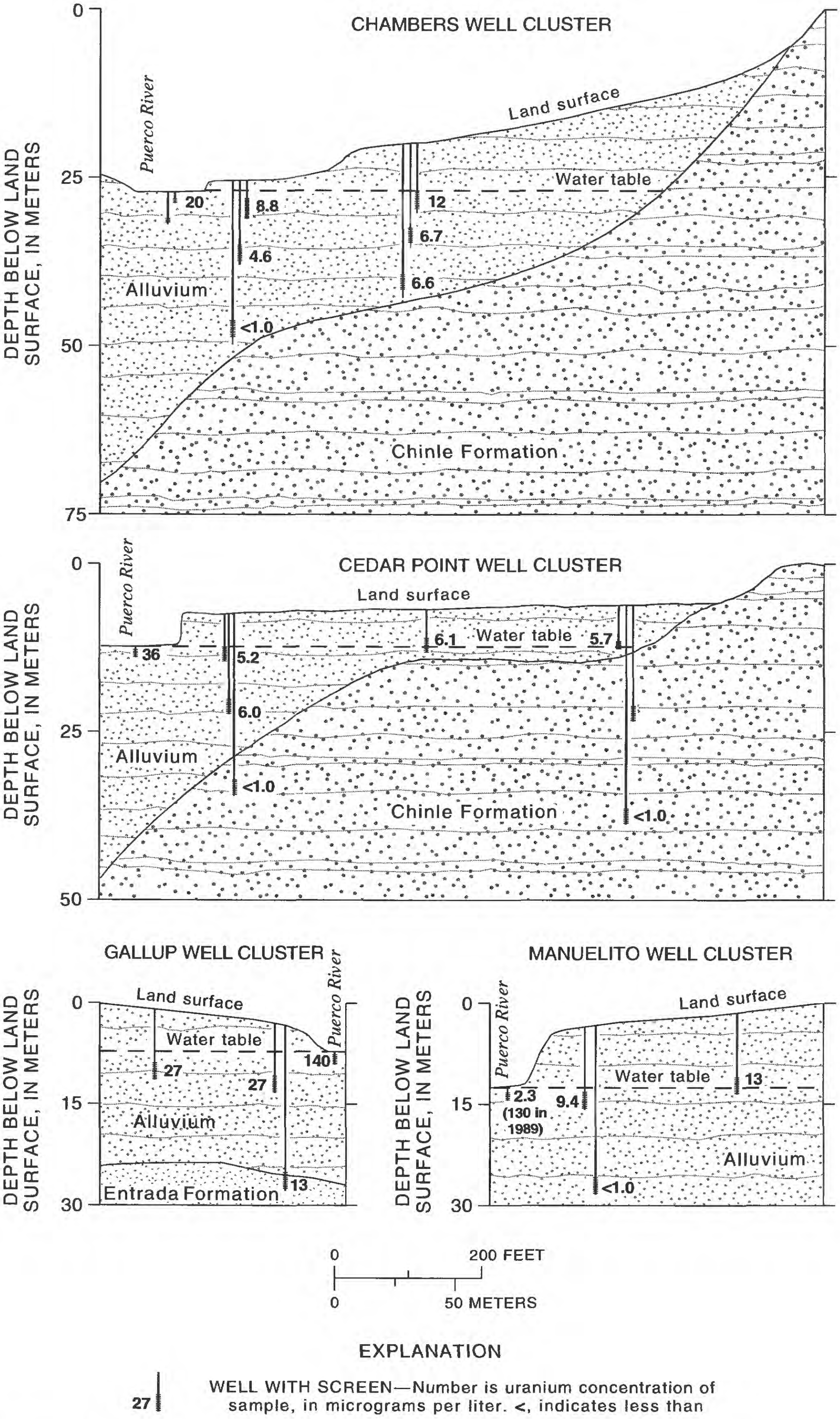


Figure 26. Concentrations of dissolved uranium under the Puerco River, 1989.



EXPLANATION

27 WELL WITH SCREEN—Number is uranium concentration of sample, in micrograms per liter. <, indicates less than

Figure 27. Concentrations of dissolved uranium at selected well clusters, 1990.

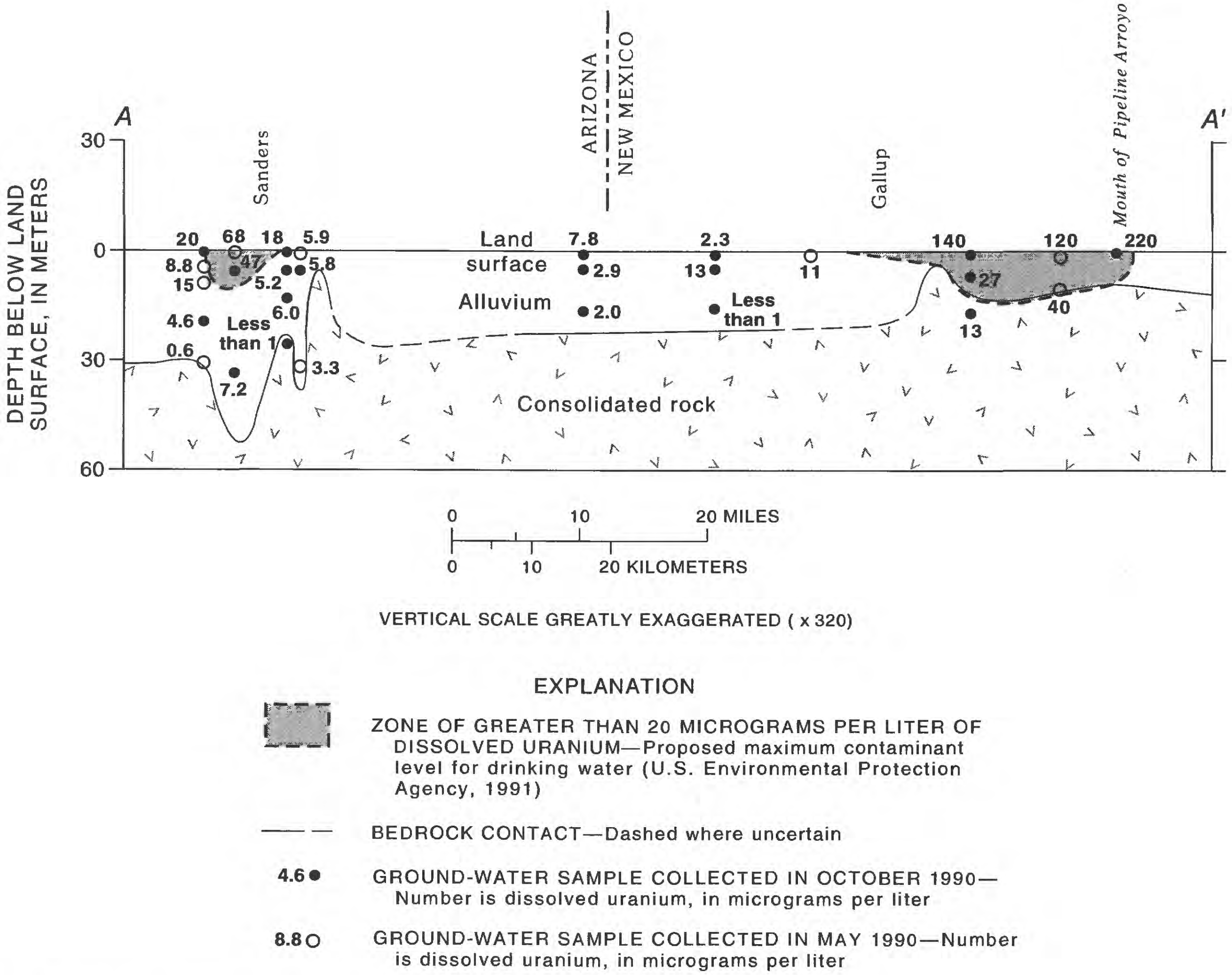


Figure 28. Concentrations of dissolved uranium under the Puerco River, 1990.

emitting daughters, ^{234}Th and protactinium–234 (^{234}Pa; fig. 5), both of which have short half-lives and are relatively insoluble (Durrance, 1986). Both, however should remain in solution in an acidified sample bottle. On the basis of their half-lives, the ingrowth of ^{234}Th and ^{234}Pa to 95 percent of secular equilibrium with ^{238}U takes 104 days (Durrance, 1986). Thus, in samples that are not analyzed for several months, the gross beta activity from ^{234}Th and ^{234}Pa would be approximately equal to twice the activity of ^{238}U. The median ratio of gross beta to ^{238}U was 2.4 for 90 samples in which gross beta was greater than 5.0 pCi/L and ^{238}U was greater than 1.0 pCi/L. The relation between gross beta activities and ^{238}U activities is evidence that much of the measured gross beta activity is from ^{234}Th and ^{234}Pa and is not indicative of gross beta activities in ground water.

Radon

Radon (^{222}Rn) is an inert gas with a half-life of 3.8 days and is a decay product of ^{226}Ra (fig. 5). Investigations of the ^{222}Rn distribution in ground water show that the range of values found in nature covers at least five orders of magnitude (Hess and others, 1985). Radon activities in samples from the alluvial aquifer ranged from less than 80 to 1,100 pCi/L (fig. 30).

Radon in ground water generally is not supplied by radium in solution but by radium in rocks and soil. Activities of ^{226}Ra in samples from the alluvial aquifer were less than 2.0 pCi/L (assuming 1 L of water weighs 1 kg, the solid-phase concentration would be 2×10^{-3} pCi/g). Activities of ^{226}Ra in 11 sediment samples from well cores at the Chambers well cluster, however, had a mean activity of 1.0 pCi/g. Assuming a porosity of 0.4, which is a representative value for a lithology of sand, silt, and clay (Freeze and Cherry,

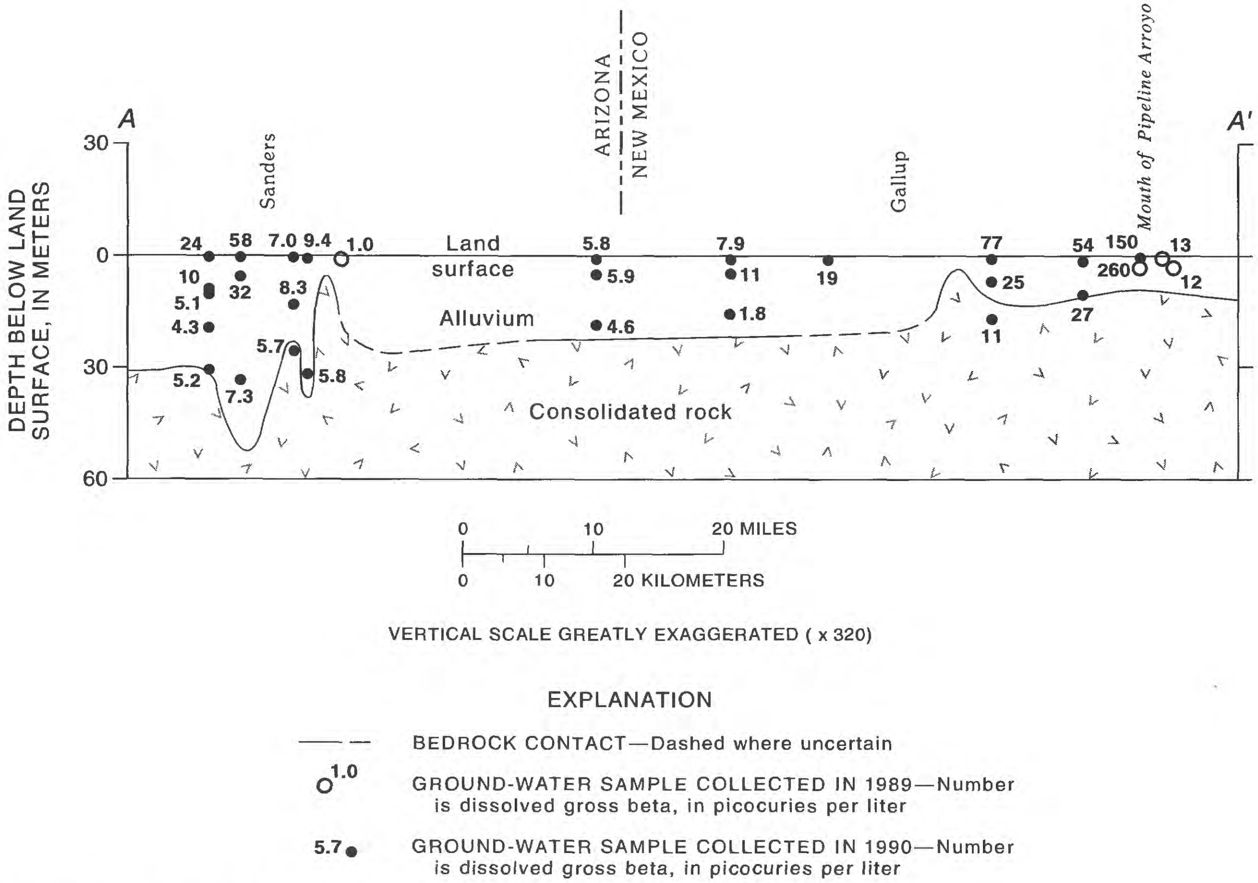


Figure 29. Activities of dissolved gross beta under the Puerco River, 1989–90.

1979), and a sediment density of 2.65 g/cm^3, 1 L of ground water is equal to about 4,000 g of sediment and, thus, about 4,000 pCi of ^{226}Ra. The source of most radon in the aqueous phase, therefore, is radium in the solid phase, and radon in water could indicate the amount of radium in the solid phase. The median ^{222}Rn concentration in water from the nine wells at Chambers was 190 pCi/L and was calculated by determining the median of samples from each well and then determining the median of those nine values. Using the estimate of about 4,000 pCi of ^{226}Ra in contact with 1 L of ground water and the median ^{222}Rn activity of 190 pCi/L, only about 5 percent of the ^{222}Rn formed is released to the water.

Ambiguous correlations often result from attempts to relate variations in the ^{222}Rn concentrations in ground water directly to the presence of uranium and ^{226}Ra in the aquifer (King and others, 1982; Livey and Morey, 1982). Radon activities for wells at the Chambers well cluster generally correlate with depth and are larger near or below the water table (fig. 30). Activities of ^{226}Ra in well-core samples from Chambers do not correlate with depth; however, a 0.76 correlation coefficient was computed between the ^{226}Ra concentration and the percent of the sample passing through a 0.062-mm sieve (the silt and clay fraction). Solid-phase data are presented in Fisk and others (1994). Furthermore, the occurrence of clay at shallow depths at Chambers is indicated by the natural gamma log at well CW–4 (fig. 31). The coincidence of larger radon activities and greater clay content suggests that some of the variation in radon activities in water could result from variations in the occurrence of clay and, therefore, ^{226}Ra in the aquifer.

GEOCHEMISTRY OF URANIUM

Sorption of uranium on sediment and the precipitation of minerals containing uranium are chemical processes that could remove uranium from solution (Stumm and Morgan, 1981). Uranium mineral saturation depends on the valance state of the uranium. U^{+4} is the more reduced form and is much less soluble than

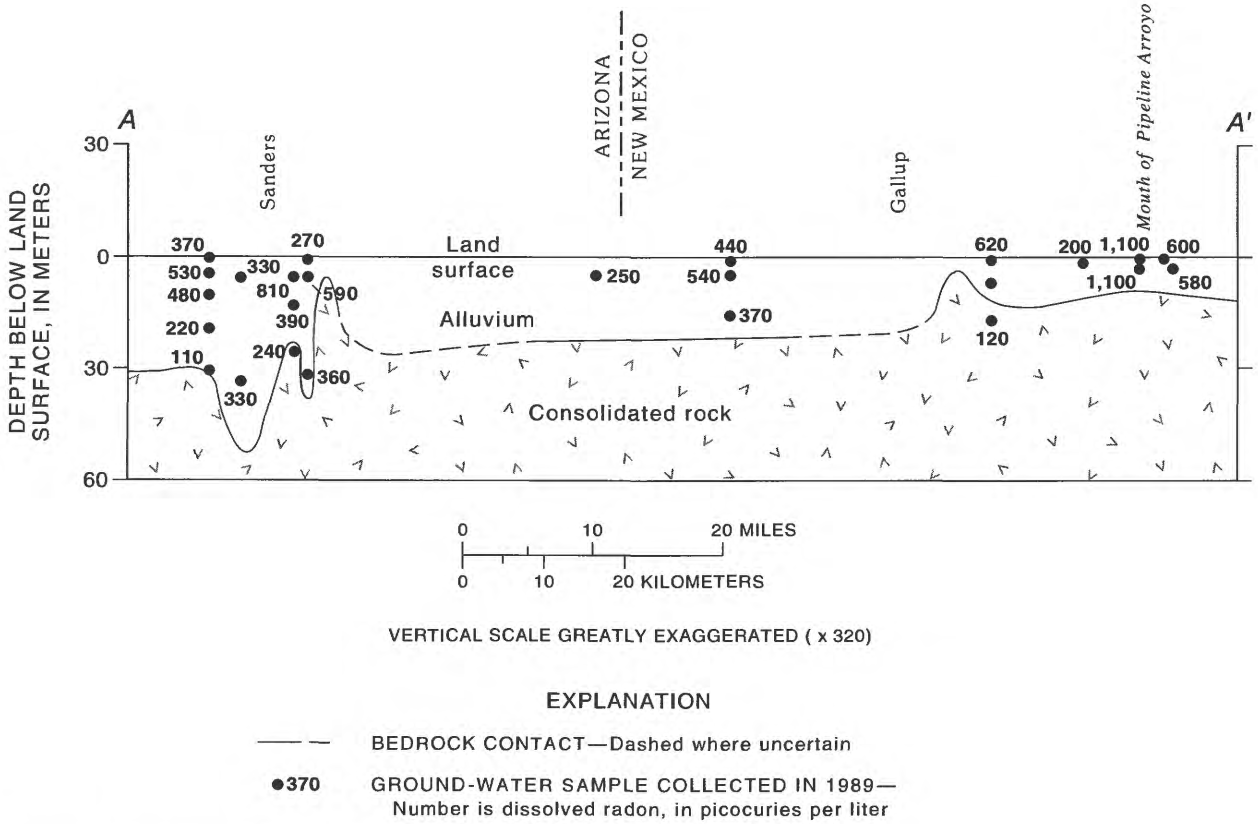


Figure 30. Activities of dissolved radon under the Puerco River.

U^{+6} (Landa, 1980). Langmuir (1978) notes that probably much of the uraninite and coffinite in sandstone-type uranium deposits is formed by reduction following adsorption of uranyl species from ground water into organic matter.

Saturation of Uranium Minerals

Speciation of uranium complexes and saturation states of selected uranium minerals were calculated by using PHREEQE (Parkhurst and others, 1980) with thermodynamic data for uranium species and minerals from Langmuir (1978) and data for vanadium species and minerals from Wanty and Goldhaber (1992). If supersaturation of uranium minerals is indicated by the model, precipitation of those uranium minerals in the environment is chemically feasible. Calculated SI values represent only one possible set of conditions because of assumptions made in the modeling process and the limited historical data available to characterize the chemistry of mine-dewatering effluent.

Mine-Dewatering Effluent

Modeling was used to calculate the saturation states of uranium minerals in mine-dewatering effluent. Because mine dewatering ended in February 1986 before this project began, this modeling relied on historical data to describe the water quality of mine effluent. Data used were collected by the NMED (Raymondi and Conrad, 1983; Gallaher and Cary, 1986; Dave Baker, NMED, written commun., 1989; and Wirt and others, 1991). Two processes were modeled that influence the SI of uranium minerals in mine-dewatering effluent—degassing of CO_2 and mixing with Gallup STP wastewater. The assumption was made that oxidizing conditions prevailed in streamflow as indicated by the presence of dissolved oxygen and a measured Eh value of 400 mV, therefore, no oxidation-reduction reactions were used in model simulations.

A sample of mine effluent collected in the Puerco River by the NMED (Raymondi and Conrad, 1983) was used in model simulations. The saturation states of uranium minerals in mine effluent at the outfall were estimated by equilibrating the sample with a partial pressure of carbon dioxide (P_{CO_2}) similar to values

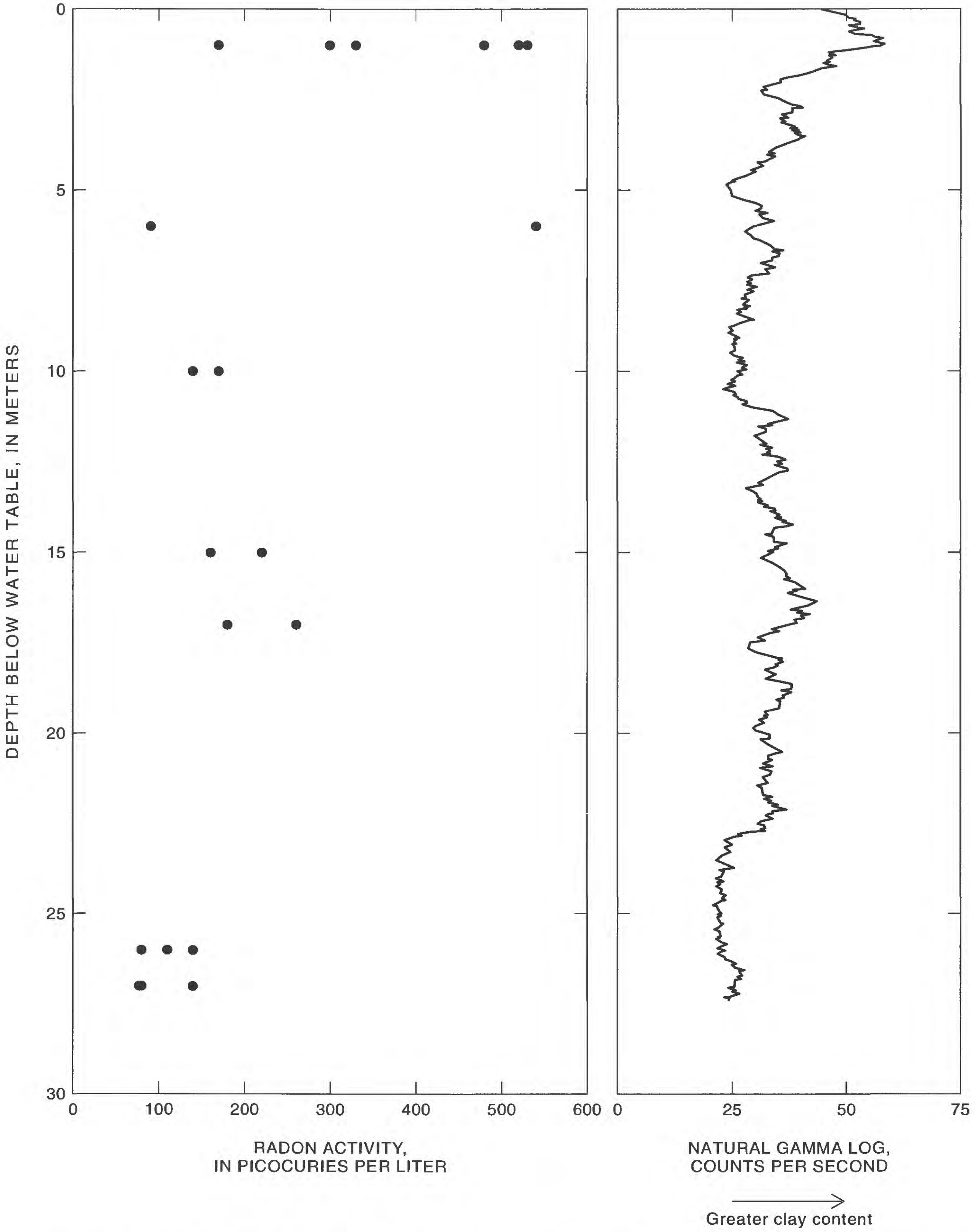


Figure 31. Gamma log at well CW–4 and dissolved-radon activities in relation to depth at the well cluster at Chambers, Arizona.

calculated for other ground-water samples collected in the area [log(P_{CO_2}) = –1.5] (fig. 32). Degassing occurs when carbon dioxide dissolved in mine effluent equilibrates with the atmospheric partial pressure of carbon dioxide [log(P_{CO_2}) = –3.5]. Calculations using PHREEQE indicate that significant degassing had already occurred before the sample of mine effluent was collected [log(P_{CO_2}) = –3.25]. Calculations using minimum, maximum, and mean uranium concentrations (0.1, 2.8, and 1.1 mg/L, respectively) and vanadium concentrations (0.006, 0.41, and 0.02 mg/L, respectively) indicate that mine effluent at the outfall was approximately in equilibrium or supersaturated with carnotite [$K_2(UO_2)(VO_4)$] and tyuyamunite [$Ca(UO_2)(VO_4)$].

The influence of carbon-dioxide degassing on uranium solubility was determined by decreasing the P_{CO_2} from log (P_{CO_2}) = –1.5 to log (P_{CO_2}) = –3.5 until equilibrium with atmospheric carbon dioxide was reached. Degassing of carbon dioxide increases pH, and the increased pH shifts the carbonate equilibrium, increasing the proportion of carbonate ions that complex with uranium. The complexation of uranium with carbonate ions decreases the SI values and results in undersaturation, which approximates the equilibrium of carnotite and tyuyamunite in mine-dewatering effluent at atmospheric P_{CO_2} (fig. 32). The relation of decreasing SI values with decreasing log (P_{CO_2}) values indicates that uranium minerals in mine effluent would remain in solution and were unlikely to precipitate in the Church Rock reach.

The effect of Gallup STP wastewater on uranium solubility was determined by simulating mixing of wastewater and mine-dewatering effluent (fig. 33). Although Gallup STP wastewater was not analyzed for uranium, a dissolved gross alpha activity of 1.3 pCi/L indicates that uranium in wastewater was negligible. Two possible equilibrium-mixing conditions were computed: (1) simple mixing of the solutions and (2) equilibrating the mix with calcite and atmospheric P_{CO_2}. Mixing proportions of the solutions were varied, and saturation states of minerals were computed for the two equilibrium-mixing conditions. Decreasing SI values with increasing proportions of Gallup STP wastewater for both mixing conditions indicate that uranium in mixed effluent and wastewater was unlikely to precipitate.

Alluvial Aquifer

Speciation of uranium complexes and saturation states of selected uranium minerals also were calculated for selected ground-water samples by using PHREEQE (Parkhurst and others, 1980). As indicated by the geochemical modeling, most ground water in the alluvial aquifer is undersaturated with respect to the common uranium minerals—uraninite, coffinite, carnotite, tyuyamunite, schoepite, and rutherfordine (fig. 34). Saturation of uranium minerals is affected primarily by the concentration of dissolved uranium and by the redox potential. Uranium concentrations used in the geochemical model represented a range of natural samples in the alluvial aquifer. The saturation indices for amorphous analogs of uraninite and coffinite (U^{+4}) species (fig. 34*A*), which may precipitate following reduction of uranyl ion, are inversely related to Eh (r = –0.93 and –0.94, respectively). Modeling results indicate that coffinite could reach saturation at Eh values near zero. Mineral species that include uranyl ion (U^{+6})—such as carnotite, tyuyamunite, schoepite, and rutherfordine (fig. 34*B*)—approach saturation at uranium concentrations greater than or equal to about 150 μg/L. On the basis of these results, uranium would not be expected to precipitate in the alluvial aquifer.

Calculated saturation indices for most wells are evidence that sorption, and not precipitation of uranium minerals, is the controlling mechanism for uranium concentrations. The state of undersaturation calculated for most ground-water samples suggests that if solid-phase uranium minerals were available, they would be dissolving. Because the average concentration of uranium measured in 45 samples of sand and clay collected from the alluvial aquifer and the streambed is 2.5 μg/g (Fisk and others, 1994), significant amounts of uranium are in the solid phase. Dissolved uranium concentrations in the alluvial aquifer, however, are decreasing as a function of time in many locations (figs. 26, 28). Observed uranium concentrations and modeling indicate that some mechanism other than precipitation of uranium minerals is removing uranium from solution. The most likely mechanism is sorption of uranium on sediments rather than precipitation of uranium minerals.

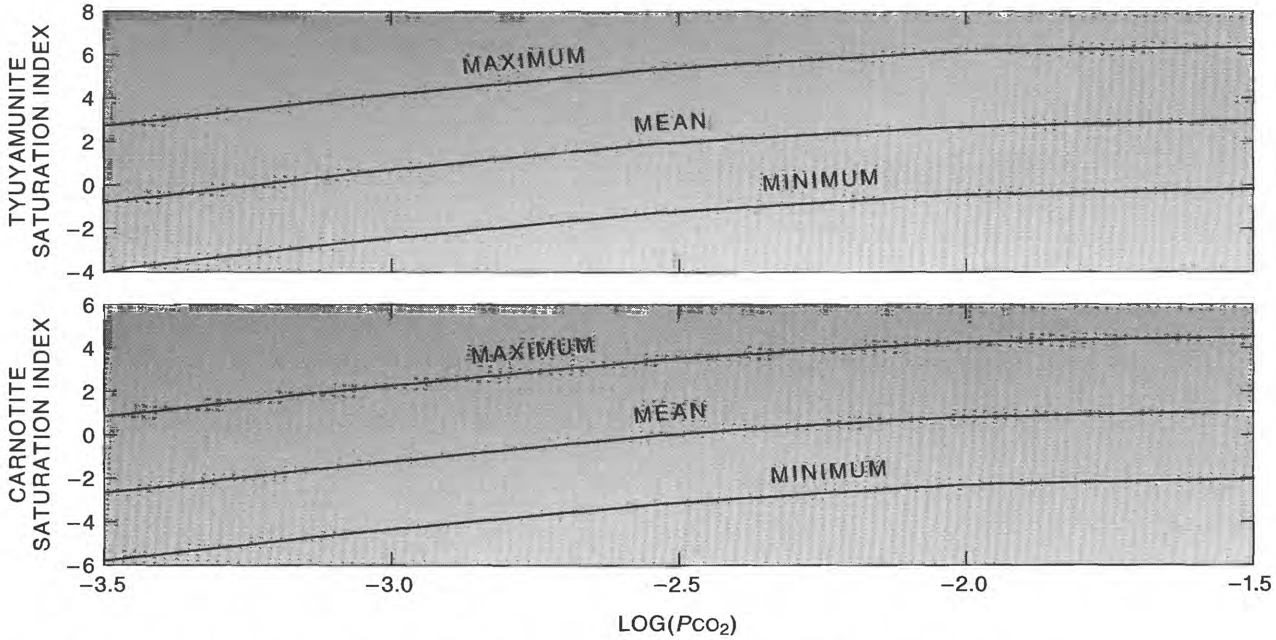


Figure 32. Influence of carbon-dioxide degassing on uranium-mineral saturation in mine effluent.

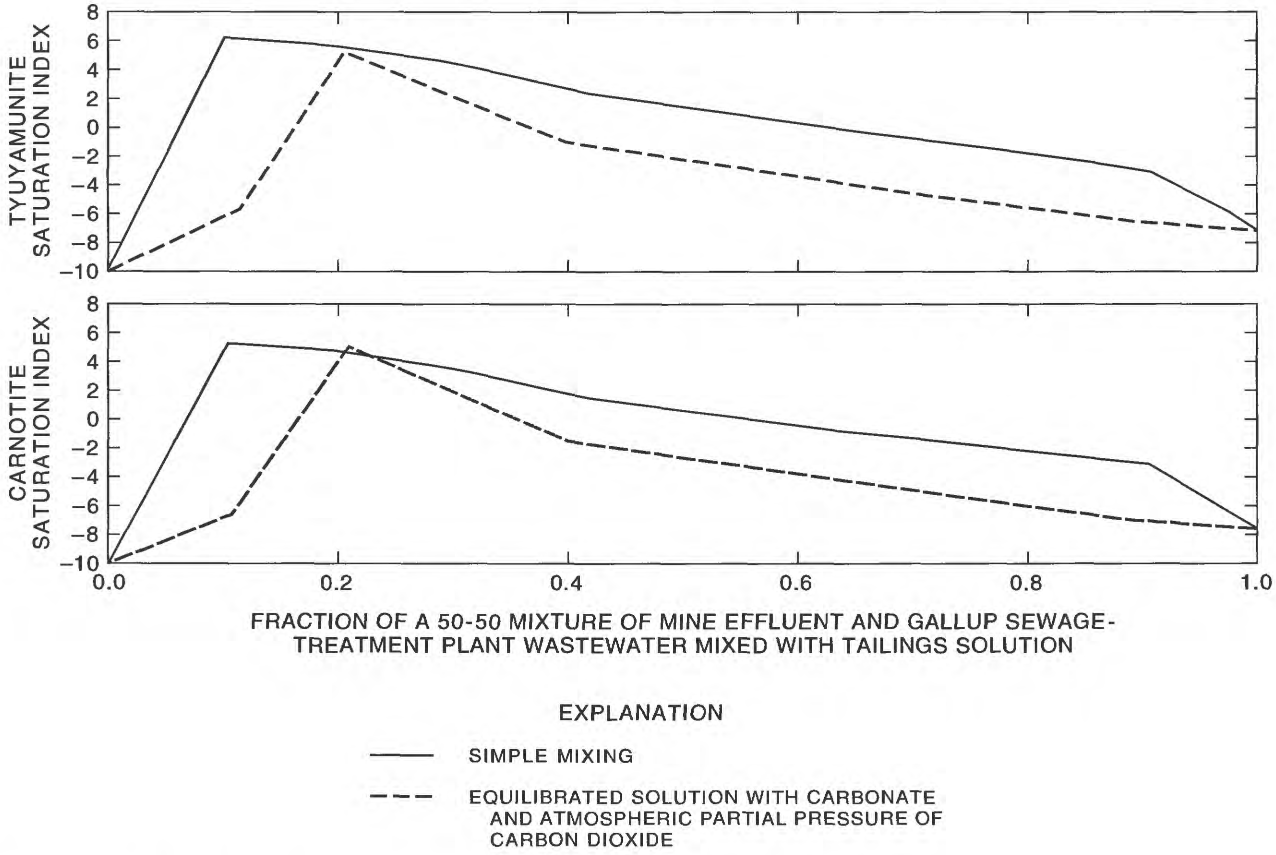


Figure 33. Effect of mixing mine effluent and Gallup sewage-treatment plant wastewater on uranium-mineral saturation.

Sorption of Uranium on Sediments

Sorption of uranium on sediment is a probable fate of the dissolved uranium from mine-dewatering effluent. The term sorption as used in this report includes ion exchange of charged uranium complexes with other ions on clays (Beard and others, 1980), adsorption on the surfaces of particles, and reactions with organic compounds that cause adsorption—ion exchange or uptake by plants (Landa, 1980). Uranium is strongly sorbed on organic compounds or clays (Ames and Rai, 1978). Uranium also can be sorbed on particles with amorphous iron-oxyhydroxide coatings, and the amount of adsorption is greatest between pH 5.5 and 8.5 (Langmuir, 1978; Hsi and Langmuir, 1985). At intermediate Eh and neutral-to-alkaline pH in the presence of phosphate or carbonate, however, the formation of uranyl phosphate or carbonate complexes

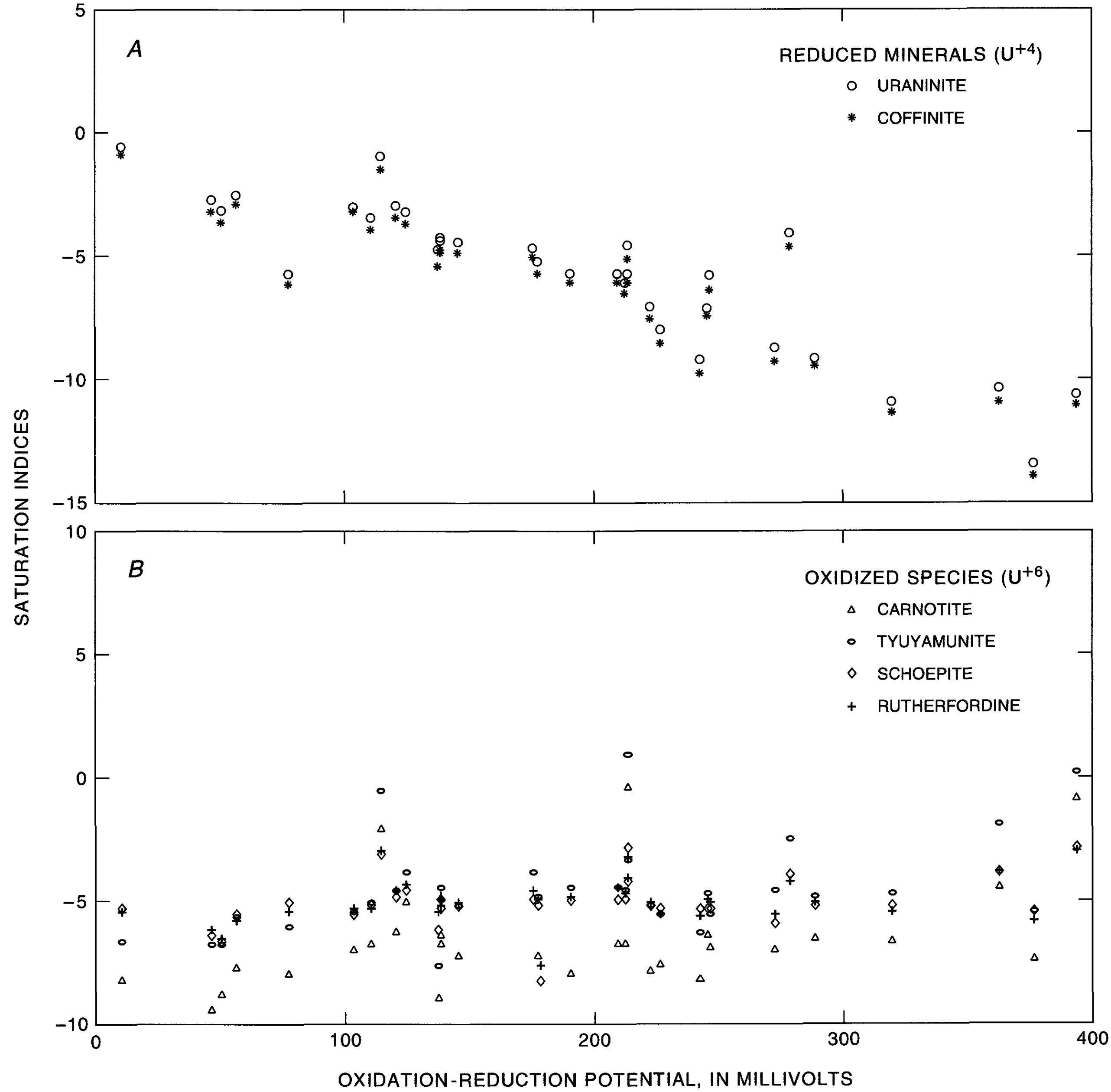


Figure 34. Comparison of oxidation-reduction potential measured in the alluvial aquifer with saturation indices of selected uranium minerals calculated by using PHREEQE geochemical model. *A*, Reduced minerals; *B*, Oxidized species (Parkhurst and others, 1980; Wanty and Goldhaber, 1992).

can severely inhibit adsorption (Langmuir, 1978; Hsi and Langmuir, 1985).

Forty-six sediment samples were collected for analysis of radionuclides to characterize the occurrence of radionuclides in the solid phase (Fisk and others, 1994). The most detailed sediment sampling was done at the Chambers well cluster where 25 samples were analyzed for gross alpha and gross beta activities. Two of those samples were collected in the streambed, and the other 23 samples were collected during drilling of monitor wells. Of those 25 samples, 11 also were analyzed for ^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra, ^{230}Th, ^{232}Th, and ^{210}Pb (Fisk and others, 1994).

Grain-size distribution and distance from the stream were determined for each sample from the Chambers well cluster. Spearman rank correlation coefficients were computed to compare the silt and clay fraction of each sample (percent of sample, by weight, passing through a screen with 0.062-mm openings) and distance from the stream to radionuclide activities (table 7). Positive correlation between trace-element concentrations and silt and clay content is an indication of sorption and usually results from the greater surface area and surface charge for fine-grained materials than for coarse-grained materials. Negative correlations between activities and distance from the stream indicate activities decrease with distance from the stream; however, most of those correlations are insignificant.

Twenty-one additional solid-phase samples near the streambed were collected and analyzed for selected radionuclides. These samples were collected several miles from the mouth of Pipeline Arroyo to the Cedar Point well cluster. Because of the strong correlation between radionuclides from the ^{238}U decay series and the percent of silt and clay determined for the samples from Chambers (table 7), these samples were wet sieved before analysis by using small amounts of distilled water. The fraction passing a 0.062-mm sieve, including the distilled water, was then oven dried and analyzed for selected radionuclides (Fisk and others, 1994).

Concentrations of uranium and thorium in fine-grained sediment have a large variance and do not show a strong relation to the presence of large uranium concentrations in ground water. The mass of a given radionuclide in a volume of typical saturated sediment from the basin, however, is much greater in the sediment than in the water of the adjacent pore space. Contaminated sediment samples, therefore, are difficult to distinguish from sediment samples with uranium from natural sources. For example, assuming a porosity of 0.4, a density of sediment of 2.65 g/cm^3, and a uranium concentration of 2.5 μg/g (the mean of these 21 samples), the sediment in contact with a liter of water would have a total mass of uranium of about 10,000 μg. If all the uranium in solution in a liter of ground water having a concentration of 1,000 μg/L (the mean concentration of uranium in treated mine effluent) were to sorb onto the sediment, the concentration would increase from 2.5 to 2.75 μg/g or 10 percent. That change is within the error of measurement for radionuclides in the solid phase and is probably well within natural variation. Sorption of all the uranium in several pore volumes of ground water with large uranium concentrations, therefore, is necessary to cause a measurable increase in the solid-phase concentration of uranium.

The activity ratio of uranium to thorium (U/Th) in the ^{238}U decay series was used to investigate uranium sorption on sediments. The ratio was calculated by averaging the concentrations of ^{238}U and ^{234}U and then dividing by the concentration of ^{230}Th. Over geologic

Table 7. Spearman rank correlations of solid-phase radionuclide concentrations to percent fines, horizontal distance from the stream, and vertical distance below the streambed, Puerco River Basin, Arizona and New Mexico

[Percent fines is percent of sample, by weight, that passes through a 0.062-millimeter sieve]

Constituent	Number of samples	Correlation coefficients: Percent fines	Correlation coefficients: Horizontal distance	Correlation coefficients: Vertical distance
Gross alpha	25	0.63	-0.24	0.02
Gross beta	25	.52	-.27	-.39
Uranium-238	11	[1].87	[2]-.45	-.18
Uranium-234	11	[1].66	-.29	-.31
Thorium-230	11	[1].65	-.10	-.09
Thorium-232	11	[2].57	.07	.17
Radium-226	11	[1].75	-.17	-.15
Radium-226	11	[2].54	.13	.35
Lead-210	11	.36	[2]-.49	-.27

[1] Relation is significant at a 95-percent confidence level.

[2] Relation is significant at an 80-percent confidence level.

time in a closed system, radionuclides in the same decay series will reach secular equilibrium (a ratio of 1.0). At secular equilibrium, all nuclides in the series will have the same activity; however, different radionuclides have different chemical and physical properties. For example, in oxidized water at near-normal pH, uranium is more mobile than thorium (Landa, 1980). If significant amounts of uranium have either been leached or have sorbed on sediment, the U/Th activity ratio will deviate from secular equilibrium. A hypothesis was proposed that near-channel sediments downstream from the mines would have U/Th activity ratios exceeding 1.0 and that sediments in areas not affected by mine-related releases of radionuclides would have U/Th activity ratios of about 1.0. Such a pattern was observed for samples from the Cedar Point well cluster (fig. 35). Only one of the nine samples from Cedar Point, however, contained significant excess uranium, and small-scale spatial variations may be large.

Further evidence for uranium sorption is provided by comparing U/Th ratios to total uranium concentrations (fig. 36). A significant positive correlation ($r = 0.89$; $n = 21$) indicates that larger concentrations of uranium correspond to samples with excess uranium relative to thorium. A more extensive sediment-sampling effort would be necessary to describe the spatial distribution of sediments containing excess uranium in the Puerco River Basin. These data, however, offer additional evidence that uranium sorption has occurred in the sediments and that sorption may be associated with near-channel sediments.

EFFECTS OF URANIUM-MINING RELEASES ON GROUND-WATER QUALITY

Determination of Sources of Uranium in Ground Water by Using Uranium-Isotope Activity Ratios

Uranium isotopes were used to distinguish sources of uranium derived from mining activities as opposed to uranium derived from natural sources in the Puerco River Basin. The ^{238}U decay series contains two isotopes of uranium—^{238}U and ^{234}U (fig. 5). Uranium-isotope activity ratios ($^{234}U/^{238}U$) are a useful conservative tracer in certain hydrologic systems and have been used to obtain information on sources of water, mixing characteristics, and circulation patterns (Osmond and Cowart, 1976; 1982). The minor mass difference between ^{238}U and ^{234}U precludes significant isotopic-fractionation effects during chemical reactions. The activity ratio of ground water, however, varies considerably because during the decay of ^{238}U to ^{234}U, the uranium atom recoils following the emission of an alpha particle. This phenomenon, known as alpha recoil, causes destruction to the mineral lattice and may position the ^{234}U in an unstable lattice configuration near the solid-liquid interface where it is more vulnerable to leaching (Osmond and Cowart, 1976; 1982).

In most unweathered rock, the $^{234}U/^{238}U$ activity ratio is close to secular equilibrium, which corresponds to a value of 1.0. The degree to which excess ^{234}U may build up in solution is a function of the original activity ratio of the water and the rock, the leach rate, and the length of time the water has been in contact with the rock (Barr and others, 1978). Uranium disequilibrium between liquid and solid phases increases with length of ground-water residence time under reducing conditions (Fröhlich and others, 1984). A significant degree of fractionation depends on a slow leach rate, a reduced environment, and for the ^{234}U daughter to stay in solution (Rich Wanty, geochemist, USGS, written commun., 1992). As the activity ratio in water becomes gradually enriched in ^{234}U, depletion of ^{238}U may not be significant in the host rock because the mass of uranium leached from the rock is small in proportion to the total uranium in the rock. The possibility of fractionation caused by geochemical processes exists but is considered unimportant (Chatham and others, 1981); therefore, once uranium is in solution and moves away from its source, the activity ratio is unaffected by dilution (as long as the dilution water contains no uranium of its own), precipitation, or changes in chemical state. Mixing with a second source of dissolved uranium would result in a value intermediate to the two end points.

Water samples from the Puerco River Basin were not collected before uranium mining (Wirt and others, 1991); therefore, background activities of uranium isotopes in the alluvial aquifer downstream from the mouth of Pipeline Arroyo are not known. In this study, several types of reference data were used to estimate uranium-isotope activity ratios of mine-dewatering effluent in the Church Rock mining district and to evaluate background conditions in the alluvial aquifer. Streamflow samples and samples from hand-driven wells were collected near a uranium mine that was discharging effluent near San Mateo, New Mexico, in

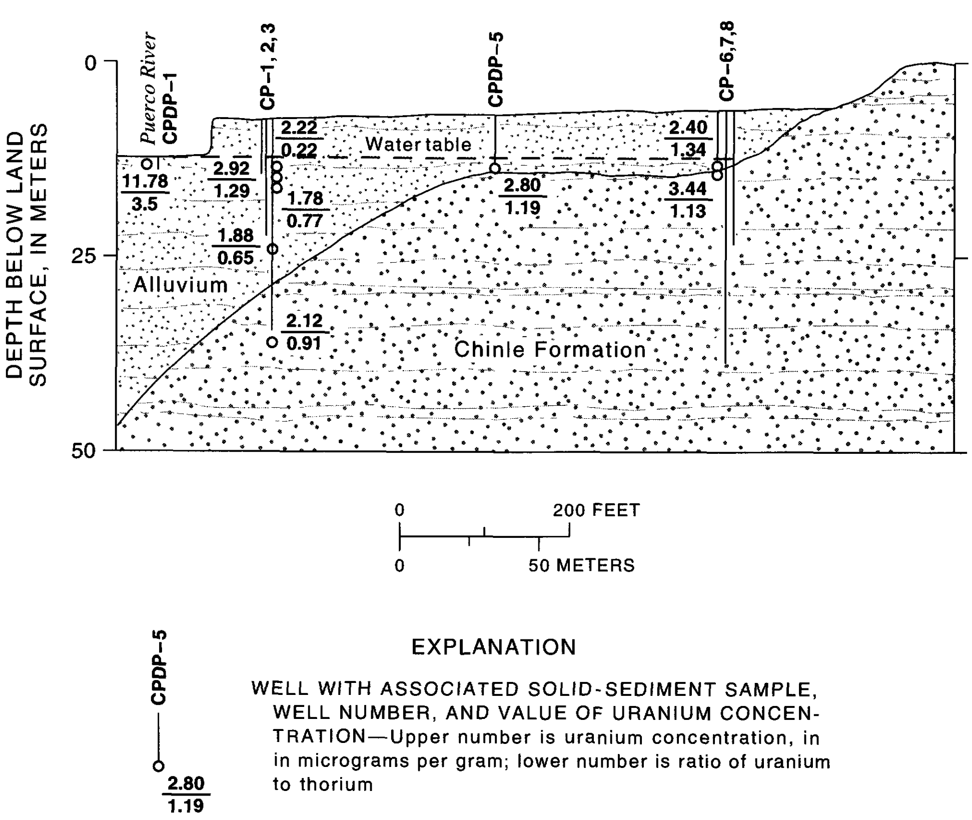


Figure 35. Comparison of ratios of uranium to thorium with uranium concentrations in sediment samples at the Cedar Point well cluster near Sanders, Arizona.

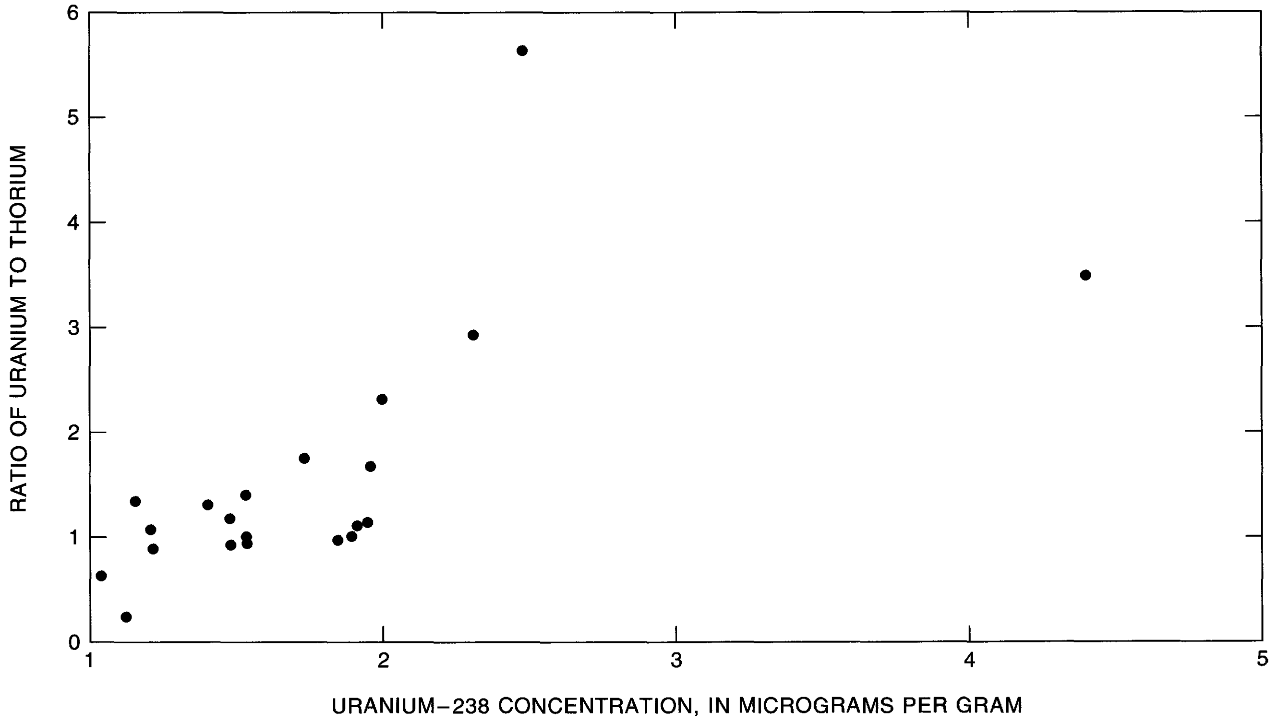


Figure 36. Comparison of ratios of uranium to thorium with uranium concentrations in sediment samples collected upstream from Pipeline Arroyo to Cedar Point well cluster.

order to sample an environment analogous to the Puerco River during mine dewatering. The San Mateo Mine is in the Grants Mineral Belt in the drainage of the nearby Rio Puerco (not the Puerco River that is the focus of this study). The Rio Puerco drains the east slope of the Continental Divide and is tributary to the Rio Grande (fig. 37). The Rio Puerco Basin is geologically and geographically similar to the Church Rock reach of the Puerco River. At the time of sampling in May 1990, the mine near San Mateo was pumping water from the Westwater Canyon Member of the Morrison Formation and discharging to Arroyo Chico, a tributary of the Rio Puerco. Additional samples were collected from runoff and from ground water upstream from the mouth of Pipeline Arroyo and from tributaries to the Puerco River that were unaffected by mining. Those samples were used to establish background uranium concentrations and background activity ratios in the basin.

Conceptual Model for Effects of Mining on Uranium-Isotope Activity Ratios

Before mining began, the uranium-isotope activity ratio of ground water in the Dakota and Morrison Formations surrounding the ore deposits was probably similar to that of ground water from other bedrock aquifers in the region. Activity ratios for samples from six bedrock wells measured in this study, believed to be unaffected by mining, ranged from 2.0 to 6.7, had a median activity ratio of 3.2, and a median dissolved-uranium concentration of 2.5 µg/L. On the basis of these results, the assumption was made that before mining began, ground water in the bedrock aquifer near the ore bodies had an activity ratio of 2.0 or greater

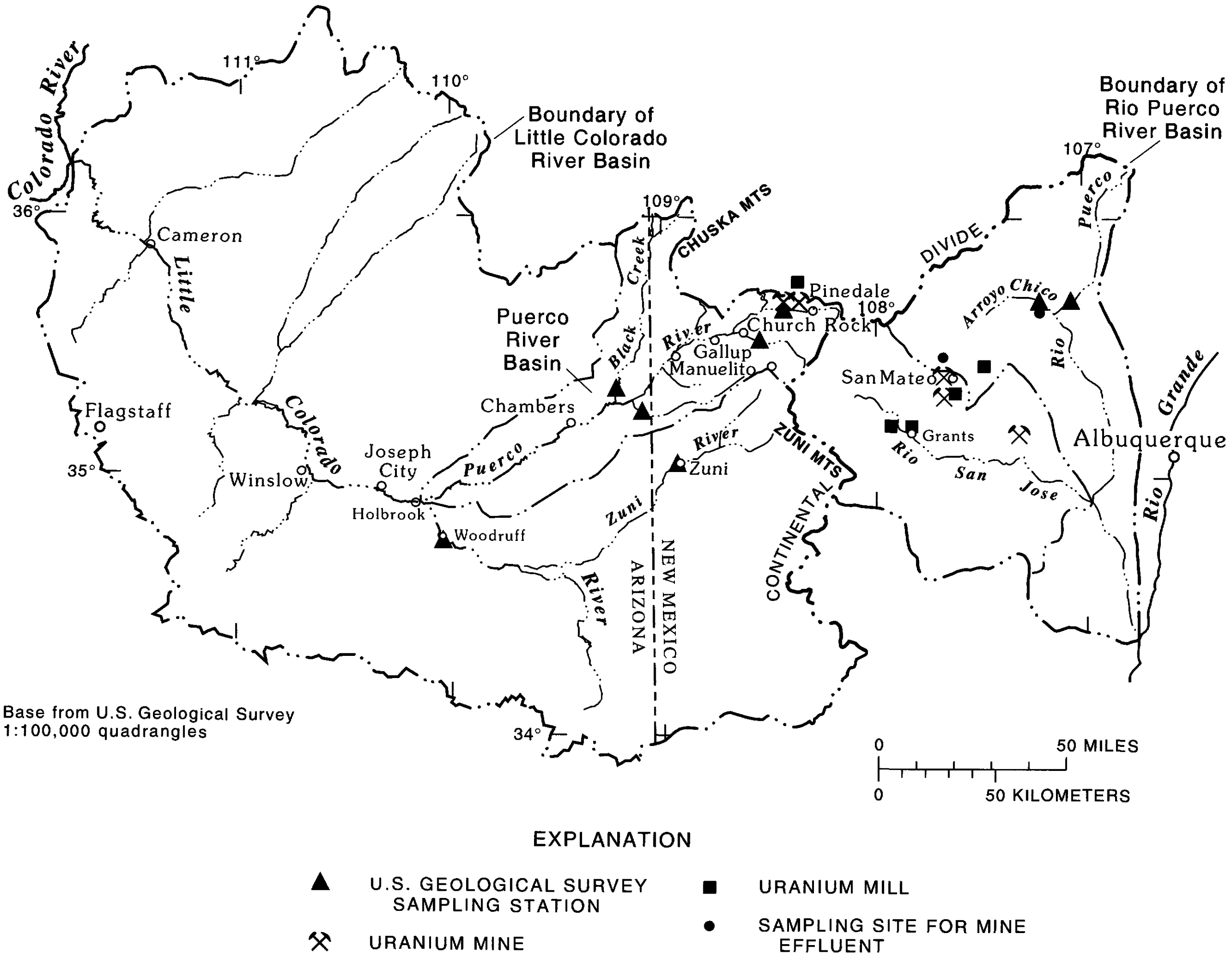


Figure 37. Location of uranium mines near San Mateo, New Mexico, and drainage of the Rio Puerco, New Mexico.

and generally had small concentrations of dissolved uranium. In contrast—as supported by multiple lines of evidence presented below in this section—mine effluent had an activity ratio of about 1.0. This hypothesis is reasonable in that highly evolved waters approaching chemical equilibrium are commonly enriched in ^{234}U because of preferential leaching from the host rock. Additionally, Chatham and others (1981) report that concentrations of dissolved uranium in reduced ground waters near uranium deposits rarely exceed 1 μg/L.

Mining processes changed the reducing environment surrounding the ore body by introducing oxygen to the subsurface through a network of mine shafts and tunnels as sediments were dewatered. Water levels declined 81 m between 1968 and 1978 in an abandoned mine shaft near Pipeline Arroyo (Hiss, 1977; Stone and others, 1983). The increase in oxygen caused uranium to dissolve to an average concentration of 7.0 mg/L in raw mine water (Gallaher and Cary, 1986), which is an increase of more than three orders of magnitude. The activity ratio of the newly dissolved uranium would have been essentially the same as in the host rock because the uranium would have dissolved rapidly without preference for ^{234}U over ^{238}U. This hypothesis is supported by Osmond and Cowart (1977) and Cowart and Osmond (1980). In a similar ground-water environment characterized by large concentrations of rapidly dissolving uranium, Osmond and Cowart (1977) and Cowart and Osmond (1980) predicted the activity ratio of dissolved uranium to be near 1.0. Treatment practices initiated in the late 1970's to remove radium and uranium from mining effluents would not have had a significant effect on the activity ratio.

As the mine-dewatering effluent was discharged to Pipeline Arroyo and travelled down the Puerco River channel, the dissolved uranium would have partitioned between the solid and liquid phases. Some uranium probably sorbed on the fine-grained silts and clays of the streambed, and some uranium infiltrated the shallow alluvial aquifer and mixed with naturally occurring uranium already in the aquifer. Because of the large volume of mine-dewatering effluent released from 1967 through 1986 (Van Metre and Gray, 1992), uranium in the streambed sediment and shallow ground water downstream from Pipeline Arroyo should have the activity ratio of the mine water. Although the concentration of dissolved uranium in the alluvial aquifer could have changed considerably due to dilution of mine effluent with native waters, isotopic fractionation of uranium due to alpha recoil would be insignificant over such a brief time. Ground water containing uranium from mine-dewatering effluent, therefore, should have a significantly smaller activity ratio than that of ground water with naturally occurring uranium.

Activities of uranium, radium, and gross alpha were measured frequently in mine effluent and streamflow in the Puerco River during the 1970's and 1980's; however, only one sample is known to have been analyzed for the dissolved isotopes of ^{234}U and ^{238}U during mine dewatering. That sample was collected from the Puerco River several kilometers below the mouth of Pipeline Arroyo on December 1, 1983, and had an activity ratio of 1.07 and a dissolved-uranium concentration of 1,330 μg/L (David Baker, NMED, written commun., 1989). That sample is perhaps the strongest evidence that mine-dewatering effluent from the Church Rock Mining District contained large concentrations of dissolved uranium with a uranium isotope-activity ratio near 1.0.

Spatial and Temporal Distribution of Uranium-Activity Ratios

Samples were collected to determine spatial and temporal variations in uranium concentrations and activity ratios in mine effluent, streamflow, and ground water. Sample sites fall into two categories—(1) sites along the Puerco River below Pipeline Arroyo that could have been affected by mining and (2) background sites. Background sampling sites in the Puerco and Little Colorado River Basins include Black Creek, South Fork of the Puerco River, North Fork of the Puerco River (above Pipeline Arroyo), Little Colorado River above Woodruff, and Zuni River (figs. 1, 37). The Rio Puerco above Arroyo Chico in the Rio Puerco Basin also was sampled (fig. 37; table 8).

Samples collected in May 1990 from an active uranium mine in a neighboring drainage provide additional evidence that mine effluent from the Church Rock mines had an activity ratio near 1.0. The activity ratios in two uranium-mine effluent samples collected from Arroyo Chico, which is in the Rio Puerco drainage below the mine-dewatering discharge point for the San Mateo mine, were 1.07 and 1.06. Concentrations of dissolved uranium for the two samples were 390 and 480 μg/L. The source of the water in Arroyo Chico was pumped ground water from the Mount Taylor mine, which mined the same geologic formation as the Church Rock mines. The activity ratios of the Arroyo

Chico samples are identical to activity ratios of the samples taken from the Puerco River in December 1983 (1.07). In contrast, a runoff sample collected from the Rio Puerco just upstream from the confluence with Arroyo Chico had an activity ratio of 1.65 and a concentration of dissolved uranium of 5.1 μg/L. A background hand-driven well at the same location had an activity ratio of 1.81 and a concentration of dissolved uranium of 13 μg/L.

Five background samples collected from hand-driven wells in the Puerco and Little Colorado River Basins (table 8) had a median uranium-isotope activity ratio of 1.55. The largest concentration of dissolved uranium for these five samples was 13 μg/L. The activity ratio for samples from 16 wells that may represent parts of the alluvial aquifer unaffected by mining ranged from 1.50 to 2.0 and had a median of 1.61. The maximum concentration of dissolved uranium for these alluvial wells was 14 μg/L. In general, uranium-isotope activity ratios of background water samples were significantly higher than mine effluent and generally had values of 1.5 or larger and concentrations of less than 13 μg/L of dissolved uranium.

Samples from streamflow, hand-driven wells, and near-stream alluvial wells that were collected downstream from Pipeline Arroyo in the Puerco River Basin had activity ratios that ranged from 1.0 to greater than 1.5. Samples that had activity ratios between 1.0 and 1.5 are assumed to have been affected by mining. Those samples that had activity ratios near 1.0 are assumed to have derived all or most of their uranium from mining sources, and those samples that had higher values were assumed to have derived their uranium from a combination of mining and natural sources. Samples that had activity ratios greater than 1.5 are assumed to have derived all of their uranium from natural sources. Fourteen streamflow samples from the Puerco and Little Colorado Rivers collected from 1988 until 1991 had activity ratios from 1.16 to 2.25 and had a median value of 1.4. This is similar to a range in activity ratios reported by Scott (1982) for major rivers of the world of from 1.1 to 2.0 with an average of about 1.2 to 1.3. All 14 samples had dissolved uranium concentrations less than 26 μg/L (table 8). Twenty-six samples were collected from hand-driven wells in the Puerco River streambed below the mouth of Pipeline Arroyo. The activity ratios for these samples ranged from 0.97 to 1.60, and the concentrations of dissolved uranium ranged from <1.0 to 650 μg/L. Uranium concentrations were inversely correlated with activity ratios for these samples (fig. 38) as shown by comparison of uranium concentrations and activity ratios under the Puerco River (figs. 26, 28, and 39). Wells CON–3 and WIN–3U are shallow wells near the stream in the Church Rock reach that are known to have been contaminated by mine-dewatering effluent (Gallaher and Cary, 1986). In 1989, activity ratios for these two wells were 1.1 and 1.2, respectively. Several other wells also had smaller activity-ratio values and larger concentrations of dissolved uranium. Well GAL–3 had a dissolved-uranium concentration of 39 μg/L and an activity ratio of 1.2. Well AD–3 had a mean activity ratio of 1.1 and a mean uranium concentration of 54 μg/L ($n = 3$). Data from monitor wells in the alluvial aquifer downstream from Gallup indicate that uranium from mine-dewatering sources occurs only in hand-driven wells and in a few shallow near-channel wells. This finding supports conclusions about the extent of infiltration and mixing from the stream and the long-term flow directions between the stream and aquifer in the Manuelito and Sanders reaches.

Wells in the alluvial aquifer in Arizona that had significant temporal variations in uranium-isotope activity ratios (notably, CW–3, AD–4, CP–4, QR–1, QR–2, and QR–3) are within about 30 m of the Puerco River and have received some recharge from anthropogenic sources as indicated by $\delta^{34}S$, $\delta^{18}O$, and δD analyses. Activity ratios for these wells ranged from 1.16 to 2.20. Significant temporal variations in activity ratios indicate nonsteady-state water-quality conditions and mixing of different sources of uranium in ground water near the stream. Many near-stream samples from the alluvial aquifer deviate significantly from background values and appear to contain uranium from mine effluent. Sixteen of 26 USGS and NMED cluster wells sampled repeatedly from 1988 to 1991 had no significant temporal variations in activity ratios, which indicate that mixing of uranium had reached steady-state conditions at most of the sites during this time period.

Relation Between Uranium-Mining Releases and Ground-Water Quality

Uranium-mine dewatering increased dissolved gross alpha, gross beta, uranium, and radium activities and concentrations of dissolved selenium and molybdenum in the Puerco River from 1967 until 1986 (Gallaher and Cary, 1986; Van Metre and Gray, 1992). Increased activities of radionuclides and concentrations of dissolved constituents extended as far downstream as Chambers (fig. 40). The occurrences

Table 8. Uranium-isotope data from mine-effluent samples, background samples, and samples collected downstream from Pipeline Arroyo for surface water and shallow ground water, Little Colorado River Basin, Puerco River Basin, and Rio Puerco Basin, Arizona and New Mexico

[pCi/L, picocuries per liter, µg/L, micrograms per liter; <, less than; ---, no data]

Sample site	Date	Uranium–234, dissolved (pCi/L)	Uranium–238, dissolved (pCi/L)	Natural uranium, dissolved (µg/L)[1]	Uranium–234/ Uranium–238
Mine effluent					
Arroyo Chico near San Mateo	05–01–90	150	140	390	1.07
Arroyo Chico near mouth	05–18–90	170	160	480	1.06
Puerco River[2]	12–01–83	470	440	1,300	1.07
Background surface water					
Rio Puerco	05–18–90	2.8	1.7	5.1	1.65
Little Colorado River above Woodruff	08–30–88	1.2	.9	2.7	1.33
Zuni River	09–06–91	.4	.3	1.0	1.33
Background hand-driven wells					
Rio Puerco DP	05–18–90	7.8	4.3	13	1.81
Black Creek DP	05–16–90	.85	.55	1.7	1.55
South Fork DP, Puerco River	11–02–90	2.2	1.7	5.1	1.29
North Fork DP, Puerco River	03–30–89	3.2	2.1	6.3	1.52
Do.	11–18–89	2.4	1.5	6.7	1.60
Background wells upstream from Pipeline Arroyo					
NF Well, Puerco River	11–18–89	5.7	3.6	11	1.58
BLM–1U[3]	01–10–89	4.4	2.8	8.4	1.57
Background wells in alluvial aquifer underlying the Puerco River					
Paulsell Ranch well, Petrified Forest	07–14–89	4.1	2.6	7.8	1.58
Petrified Forest well No. 2	01–20–89	.20	.10	<.3	2.00
CW–2	12–09–88	3.5	2.2	6.6	1.59
Do.	12–09–88	4.0	2.4	6.7	1.67
Do.	11–16–89	[4].90	[4].20	<1.0	-----
Do.	05–02–90	4.1	2.7	7.6	1.52
Do.	05–02–90	7.3	4.0	15	1.83
CW–7	12–06–88	3.7	2.3	7.2	1.61
Do.	11–14–89	3.7	2.1	2.2	1.61
Do.	11–01–90	3.6	2.4	6.6	1.50
CW–8	12–06–88	4.1	2.5	7.3	1.64
Do.	11–14–89	3.7	2.3	3.3	1.61
Do.	10–18–90	3.9	2.6	6.7	1.50
AD–1	11–14–89	7.7	5.0	6.2	1.54
Do.	05–01–90	5.8	3.3	8.9	1.76
Do.	10–13–90	4.3	2.6	7.2	1.65
AD–5	07–13–89	4.1	2.7	8.1	1.52
Do.	11–13–89	4.0	2.5	7.0	1.60
Do.	05–04–90	4.0	2.4	7.0	1.67
Do.	10–19–90	4.3	2.8	8.3	1.54

See footnotes at end of table.

Table 8. Uranium-isotope data from mine-effluent samples, background samples, and samples collected downstream from Pipeline Arroyo for surface water and shallow ground water, Little Colorado River Basin, Puerco River Basin, and Rio Puerco Basin, Arizona and New Mexico—Continued

Sample site	Date	Uranium–234, dissolved (pCi/L)	Uranium–238, dissolved (pCi/L)	Natural uranium, dissolved (μg/L)[1]	Uranium–234/ Uranium–238
Background wells in alluvial aquifer underlying the Puerco River—Continued					
Sanders School well	08–10–88	6.5	4.3	13	1.51
Do.	08–10–88	6.3	4.4	13	1.43
Do.	01–20–89	6.4	4.5	**14**	1.42
Do.	05–09–90	6.3	4.2	9.2	1.50
ADOT inspection well	05–09–90	5.1	3.0	6.1	1.70
CP–1	09–21–89	0.20	<0.10	**<.3**	-----
Do.	05–03–90	.20	.10	<1.0	2.00
Do.	10–12–90	.10	<.10	<1.0	-----
CP–2	09–21–89	2.6	1.4	**4.2**	1.86
Do.	05–03–90	2.5	1.6	6.9	1.56
Do.	10–12–90	3.2	1.9	6.0	1.68
CP–3	09–21–89	3.2	2.1	**6.3**	1.52
Do.	10–17–90	2.9	1.8	5.2	1.61
CP–5	09–20–89	3.3	1.9	**5.7**	1.74
Do.	05–07–90	3.3	2.1	4.2	1.57
Do.	10–17–90	3.5	2.2	6.1	1.59
CP–6	09–20–89	3.6	2.1	**6.3**	1.71
Do.	10–12–90	3.0	1.8	5.7	1.67
MAN–2	06–06–90	7.3	4.5	8.8	1.62
Do.	10–10–90	7.5	4.5	13	1.67
MAN–3	06–06–90	6.4	3.7	<1.0	1.73
Do.	10–11–90	6.1	3.6	9.4	1.69
Streamflow downstream from Pipeline Arroyo					
Puerco River near Church Rock	08–15–90	1.2	1.0	3.1	1.20
Puerco River near Manuelito	04–05–89	2.1	1.5	**4.5**	1.40
Do.	08–14–90	1.5	.90	1.9	1.66
Do.	08–15–90	1.0	.80	2.2	1.25
Puerco River near Chambers	08–10–88	7.1	5.4	**16**	1.31
Do.	07–11–90	9.3	6.8	13	1.37
Little Colorado River near Joseph City	08–02–88	10	8.6	**26**	1.16
Little Colorado River near Grand Falls	03–05–91	2.5	1.7	**5.1**	1.47
Do.	03–05–91	2.3	1.5	**4.5**	1.53
Little Colorado River near Cameron	08–04–88	.8	.50	**1.5**	1.60
Do.	03–07–91	2.1	1.5	**4.5**	1.40
HBSW–1, Holbrook	05–15–90	1.8	.80	<1.0	2.25
Puerco River at Sanders	03–09–90	6.5	4.2	**13**	1.55
Puerco River near Lupton at Route 66 bridge	03–08–90	3.7	2.3	**6.9**	1.61
Hand-driven wells downstream from Pipeline Arroyo					
Holbrook DP	05–14–90	.40	.30	<1.0	1.33
Navajo DP	06–12–91	6.8	5.3	9.5	1.28

See footnotes at end of table.

Table 8. Uranium-isotope data from mine-effluent samples, background samples, and samples collected downstream from Pipeline Arroyo for surface water and shallow ground water, Little Colorado River Basin, Puerco River Basin, and Rio Puerco Basin, Arizona and New Mexico—Continued

Sample site	Date	Uranium–234, dissolved (pCi/L)	Uranium–238, dissolved (pCi/L)	Natural uranium, dissolved (μg/L)[1]	Uranium–234/ Uranium–238
Hand-driven wells downstream from Pipeline Arroyo—Continued					
CDP–1	08–11–88	6.8	6.3	19	1.08
Do.	12–07–88	7.1	7.3	19	.97
Do.	11–16–89	6.8	5.2	7.2	1.31
Do.	10–17–90	12	11	20	1.09
CDP–2	11–16–89	6.7	6.6	11	1.02
ADDP–1	05–15–90	32	29	68	1.10
CPDP–1	11–17–89	10	8.9	18	1.12
Do.	10–16–90	19	14	36	1.36
CPDP–1	11–17–89	10	8.9	18	1.12
Do.	10–16–90	19	14	36	1.36
CPDP–2	05–16–90	8.7	7.7	20	1.13
QRDP	05–16–90	.90	.60	1.3	1.50
Do.	05–16–90	.80	.50	1.6	1.60
LPDP–1	11–17–89	9.4	7.7	11	1.22
Do.	10–16–90	2.7	1.9	7.8	1.42
Do.	06–11–91	7.8	6.1	7.6	1.27
MANDP–1	04–05–89	51	43	**130**	1.19
Do.	10–16–90	.60	.50	2.3	1.20
Do.	06–11–91	5.9	4.4	10	1.34
BRIDGE–83DP	10–16–90	5.6	4.3	11	1.30
Do.	06–11–91	18	15	44	1.20
GALDP–1	05–17–90	52	50	140	1.04
Do.	10–15–90	46	41	140	1.12
CONDP–1	03–30–89	220	220	**650**	1.00
Do.	10–18–90	95	96	220	.99
Do.	06–10–91	45	42	130	1.07
Wells in alluvial aquifer downstream from Pipeline Arroyo					
CON–3	01–11–89	320	290	**900**	1.10
WIN–3U	01–11–89	67	54	**160**	1.24
Do.	10–24–90	49	39	120	1.25
GAL–3	01–12–89	15	13	**39**	1.15
Do.	10–24–90	15	12	27	1.25
AD–3	07–13–89	16	16	**48**	1.00
Do.	07–13–89	11	8.9	**28**	1.23
Do.	09–22–89	17	16	**48**	1.06
Do.	05–01–90	22	20	49	1.10
Do.	10–19–90	20	18	47	1.11

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[1] Bold type indicates that natural uranium values were calculated from isotopic activities of uranium–234 and uranium–238.

[2] Sample collected by New Mexico Environmental Improvement Division (Dave Baker, environmental engineer, written commun., 1989).

[3] Bureau of Land Management well at Lupton, Arizona.

[4] Analytical error suspected because of low-level uranium–234 and uranium–238.

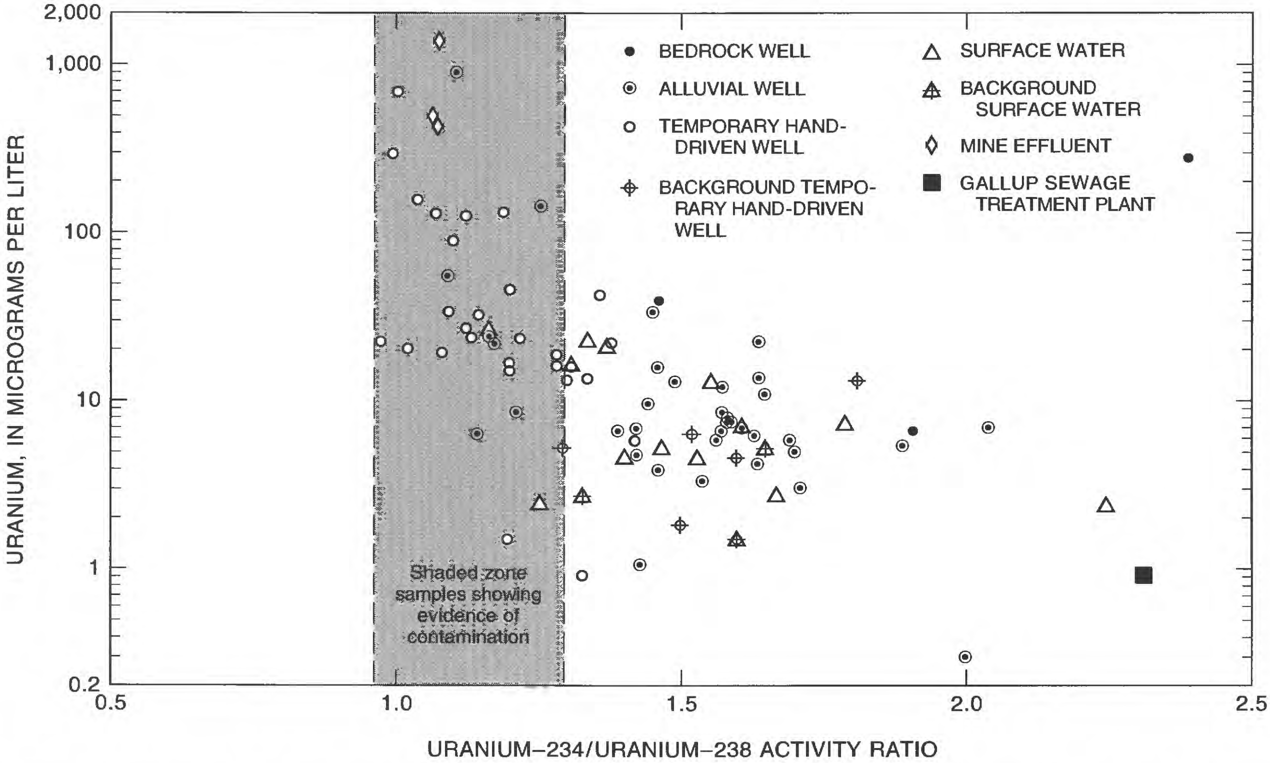


Figure 38. Concentrations of uranium in relation to uranium activity ratios in surface-water and ground-water samples, Puerco River Basin, Arizona and New Mexico.

of dissolved uranium, dissolved gross alpha, and dissolved gross beta activities in hand-driven wells in 1989 correlate with the occurrence of increased activities in streamflow during mining (figs. 26, 29, and 40). In 1989, a significant correlation (Spearman rank correlation coefficient, $r = 0.76$; $n = 6$) existed between the dissolved gross alpha activity in samples from hand-driven wells and the average dissolved gross alpha activity in the Puerco River during mining at corresponding locations. Samples from the alluvial aquifer in this study did not have increased activities or concentrations of radium, thorium, molybdenum, or selenium that could be attributed to mine dewatering or the tailings-pond spill.

The total mass of uranium and activity of gross alpha released to the Puerco River by mine dewatering were estimated to be 560 metric tons and 260 curies, respectively. In comparison, the tailings-pond spill on July 16, 1979, released an estimated 1.5 metric tons of uranium and 46 curies of gross alpha activity (Van Metre and Gray, 1992). Van Metre and Gray (1992) calculated the expected average concentration of dissolved uranium in ground water in the alluvial aquifer resulting from infiltration of mine effluent to be 330 μg/L, on the basis of the assumption that uranium was not removed by precipitation or sorption. Comparison of the calculated concentration with measured data indicates that only a small part of the total amount of dissolved uranium released by mining was in solution in ground water in 1989 (fig. 26) and strongly suggests that the uranium may now be in the solid phase. Geochemical modeling of uranium-mineral saturation indicates that precipitation of uranium minerals from solution is unlikely. The most likely mechanism for the removal of uranium from solution, therefore, is sorption of uranium on sediments. Evidence for sorption is provided by analyses of enriched U/Th ratios in sediment samples from the Cedar Point well cluster and by correlations between concentrations of ^{238}U in sediment, grain size, and distance from the stream at the Chambers well cluster.

Uranium concentrations decreased from 1989 to 1991 in water from hand-driven wells and wells that had the largest measured uranium concentrations in 1989. For example, CONDP–1 had concentrations of dissolved uranium of 660 μg/L on March 3, 1989 (calculated by conversion of ^{238}U activity to equivalent concentration), 220 μg/L on October 18, 1990, and 130 μg/L on June 10, 1991. Concentrations of dissolved uranium at MANDP–1 decreased from 130

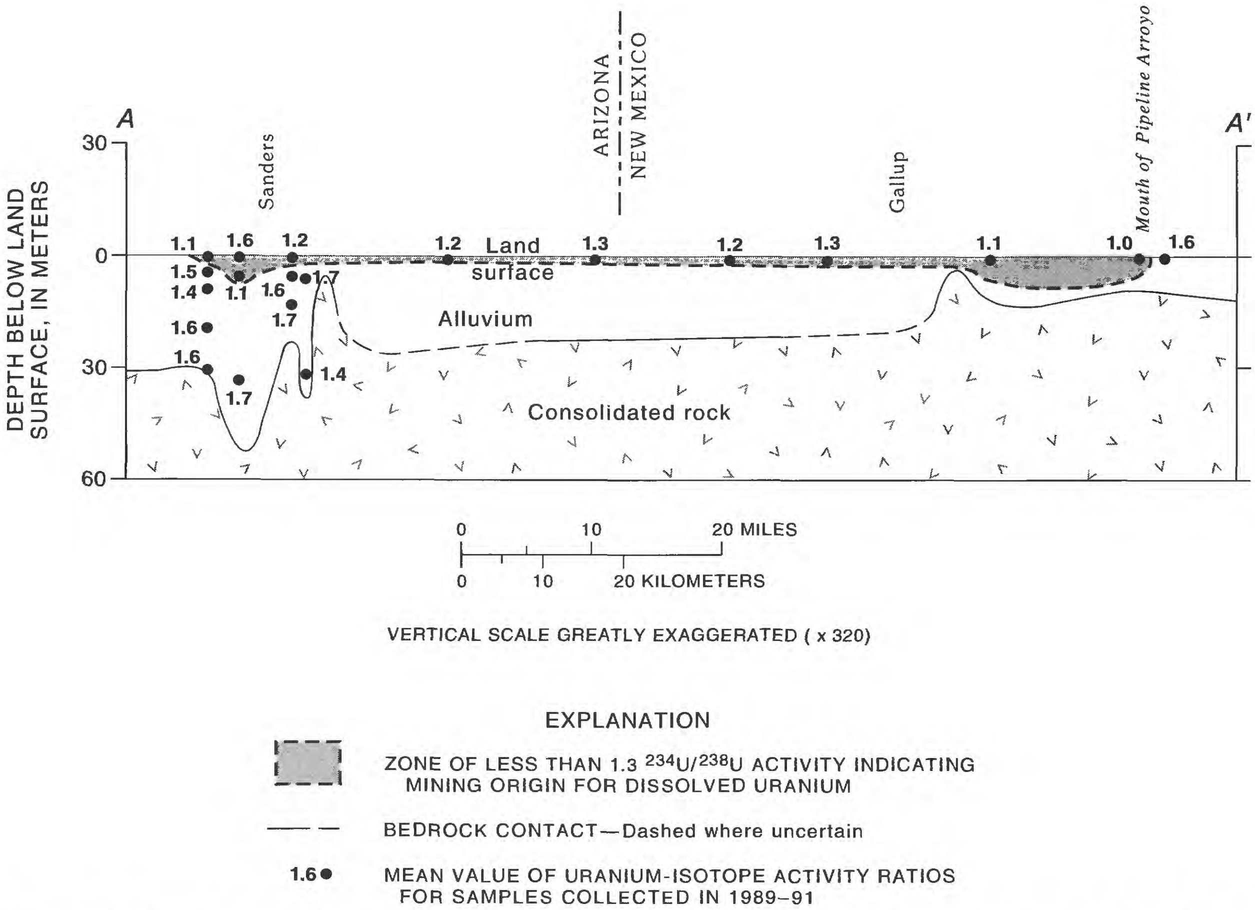
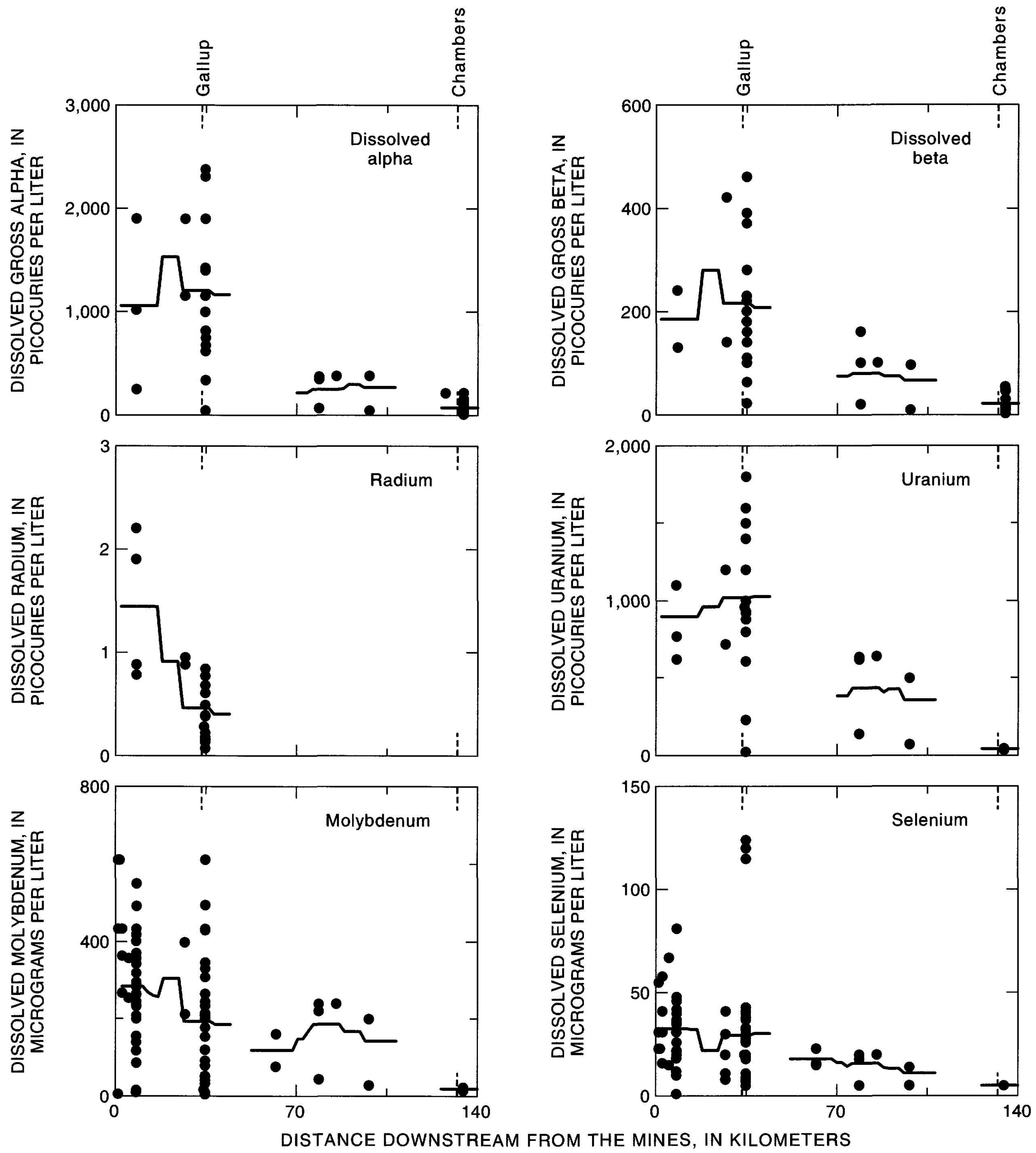


Figure 39. Concentrations of uranium and uranium–234 to uranium–238 activity ratios under the Puerco River, 1989–91.

μg/L on April 5, 1989 (calculated by conversion of ^{238}U activity to equivalent concentration), to 10 μg/L on June 11, 1991. Those decreases could have been caused by removal of uranium from solution by sorption. Therefore, improvements in water quality may be coming at the expense of sediment quality. If water-quality conditions remain fairly constant, uranium on sediment will probably remain immobile. It is possible, however, that an unforeseen change in water quality to a condition that favors uranium mobility could cause leaching of uranium and the subsequent degradation of water quality.

Variations in concentrations of uranium and gross alpha and gross beta activities in ground water are related to flow relations between the stream and aquifer described for each of the three reaches of the stream. The Church Rock reach (fig. 10), where large amounts of mine effluent infiltrated, had the largest uranium concentrations and gross alpha and gross beta activities measured in the alluvial aquifer. Uranium-isotope activity ratios identify the source of those large uranium concentrations as mine-dewatering effluent.

In the Manuelito reach (fig. 10), ground-water flow is toward the stream with negligible deep infiltration from the perennial flow of treated wastewater. Radionuclide activities in wells were small (13 μg/L or less dissolved uranium) and uranium-isotope activity ratios indicate the uranium is not from mine-related sources. Hand-driven wells, MANDP–1 and BR83DP–1, sampled in 1989, however, had 120 and 170 pCi/L of dissolved gross alpha, respectively. The uranium concentration in the MANDP–1 sample was 130 μg/L, and the activity ratio was 1.2. These values indicate that the source of the uranium was mine effluent. Uranium was not measured at BR83DP–1 in 1989. The two hand-driven wells were sampled again in 1990 and 1991. In 1990 and 1991, dissolved gross alpha activities decreased to 15 and 29 pCi/L at BR83DP–1 and to 2.3 and 11 pCi/L at MANDP–1. The decrease in gross alpha activity indicates removal of dissolved uranium by sorption or transport by streamflow.



EXPLANATION

—— MOVING AVERAGE FOR SAMPLES COLLECTED FROM 1975 UNTIL 1984—Calculated as a mean of all data collected within 20-kilometer reaches, centered on successive 5-kilometer intervals

Figure 40. Activities and concentrations of selected constituents in streamflow in the Puerco River and distance downstream from the mines, 1975–84.

In the Sanders reach, infiltration of Gallup STP wastewater and possibly mine-dewatering effluent is indicated by ratios of stable isotopes. Infiltration of uranium from mine-dewatering effluent is indicated by analyses of uranium-activity ratios in samples from hand-driven wells and a few shallow wells. Concentrations of uranium and the depth to which uranium from mine dewatering has penetrated the alluvial aquifer also appear to be affected by the flow system and by removal of uranium by sorption. Larger concentrations of uranium were measured at the ADOT well cluster than at other wells and hand-driven wells in the Sanders reach. One well and one hand-driven well at ADOT had large uranium concentrations (greater than 35 μg/L) and small uranium activity ratios. These concentrations and ratios indicate the source of uranium is mine-dewatering effluent. The ADOT well cluster is the only cluster in the Sanders reach where consistent downward gradients in water levels were measured in near-channel wells.

Large radionuclide activities (in excess of MCL's) in wells completed in the Chinle Formation are not associated with mining-related sources or the Puerco River. Three independent pieces of information support that conclusion. First, tritium activities in wells completed in the Chinle Formation in the Sanders area are less than 3 pCi/L and indicate that the water was recharged prior to 1952 before uranium mining began in the Puerco River Basin. Second, uranium-isotope activity ratios in ground-water samples indicate that in the Sanders area, mine-released uranium is confined to a zone a few meters or less below and a few tens of meters laterally from the stream channel and is not found in the Chinle wells. Third, the radium activity from well INDIAN RUINS and the gross alpha and gross beta activities from well ADOT YARD (Fisk and others, 1994) were higher than activities measured in all alluvial aquifer samples from the Sanders reach and were higher than activities measured in streamflow in Arizona during mining (fig. 40).

SUMMARY

The Puerco River of Arizona and New Mexico is an ephemeral stream that received effluent from mine-dewatering operations from 1960 until 1961 and from 1967 until mining ceased in February 1986. Dissolved gross alpha, gross beta, uranium, and radium activities and dissolved molybdenum and selenium concentrations were elevated in streamflow as far as 140 km downstream from the mines. Mine dewatering released an estimated 560 metric tons of uranium and 260 curies of gross alpha activity to the river. Additionally, in 1979, a tailings-pond dike failed, releasing an estimated 1.5 metric tons of uranium and 46 curies of gross alpha activity to the Puerco River.

The distribution of uranium in ground water in the alluvial aquifer downstream from the mines is related to flow relations between the stream and alluvial aquifer. Flow relations between the stream and aquifer were evaluated for three hydrologically distinct reaches of the Puerco River by using historical records of streamflow and mine-dewatering discharges; variations in water levels; a numerical ground-water flow model; and differences in isotopes of oxygen, hydrogen, tritium, and sulfur; and proportions of major ions. In the reach of the Puerco River from the mines to near Gallup, New Mexico, flow during mine dewatering was from the stream downward into the alluvium. The largest concentrations of uranium in the alluvial aquifer are found downstream from the mines in this reach. Downward flow was partly caused by mine-dewatering pumpage and associated drawdown in bedrock aquifers underlying the alluvial aquifer. In the reach from Gallup to near Lupton, Arizona, flow was predominantly toward the stream as indicated by upward water-level gradients and by isotopes of oxygen, hydrogen, and sulfur. Upward flow in the alluvial aquifer is caused by upward leakage from underlying bedrock aquifers. Uranium concentrations in wells in this reach were small. In the reach from about 8 km upstream from Sanders, Arizona, to about 4 km downstream from Chambers, Arizona, vertical water-level gradients in near-channel wells were small, and flow was toward the stream at certain times, and away from the stream at other times. Larger uranium concentrations occurred below the streambed at sites with downward gradients in the alluvial aquifer near the stream than at sites with no vertical or upward gradients. Water levels were controlled by the elevation of the streambed and by seasonal variations in evapotranspiration. The interpretation of flow at one location was supported by the development of and simulations from a two-dimensional ground-water flow model.

Measurement of ground water from 69 ground-water sampling points in the Puerco River Basin from 1988–91 supports the following conclusions:

- Because water levels in the alluvial aquifer are typically shallow—within about 0.6 m of the elevation of the lowest part of the streambed—

near-stream ground water potentially can be affected by contaminants in streamflow.

- Except for several samples collected within several meters of the streambed, ground-water samples collected from the alluvial aquifer downstream from Gallup, New Mexico, meet the MCL's of the USEPA for gross alpha and radium–226 plus radium–228, and the proposed MCL for uranium. Alluvial ground water, however, commonly exceeds SMCL's of the USEPA for dissolved solids, iron, and manganese, which are constituents that are unrelated to mining releases.
- Concentrations of dissolved uranium and $^{234}U/^{238}U$ activity ratios in shallow alluvial wells as far downstream as Chambers indicate some residual contaminated water was still present in October 1990. Data indicate it is unlikely that radionuclides released to the Puerco River by mining could infiltrate to bedrock aquifers in the New Lands area.
- In 1990–91, shallow ground-water samples collected beneath the streambed had smaller concentrations of dissolved uranium than in 1989.
- In parts of the alluvial aquifer unaffected by mining, ground water contains less than 13 µg/L of dissolved uranium.
- Natural sources of recharge include (1) direct infiltration of precipitation and runoff and (2) interformational flow from the underlying bedrock aquifer. Anthropogenic sources include (1) discharge of sewage effluent and (2) historical releases of mining effluent. Discharge from the alluvial aquifer is predominantly by ET and to streams.
- Extent and concentration of uranium is related to (1) concentration of uranium in the Puerco River during mining, (2) variation in mixing between native ground water and recharge from streamflow, and (3) removal of uranium in solution by sorption on sediments.
- Estimated total volume of uranium released by mining activities was not found at predicted levels in 1989–91. As indicated by the results of sample analyses from the alluvial aquifer, sorption on sediment is a probable fate of the missing uranium.
- Radionuclide concentrations and uranium-series isotope ratios on sediment suggest that concentrations of radionuclides on sediment near the channel are larger than on sediment away from the channel. Improvements in water quality, therefore, may be at the expense of sediment quality.

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