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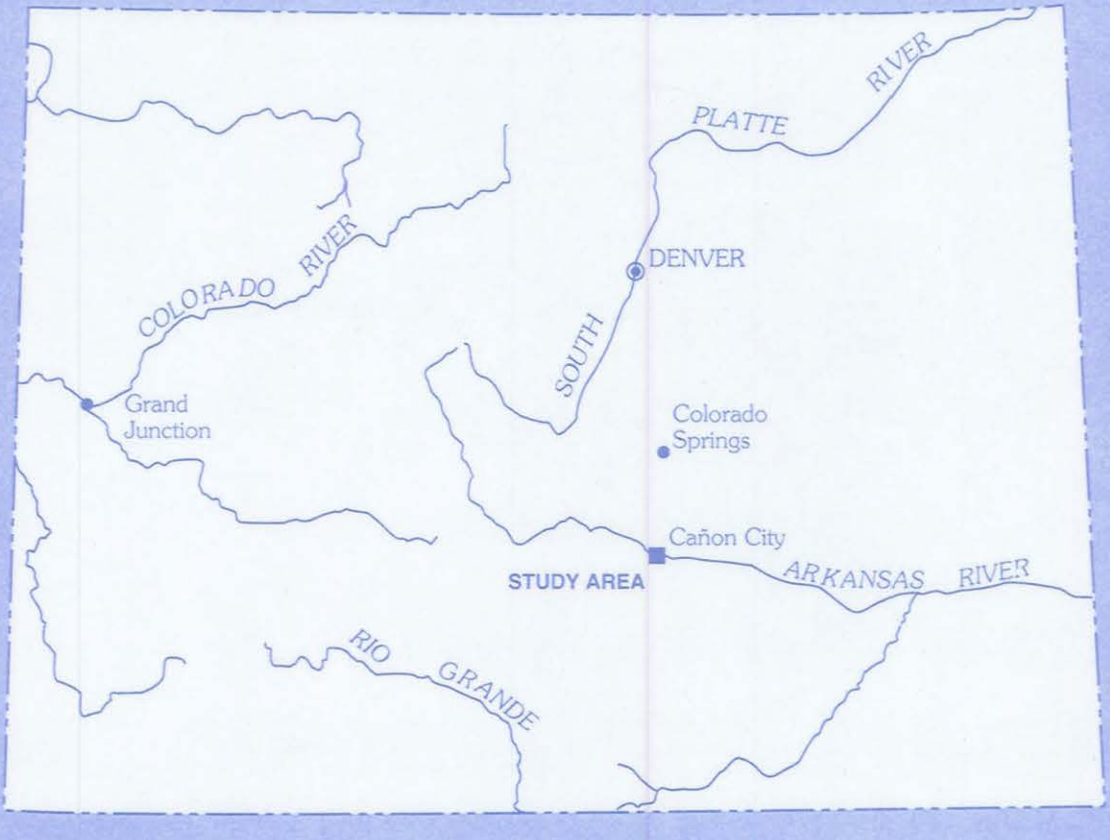
MIGRATION AND GEOCHEMICAL EVOLUTION OF GROUND WATER AFFECTED BY URANIUM-MILL EFFLUENT NEAR CAÑON CITY, COLORADO

U.S. GEOLOGICAL SURVEY



Water-Resources Investigations Report 98–4228

Prepared in cooperation with the
COLORADO DEPARTMENT OF PUBLIC HEALTH AND ENVIRONMENT

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Denver, Colorado
1999

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
foot (ft)	0.3048	meter
inch (in.)	2.54	centimeter
mile (mi)	1.609	kilometer
square foot	0.0929	square meter
square mile (mi^2)	2.589	square kilometer
foot per day (ft/d)	0.0003528	centimeter per second
foot per mile (ft/mi)	0.4904	meter per kilometer
gallon per minute (gal/min)	5,450	liter per day

Temperature in degree Celsius (°C) may be converted to degree Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32$$

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.

Other abbreviations, terms, and symbols used in this report:

gram per day (g/d)

microgram per liter (µg/L)

micrometer (µm)

milliequivalent per liter (meq/L)

milliequivalent per 100 grams (meq/100g)

milligram per kilogram (mg/kg)

milligram per liter (mg/L)

millimole per liter (mmol/L)

Migration and Geochemical Evolution of Ground Water Affected by Uranium-Mill Effluent Near Cañon City, Colorado

By Daniel T. Chafin *and* Edward R. Banta

ABSTRACT

A uranium-ore processing mill began operating about 2 miles south of Cañon City, Colorado, in 1958 and remained active until January 1986. This report presents information on migration pathways of ground water affected by mill activities and on geochemical processes that affect the quality of this ground water, especially with respect to dissolved uranium and dissolved molybdenum.

Both deep and near-surface pathways were evaluated. Analysis of water-level and chemical data indicates that neither of the two hypothesized deep pathways nor a near-surface pathway northeast of the mill are likely to exist. The primary near-surface pathway is from the vicinity of the old unlined mill-tailings ponds, along Sand Creek drainage and into Lincoln Park, an unincorporated neighborhood that is immediately south of Cañon City and between the mill and the Arkansas River. The near-surface pathway is in alluvium and in fractured bedrock immediately underlying the alluvium, probably extending no deeper than 100 feet. A much smaller quantity of water probably has migrated from the vicinity of the mill northward into a small, unnamed drainage west of Sand Creek and through a gap in the Raton ridge.

Remediation activities at the uranium-mill site, which began in 1979, have substantially decreased concentrations of dissolved uranium and dissolved molybdenum in ground water downgradient from the mill. For example, at well 138 in Lincoln Park, dissolved-uranium concentrations decreased from 3,570 micrograms per liter in 1979 to less than 600 micrograms per liter in 1994.

Ground-water flow along the primary pathway through the gap formed by Sand Creek in the ridge between the uranium mill and Lincoln Park was estimated to be 1,900 to 12,000 liters per day. Uranium flux was estimated as 8.3 to 52 grams per day, and molybdenum flux was estimated as 48 to 300 grams per day.

Mass-balance chemical-reaction modeling indicates that dilution is a major process affecting downgradient evolution of water along the primary pathway. Near the uranium mill, most dilution is accomplished by ground-water flow into the structural basin where the mill is located, injection of municipal water at an injection-withdrawal system downgradient from the old tailings ponds, and infiltration of streamflow along the channel of Sand Creek. Near Lincoln Park, water from a leaky irrigation ditch causes additional dilution of mill contaminants.

The modeling also indicates that cation exchange is much greater near the uranium mill than near Lincoln Park. Most of the pathway had exchange of calcium (and sometimes magnesium and potassium) for sodium. Uranyl (UO_2^{++}) ions generally are sorbed, except in alluvium in Lincoln Park where these ions are desorbed (flushed) by calcium-rich water that is injected and that infiltrates from the DeWeese Dye Ditch and associated irrigation. Powellite ($CaMoO_4$) generally is dissolved where recharge of precipitation or injected municipal water occurs.

Powellite probably is dissolved in the unsaturated zone by fresh recharge water and is precipitated in the saturated zone. Powellite also is flushed (dissolved) where uranyl ions are desorbed by freshwater that is injected and that infiltrates from irrigation. Dissolved molybdenum generally is more mobile than dissolved uranium in the study area. As a result, the ratio of dissolved molybdenum to dissolved uranium generally increases in the downgradient direction from the mill to the DeWeese Dye Ditch.

INTRODUCTION

A uranium-ore processing mill owned by the Cotter Corporation began operating at a site 2 mi south of Cañon City, Colorado, in 1958. Production increased to a peak in 1981 and, thereafter, declined until the mill was put on standby status in January 1986. The mill remained inactive through 1996 (Preston Niesen, Cotter Corporation, written commun., 1997). From 1958 through 1979, mill wastes were discharged to a series of unlined tailings ponds adjacent to the mill. By 1968, ground water from some wells in Lincoln Park, an unincorporated suburban and semirural area that is immediately south of Cañon City and between the mill and the Arkansas River, was affected by contaminants apparently originating from the old tailings ponds; dissolved uranium and dissolved molybdenum were identified as two constituents of particular concern (W.A. Wahler and Associates, 1978a). In 1983, the Colorado Department of Public Health and Environment (CDPHE), which licenses the mill, filed a claim against Cotter Corporation under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). In 1984, Lincoln Park was placed on the National Priorities List (U.S. Environmental Protection Agency, 1984) required by CERCLA.

In 1994, the CDPHE entered into a cooperative agreement with the U.S. Geological Survey (USGS) to evaluate areas affected by the uranium mill. The purposes of the study were (1) to characterize the ground-water hydrology and geochemistry of the uranium mill and the immediate surrounding area, including Lincoln Park; and (2) to compare the likely effects of proposed remediation strategies.

Purpose and Scope

This report discusses the migration pathways of ground water directly or indirectly contaminated by liquid and solid wastes from uranium-mill processing and processes that affect the geochemical evolution of this ground water, especially with respect to the concentrations of dissolved uranium and dissolved molybdenum. In this report, the term "raffinate" refers to liquid wastes discharged directly from the uranium mill and to leachate derived from mill tailings. The interpretations are based on historical water-quality data collected by Cotter Corporation from 1968 through 1994 and on data collected in 1995 and 1996 by the USGS. Data collected by the USGS include chlorofluorocarbon concentrations in 7 selected ground-water samples for interpretation of recharge dates; 13 sets of stable-isotope ratios for selected ground-water (11), surface-water (1), and municipal-water (1) samples; and various solid-phase analyses for selected well cuttings. Historical water-quality data collected by the Cotter Corporation and water-quality (except for the chlorofluorocarbon-age dates) and solid-phase data analyzed by the USGS for this study are reported in Banta (1997). Water-quality data collected by the USGS for this study also are presented in this report.

Site Description

The uranium mill is located about 2 mi south of Cañon City in south-central Colorado (fig. 1). The climate of the Cañon City area is semiarid; average annual precipitation is 12.7 in., about one-third of which occurs as snow and about two-thirds as rain (W.A. Wahler and Associates, 1978a, p. II-1).

The uranium mill (elevation 5,600 ft) is located in a small structural basin bounded by a hogback-shaped ridge immediately to the south and a lower ridge situated between the mill and Lincoln Park (fig. 1). For simplicity in this report, the hogback-shaped ridge south of the mill is referred to as the hogback, and the ridge between the mill and Lincoln Park is referred to as the Raton ridge. Between the hogback and the Raton ridge, the land surface is moderately rolling and slopes generally northeastward at about 100 ft/mi. In addition to the mill and its associated facilities, the area includes a golf course, located north of the mill.

Lincoln Park (approximate population 4,000) is on relatively flat land that forms a terrace between the Raton ridge and an escarpment on the south side of the Arkansas River. The land surface slopes northeastward at about 80 ft/mi. Lincoln Park, which is separated from the Raton ridge by a band of undeveloped land that is about 0.5 mi wide, consists of a rural-suburban mixture of single-family dwellings on small plots, small ranches, farms, and orchards. Scattered services include restaurants, small shops, and stores. Municipal water is available throughout Lincoln Park, and private water wells are used primarily for stock watering and irrigation.

Mining of coal from the Vermejo Formation (see "Geology" section) beneath the uranium-mill site began in 1908 and ceased in 1934. This mining resulted in shafts and underground rooms where the coal was removed. The locations of the mines are shown in Hearne and Litke (1987, fig. 2). The shaft having the most potential effect on ground-water flow in the study area is the Littell shaft, which is located near the old tailings ponds (fig. 1). This shaft was originally about 1,060 ft deep (Washburne, 1910), was later deepened to 1,084 ft (W.A. Wahler and Associates, 1978b), and was finally plugged in 1978.

Earth-moving operations on uranium-mill property have resulted in substantial changes to the natural physiography locally. Earth-fill flood-control dams were constructed by the Soil Conservation Service (SCS) [now (1999) the Natural Resources Conservation Service] of the U.S. Department of Agriculture in both gaps in the Raton ridge in 1971. The dam at the Sand Creek gap is referred to as the SCS dam (fig. 1) in this report. The dam at the west gap is referred to as the west SCS dam (fig. 1). The SCS dam and the west SCS dam were constructed of fill that was largely derived from nearby upstream earth. Between 1978 and 1980, an impoundment was constructed adjacent to the mill with clay layers, gravel drains, and a synthetic liner. The impoundment was used to accept mill wastes and tailings from the old tailings ponds. In about 1979, gravel-filled trenches were constructed to intercept ground-water flow in the vicinity of the old tailings ponds and immediately upgradient from the SCS reservoir (fig. 1). In 1988, a clay barrier was constructed on the south side of the SCS dam to further decrease ground-water flow through the Sand Creek gap.

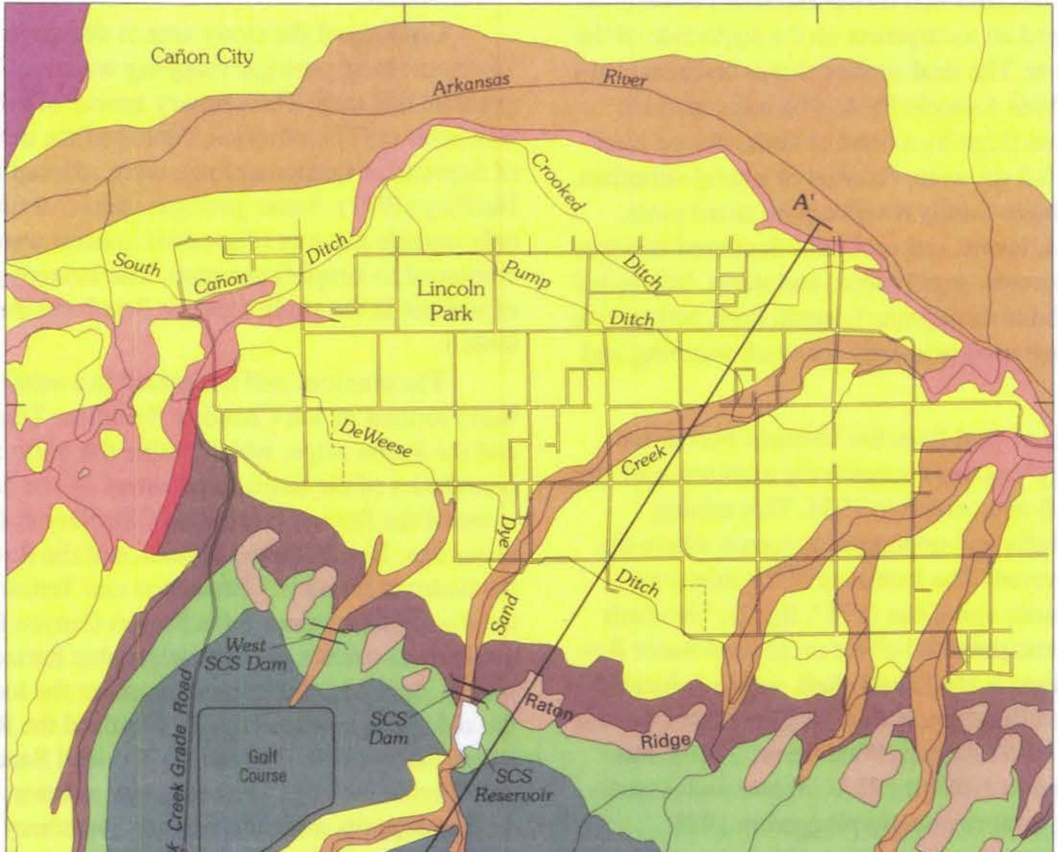
Geology

Geology of the study area is shown in figure 1. Two sources of geologic mapping were used to generate this map. The primary source of information was Scott (1977); however, details of the distribution of deposits of Quaternary age were adapted from Hershey (1977). Some geologic units that crop out only outside the area of greatest interest were combined to simplify the map. The stratigraphic units of interest in the study area are listed and described in table 1.

The uranium mill is situated in a small structural basin formed by the Chandler Syncline. The hogback and the Raton ridge, which define the north and south boundaries of the basin, are formed by the hard sandstone of the Raton Formation of Tertiary and Cretaceous age. Between the hogback and the Raton ridge, the bedrock layers of Cretaceous and Tertiary age of the Pierre Shale through the Poison Canyon Formation are folded so that a given stratigraphic horizon is at its lowest elevation approximately under the location of the old tailings ponds (fig. 2). North of the Raton ridge, the Vermejo Formation, Trinidad Sandstone, and Pierre Shale of Cretaceous age subcrop under terrace deposits and alluvium of Quaternary age. Terrace deposits underlie most of Lincoln Park, and alluvium occupies a narrow band along Sand Creek. Alluvium-filled channels cut the ridge formed by the Raton Formation at two places. The gap in the ridge through which Sand Creek passes is referred to as the Sand Creek gap in this report; the gap to the west is referred to as the west gap. Additional discussion of the geology of the study area is in Hearne and Litke (1987).

Hydrology

Ground-water flow and associated transport of solutes in the study area are largely controlled by such natural factors as rate of recharge from precipitation, lithology, geologic structure, and fractures. In addition, the anthropogenic modifications (described in the "Site Description" section) have substantially altered the ground-water system. A map showing median water levels for most of the study area is included in Banta and Chafin (in press). Because of the historically and annually variable nature of the ground-water system, this map does not adequately indicate some



Base from U.S. Geological Survey, 1:24,000 scale map State Plane Coordinate System Zone 3476

Geology modified from Hershey, 1977; Scott, 1977

Figure 1. Geology of the study area.

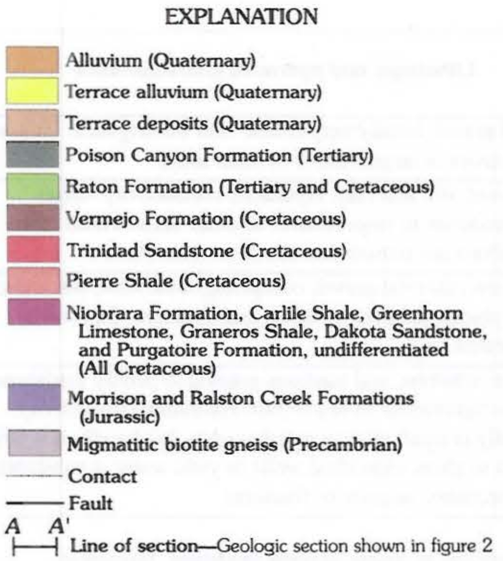


Figure 1. Geology of the study area—Continued.

important ground-water-flow directions, and some of the interpretations in this report are based on chemical gradients.

The ground-water system in the study area can be conceptually divided by the Raton ridge into two areas: (1) The upgradient area near the uranium mill, where hydraulic conductivities generally are small and where ground-water flow in the bedrock, although small in magnitude, is an important part of the ground-water system; and (2) the downgradient area in Lincoln Park, where flow in permeable, unconsolidated sediments dominates the ground-water system. This section describes the two areas of the ground-water system.

Upgradient Area

In the upgradient area, ground water is in the alluvium along Sand Creek; in the terrace alluvium adjacent to the alluvium; in the Poison Canyon, Raton, and Vermejo Formations; in the Trinidad Sandstone; and in the Pierre Shale. Of these geologic units, only alluvium and terrace alluvium generally are permeable enough to transmit large volumes of ground water at substantial rates. In the bedrock units (Tertiary and older), the rate of ground-water flow generally is limited by small hydraulic conductivities, although fractures in the bedrock, where present, allow small amounts of water to travel at substantial velocities.

Weathered zones and fractures are commonly observed in cuttings and cores obtained from the near-surface parts of the Poison Canyon and Vermejo Formations. The Raton Formation also is fractured (Hershey, 1977). Fractures and weathering tend to enhance the ability of the units to transmit water. Most of the monitoring wells constructed in the upgradient area are completed in the Poison Canyon Formation and yield only small amounts of water; these wells generally need several hours or overnight to recover when purged for sampling.

Recharge to the unconsolidated units in the upgradient area is predominantly by inflow of ground water through Alkali Gap (fig. 1). On occasions when there is flow of stormwater in Sand Creek, infiltration of surface water also contributes to recharge. In the areas mapped as bedrock, terrace deposits, or terrace alluvium, recharge comes from precipitation that exceeds evapotranspiration. Because the two gaps in the Raton ridge provide the major outlets for ground water from the upgradient area, the direction of ground-water flow in the upgradient area generally is toward one or the other of these gaps. Flow downward across the bedding planes of the Poison Canyon, Raton, and Vermejo Formations likely accounts for a small part of the ground-water discharge from the upgradient area because of the generally small hydraulic conductivities of these units. The interbedded shales of the Poison Canyon and Vermejo Formations also tend to further decrease the potential for flow across the bedding planes. Since construction of the SCS dam, the existence of a surface-water body upgradient from the dam (the SCS reservoir) has provided an area where evaporation causes some additional loss of water from the hydrologic system.

In 1989, a network of injection and withdrawal wells began operation downgradient of the lined impoundment. Piped municipal water (represented by site 997; location unspecified) was injected to attempt to reverse the hydraulic gradient to prevent northward migration of raffinate-affected ground water.

Downgradient Area

In the area north of the Raton ridge, alluvium along Sand Creek and terrace alluvium are the principal units capable of transmitting ground water at substantial rates. These unconsolidated units are underlain by the Vermejo Formation, Trinidad Sandstone, and Pierre Shale (in northward order). Each of

Table 1. Stratigraphic units of interest in the study area

System	Series	Geologic unit and thickness (feet)	Lithologic and hydraulic characteristics
Quaternary	Holocene	Alluvium, 0-10	Sand and gravel, locally very coarse near the hogback. Hydraulic conductivity is large relative to other units.
	Holocene and Pleistocene	Terrace alluvium, 0-60	Gravel, sand, silt, and clay. Hydraulic conductivity ranges from moderate to large relative to other units. Yields 10 to 400 gallons per minute to wells in Lincoln Park.
	Pleistocene	Terrace deposits, 0-20	Alluvial and colluvial gravel, containing some sand, silt, and clay, and in places, pebbles, cobbles, and boulders. Generally unsaturated.
Tertiary	Paleocene	Poison Canyon Formation, 0-1,000	Claystone, siltstone, and medium-grained to pebbly sandstone; some conglomerate in lower part. Hydraulic conductivity generally is small relative to other units, but locally it is large enough to allow individual wells to yield water at substantial rates, probably because of fractures.
Tertiary and Cretaceous	Paleocene and Upper Cretaceous	Raton Formation, 0-500	Hard, medium- to coarse-grained sandstone. Hydraulic conductivity is small relative to other units.
Cretaceous	Upper Cretaceous	Vermejo Formation, 0-1,100	Shaley, fine- to medium-grained sandstone interlayered with sandy to clayey shale and coal. In some areas, removal of coal layers by mining has resulted in water-filled voids. Some of the coal beds are fractured. Hydraulic conductivity is variable; it probably is small in the shale or shaley intervals and moderately large in zones of fractured coal relative to other units.
		Trinidad Sandstone, 0-90	Fine- to medium-grained sandstone interlayered with carbonaceous shale. Hydraulic conductivity is unknown, but is likely to be small to moderate relative to other units.
		Pierre Shale, 3,900	Clayey, silty, and sandy shale containing bentonite beds. Hydraulic conductivity is small relative to other units.

these bedrock units probably has an upper part that is weathered and fractured. In this report, the term "alluvial aquifer" is used to refer to the saturated alluvium, terrace alluvium, and underlying weathered or fractured bedrock in the downgradient area.

Recharge to the alluvial aquifer comes from seepage from irrigation ditches and ponds, from infiltration of excess irrigation water, and from infiltration of precipitation. Water also enters the alluvial aquifer through the two gaps in the Raton ridge as ground water in the alluvium-filled channels. However, the clay barrier (noted in the "Site Description" section), which was installed against the upgradient (south) toe of the SCS dam in 1988, has eliminated most groundwater flow through the Sand Creek gap. In 1990, injection trenches were constructed about 100 ft northeast of wells 329, 330, and 331 (fig. 3, inset). During the irrigation seasons of 1990 through 1994, municipal water was injected into these trenches at average rates ranging approximately from 30 to 60 gal/min in a remediation effort referred to as the dam-to-ditch flush. In 1995, injection at these trenches was performed only during August and September; water was not injected in 1996 and 1997.

The alluvial aquifer discharges water to Sand Creek, which is perennial for about 0.5 mi upstream from its mouth. The aquifer also discharges to a series of springs and seeps at the contact between terrace alluvium and the Pierre Shale along the Arkansas River. Substantial evapotranspiration is indicated by abundant vegetation along the scarp between Lincoln Park and the flood plain of the Arkansas River. Saturated thickness of the alluvial aquifer ranges from 0 ft along the Raton ridge to about 60 ft, according to Colorado State Engineer well records. Saturated thickness varies seasonally; it is largest during the irrigation

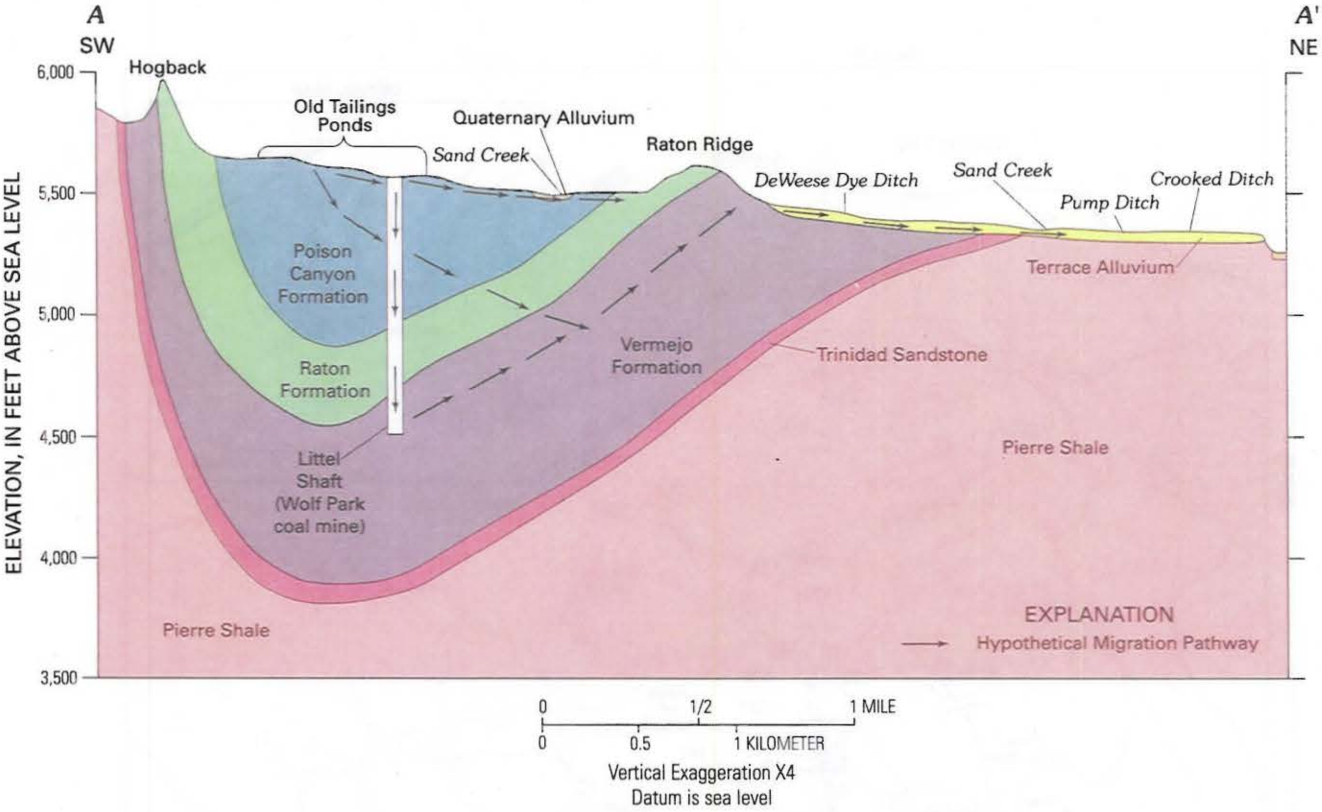


Figure 2. Geologic section of the study area. Location of Littell shaft projected onto line of section (line of section is shown in fig. 1).

season and decreases during the nonirrigation season. The alluvial aquifer yields water to numerous wells in Lincoln Park, which are used mainly for irrigation.

Sample Collection

Data used for this study consist of extensive water-quality data collected prior to this study and water-quality and solid-phase data collected during this study. Most of the data collected prior to this study were collected by the Cotter Corporation and are reported in Banta (1997). This section describes the sampling conducted for this study.

Fifty-five wells, one spring, one surface-water site, and one pipe outlet of municipal water at the uranium mill (which represents water injected for the injection-withdrawal system and the dam-to-ditch flush) were sampled for this study. Seven wells were sampled for chlorofluorocarbon (CFC) analysis (age dating). Thirty-nine wells, one spring, one surface-water site on the DeWeese Dye Ditch, and municipal water were sampled to determine $^{234}U/^{238}U$ isotopic ratios, which are reported in Zielinski and others (1997). Twenty-two wells, one surface-water site, and municipal water were sampled for concentrations of major ions, ammonia, nitrite plus nitrate, bromide, fluoride, silica, aluminum, iron, manganese, selenium, laboratory alkalinity, and dissolved-solids residue on evaporation at 180°C; all but 11 wells from this group also were sampled for the following isotopic ratios: $^{2}H/^{1}H$ and $^{18}O/^{16}O$ of water, $^{13}C/^{12}C$ of inorganic carbon, and $^{34}S/^{32}S$ of sulfate. Samples from all 58 sites were analyzed for dissolved uranium and dissolved molybdenum; temperature, specific conductance, and pH were measured onsite. In addition, alkalinity and dissolved oxygen were measured in samples from most of the sites.

All ground-water samples were collected following adequate purging of the well, except for subsurface-drain collector 701, which had insufficient water. Many small-yield wells completed in the Poison Canyon and Vermejo Formations required evacuation

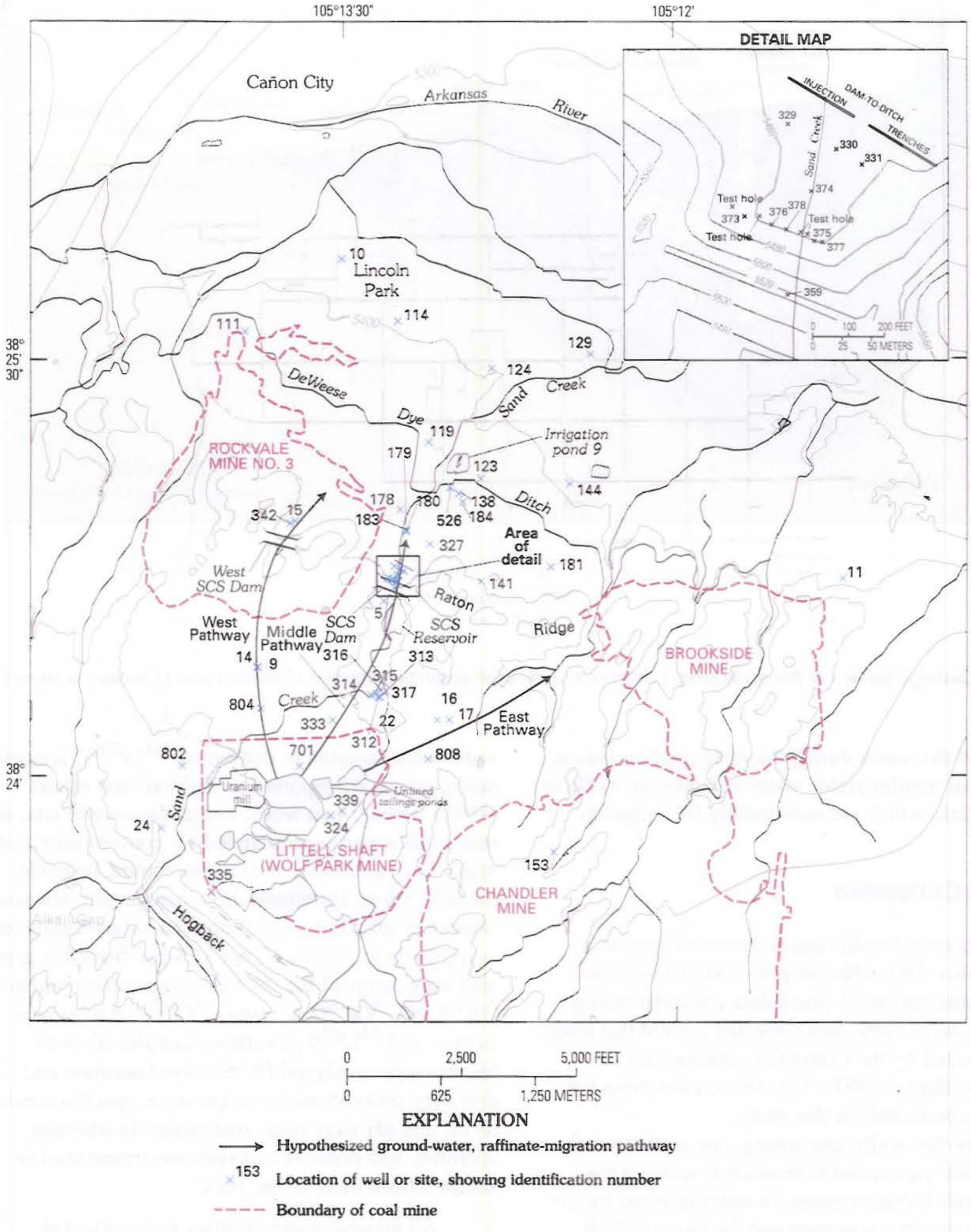


Figure 3. Hypothesized near-surface pathways of contaminant migration and locations of selected ground-water sites.

and recovery before sampling. Most wells were sampled with a portable, electric, submersible pump or a piston pump driven with compressed air. Three sites (15, 377, and 701) were sampled with bailers. Pumps delivered sample water through polyethylene tubing, which was decontaminated between sampling at the sites by flushing with a soap solution and rinsing with municipal water and deionized water.

Wells that had adequate yield were pumped from near the top of the water column to remove stagnant water from the casing before the pump intake was lowered into or near the slotted interval of the well for additional purging and sampling. Most wells were sampled after stabilization of temperature, pH, specific conductance, and dissolved-oxygen concentrations for three consecutive readings taken at 5-minute intervals. Stabilized measurements of these parameters are the reported values. These measurements were taken in water flowing upward through a graduated cylinder or in grab samples from other wells and springs.

Samples collected for analysis of alkalinity, major ions, ammonia, nitrite plus nitrate, bromide, fluoride, silica, aluminum, iron, manganese, molybdenum, selenium, uranium, and dissolved-solids residue on evaporation at 180°C were filtered through nominal 0.45-µm openings. Samples collected for analysis of major ions, silica, aluminum, iron, manganese, molybdenum, selenium, and uranium were stabilized with nitric acid. Samples collected for analysis of ammonia and nitrite plus nitrate were chilled on ice between sample collection and analysis. Samples collected for isotopic analysis of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ of water, $^{13}C/^{12}C$ of inorganic carbon, and $^{34}S/^{32}S$ of sulfate required neither filtering nor chemical treatment prior to delivery to the laboratory. Incremental alkalinity titrations were done onsite at all sites where major ions were sampled and at numerous other sites. Constituents were analyzed by USGS laboratories in Denver, Colorado, and Reston, Virginia. Results of analyses are listed in table 7 in the "Supplemental Information" section at the back of this report.

Seven wells were sampled for CFC analysis to determine approximate recharge ages for ground water. The theory, sampling, and analytical techniques for CFC dating of ground water are described by Busenberg and Plummer (1992), Dunkle and others (1993), and Reilly and others (1994). Results of CFC sampling are listed in table 8 in the "Supplemental Information" section at the back of this report.

Twenty-eight samples from borehole cuttings and core collected by the Cotter Corporation were selected for various solid-phase analyses. All samples were analyzed for mineralogical composition by X-ray diffraction. Thirteen samples were selected for size-fraction analysis, and the <2-µm size fractions for these 13 samples and a powdered sample (total of 14 samples) were analyzed for clay-mineral composition by X-ray diffraction. In addition, ion-exchange capacity and relative exchangeable-cation abundances were determined for the <2-µm size fractions for these 14 samples. Sample descriptions for the >62-µm size fractions of all 28 samples and results of analyses for the 14 samples are listed in Banta (1997).

MIGRATION OF RAFFINATE-AFFECTED GROUND WATER

Migration of raffinate-affected ground water in the vicinity of the uranium mill has been hypothesized to occur along near-surface (≤100 ft deep) and deep pathways. The hypothesized near-surface pathways are (1) a middle pathway down the Sand Creek drainage, (2) a west pathway, and (3) an east pathway. These hypothesized pathways are shown in figure 3. This section evaluates the likelihood of contaminant transport along these hypothesized pathways. Most of these evaluations are based on a review of data collected by the Cotter Corporation and reported in Banta (1997).

Middle Near-Surface Pathway

Previous investigations (W.A. Wahler and Associates, 1978a; Geotrans, Inc., and others, 1986; Hearne and Litke, 1987; ENVIRON Corporation and others, 1991; Adrian Brown Consultants, Inc., 1993) have established that the primary migration pathway of raffinate-affected ground water was from the vicinity of the uranium-mill site and the old tailings ponds, down the Sand Creek drainage, through the Sand Creek gap, and into Lincoln Park (the middle pathway in fig. 3). Ground-water-collection and pumpback systems, which were first installed in 1979, and the clay barrier installed at the SCS dam in September 1988 were designed to decrease the flow of raffinate-affected ground water into Lincoln Park. The effects of these remediation efforts are discussed in subsequent subsections.

Determination of the areal distribution of raffinate-affected ground water requires an estimate of background concentrations of dissolved uranium and dissolved molybdenum. In this report, the term "background" describes concentrations of dissolved uranium and dissolved molybdenum not affected by raffinate migration. Historical water-quality analyses for three wells (10, 11, and 114; locations shown in fig. 3) completed in Quaternary alluvium (table 2) provide an estimate of background concentrations of dissolved uranium and dissolved molybdenum in alluvial ground water in Lincoln Park. Banta (1994) described selection of wells 10 and 114 as background sites in a statistical determination of raffinate contamination in selected wells in Lincoln Park; well 11 is located near the Raton ridge far to the east of the general area affected by migration of raffinate and, therefore, can be confidently considered to yield water with background concentrations. Dissolved-uranium concentrations for these three wells ranged from 4 to 31 μg/L. Thus, the general area in Lincoln Park affected by raffinate-derived uranium is defined in this report by uranium concentrations exceeding 31 μg/L. Dissolved-molybdenum concentrations ranged from <5 to 40 μg/L, and the general area in Lincoln Park affected by raffinate-derived molybdenum migration is approximated by areas with molybdenum concentrations exceeding 40 μg/L.

The use of these background concentrations for dissolved uranium (31 μg/L) and dissolved molybdenum (40 μg/L) do not imply that smaller concentrations in samples from other wells are not affected by raffinate. Concentrations (table 2) as small as 4 μg/L for uranium and <5 μg/L for molybdenum and median concentrations averaging about 14 μg/L for uranium and 7 μg/L for molybdenum in water from the three background wells indicate that raffinate-affected concentrations can be substantially smaller than 31 μg/L for uranium and 40 μg/L for molybdenum. However, because information is not available to determine which of the smaller concentrations are affected by raffinate, this report uses the more conservative maximum background concentrations to ensure that concentrations that exceed these background concentrations have a very high probability of being affected by raffinate.

Background concentrations of dissolved uranium and dissolved molybdenum in the area south of the Raton ridge are more difficult to determine. Because of large concentrations of dissolved uranium and dissolved molybdenum in this area, background concentrations used for Lincoln Park are used for the middle near-surface pathway in the area south of the Raton ridge for the purpose of outlining general areas of raffinate-affected ground water. More specific background concentrations are discussed on a case-by-case basis.

Various statistics for dissolved-uranium and dissolved-molybdenum concentrations in ground water, including median and maximum concentrations for 1987–89 and 1990–95, were plotted on maps of the study area. These time frames approximately represent

Table 2. Summary statistics for dissolved-uranium and dissolved-molybdenum concentrations in background alluvial wells in the Lincoln Park area (modified from Zielinski and others, 1997)

Site number	Sampling period	Constituent	Number of determinations	Concentration (micrograms per liter)				
				Mean	Standard deviation	Median	Minimum	Maximum
10	2/89-3/95	Uranium	31	17.3	5.4	18	6	30
		Molybdenum	[1]27	7.1	2.1	7	<5	11
11	2/89-3/95	Uranium	32	15.5	7.4	18	5	31
		Molybdenum	[1]25	9.5	6.2	8	<5	30
114	[2]8/84-3/95	Uranium	68	11.8	3.4	11	4	24
		Molybdenum	[1]52	8.3	6.1	7	<5	40

[1] Number indicates the number of determinations exceeding the detection limit of 5 micrograms per liter. A value of 0.7 times the detection limit (3.5 micrograms per liter) was assigned to determinations <5 micrograms per liter when calculating mean and standard deviation of molybdenum concentrations. The total number of determinations was the same as for uranium and was used to calculate medians.

[2] Prior data for well 114 were not included because of unsuitably large detection limits.

conditions before and after the installation of the clay barrier at the SCS dam. Because of the lack of data in many of these plots, the plots of the maximum concentrations of dissolved uranium and dissolved molybdenum for 1987–89 (figs. 4 and 5) provide the best estimate of the area affected by raffinate migration in the past.

The general area of near-surface ground water affected by migration of raffinate-derived uranium is shown by maximum dissolved-uranium concentrations exceeding 31 µg/L in near-surface ground water during 1987 through 1989 (fig. 4). The data indicate that the largest concentrations were in the vicinity of the old tailings ponds. From that area, large, but generally decreasing, concentrations of uranium were present down the Sand Creek drainage, in the gap in the Raton ridge, and in Lincoln Park. Maximum uranium concentrations of 3,400 and 4,400 µg/L were measured at wells 330 and 331 (fig. 3) near the downgradient (north) toe of the SCS dam. From there, raffinate-affected ground water migrated to the north-northeast for about 1.2 mi and then eastward for about 0.5 mi. In the vicinity of the DeWeese Dye Ditch, about 0.33 mi north-northeast of well 330, the area of raffinate-affected ground water splits, and another uranium plume extends eastward about 0.5 mi. This split may be caused by hydrologic stresses and dilution associated with infiltration of water from the DeWeese Dye Ditch and irrigation pond 9 (fig. 3) and possibly is enhanced by a subsurface high in the Vermejo Formation and by lithologic heterogeneity in the alluvial aquifer. The data also appear to indicate two westward projections of raffinate-affected ground water (relative to the main axis of migration). The southernmost projection probably is a result of hydrologic stresses caused by infiltration of water from the DeWeese Dye Ditch. The cause of the northernmost projection is not known, but the projection possibly results from migration of raffinate-affected ground water that traveled via the west near-surface migration pathway (fig.3). Water-quality data are not adequate to evaluate this hypothesis.

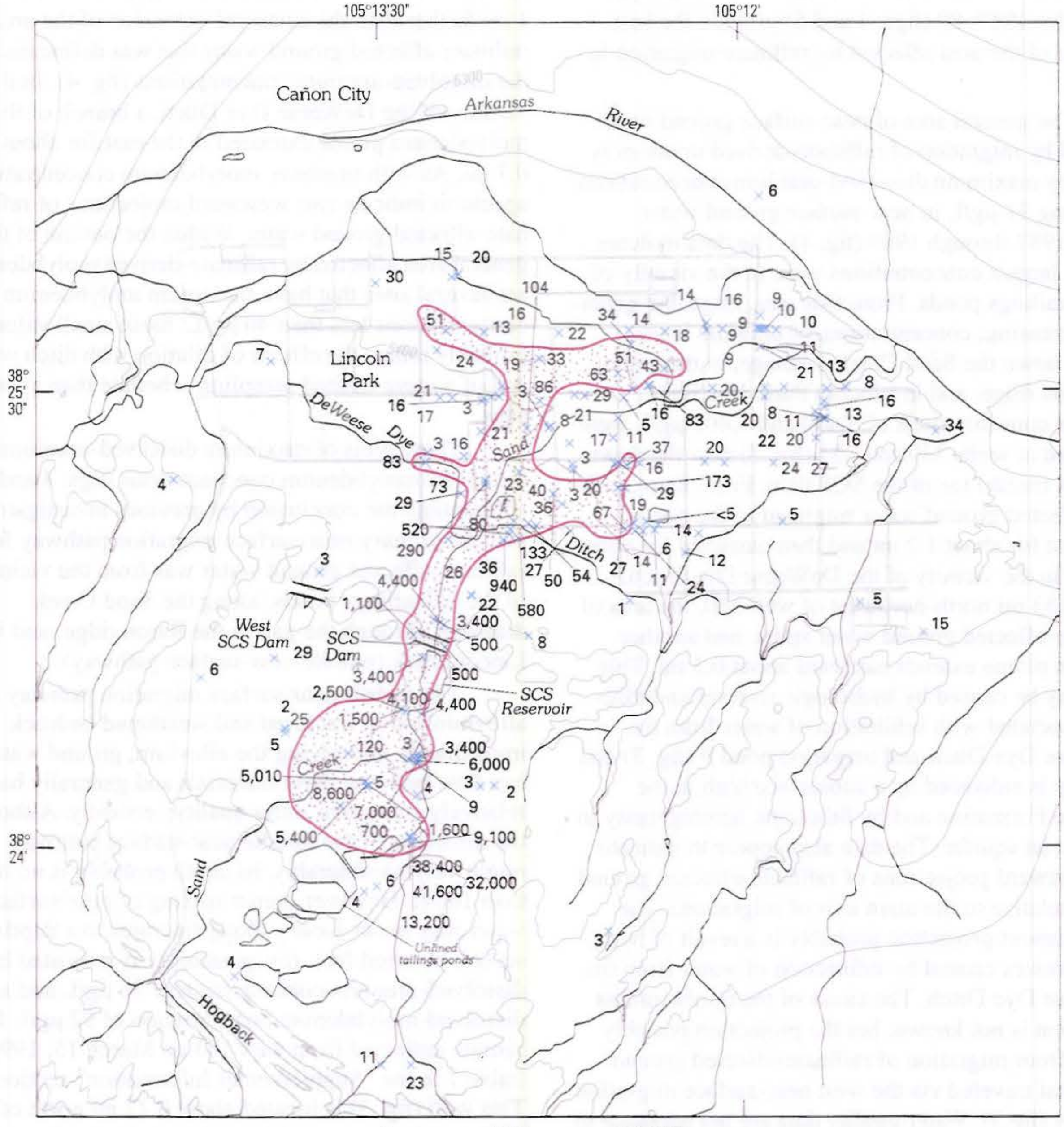
The area of near-surface ground water affected by migration of raffinate-derived molybdenum is indicated by maximum dissolved-molybdenum concentrations exceeding 40 µg/L during 1987 through 1989 (fig. 5). The affected area was similar to the area affected by raffinate-derived uranium. The data indicate large molybdenum concentrations of 17,300 µg/L at well 330 and 16,200 µg/L at well 331 near the downgradient toe of the SCS dam and migration to the north-northeast for about 1.2 mi. From there, the area of raffinate-affected ground water extended eastward about 1.5 mi to near the mouth of Sand Creek at the Arkansas River. This eastward extension was about 1 mi farther than the eastward extension of the area of raffinate-affected ground water that was delineated by the dissolved-uranium concentrations (fig. 4). In the vicinity of the DeWeese Dye Ditch, a branch of the molybdenum plume extended to the east for about 0.7 mi. As with uranium, molybdenum concentrations appear to indicate two westward projections of raffinate-affected ground water. Within the outline of the general area affected by raffinate-derived molybdenum are several sites that have maximum molybdenum concentrations less than 40 µg/L; these small values probably reflect the effects of dilution with ditch water and of a more limited sampling schedule than at other sites.

These plots of maximum dissolved-uranium and dissolved-molybdenum concentrations (figs. 4 and 5) substantiate the conclusion by previous investigators that the primary near-surface migration pathway for raffinate-affected ground water was from the vicinity of the old tailings ponds, along the Sand Creek drainage, through the gap in the Raton ridge, and into Lincoln Park (middle near-surface pathway).

The middle near-surface migration pathway is in alluvium and in fractured and weathered bedrock immediately underlying the alluvium; ground water can flow between these materials and generally has relatively consistent water quality vertically. Although the thickness of the middle near-surface pathway might vary considerably, its depth probably is no more than 100 ft. However, minor mixing of near-surface water may occur locally along fractures to a depth of several hundred feet; this possibility is indicated by a dissolved-uranium concentration of 76 µg/L and a dissolved-molybdenum concentration of 92 µg/L for a sample collected from well 183 on March 15, 1996, (table 7 in the "Supplemental Information" section). This well (fig. 3) is located about 0.22 mi north of the SCS dam in the area of the raffinate plume (figs. 4 and 5) and is open to the Vermejo Formation at depths between 190 and 243 ft.

Temporal Variations

Historical plots of dissolved-uranium concentrations for several wells indicate long-term and seasonal changes in the migration of raffinate. The historical plot for well 312 (fig. 6), located about 0.4 mi upgradient from the SCS dam (fig. 3), shows a

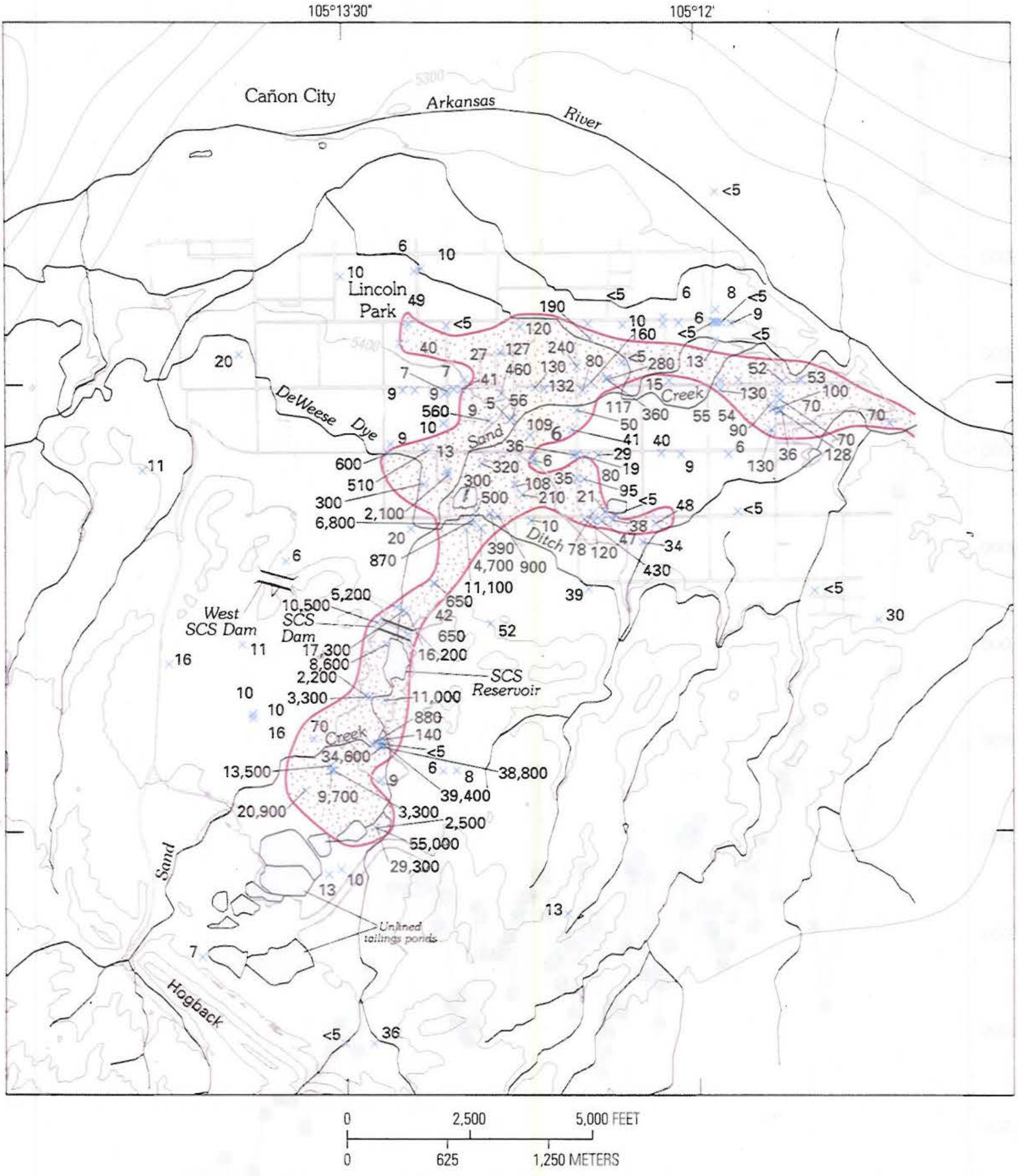


EXPLANATION

× 6 Location of datum, showing concentration of dissolved uranium, in micrograms per liter

▨ Area where uranium concentration exceeds 31 micrograms per liter

Figure 4. Distribution of maximum dissolved-uranium concentrations in water from wells less than 100 feet deep, 1987–89.



EXPLANATION

$^{6}_{\times}$ Location of datum, showing concentration of dissolved molybdenum, in micrograms per liter

▨ Area where molybdenum concentration exceeds 40 micrograms per liter

Figure 5. Distribution of maximum dissolved-molybdenum concentrations in water from wells less than 100 feet deep, 1987–89.

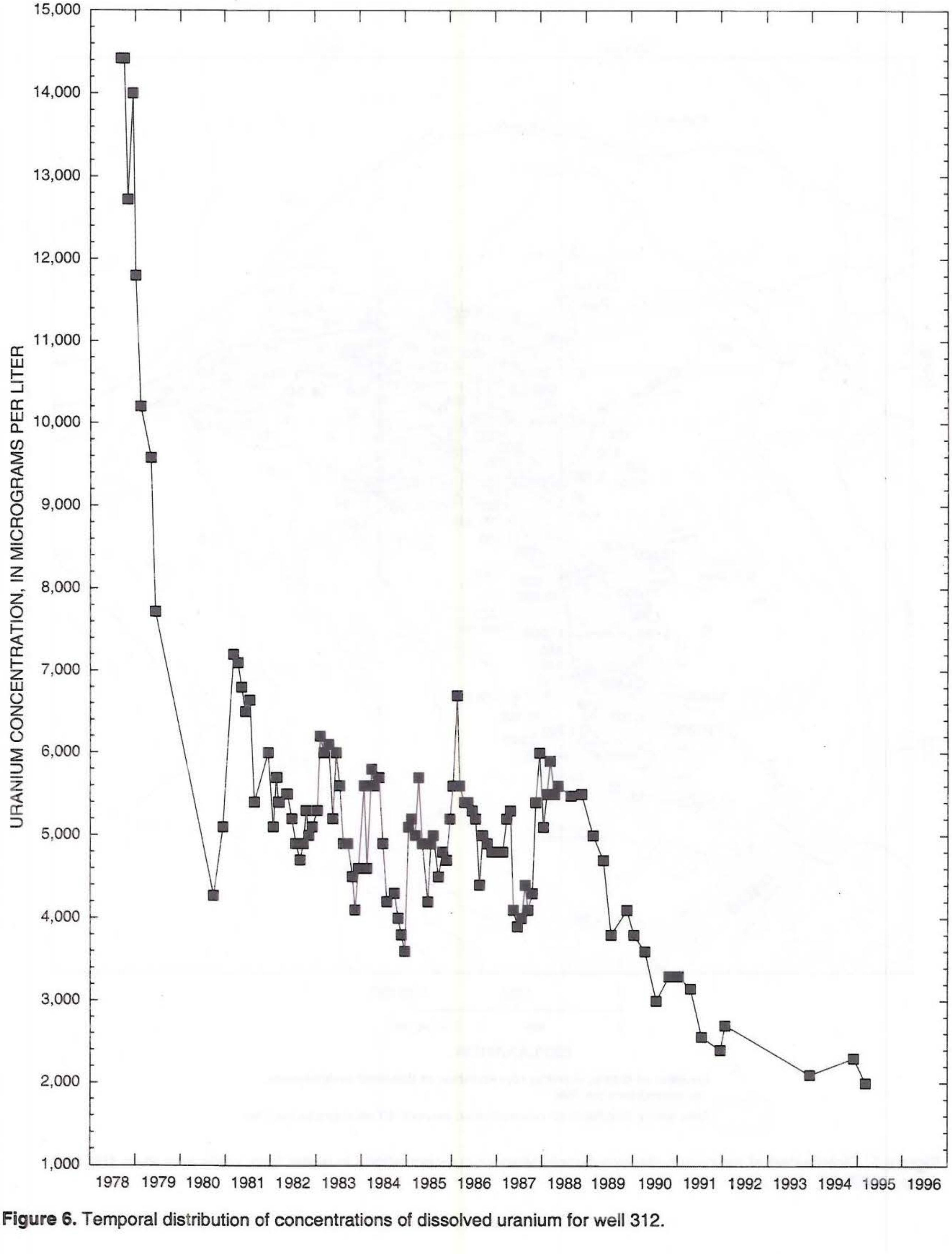


Figure 6. Temporal distribution of concentrations of dissolved uranium for well 312.

pronounced decline in uranium concentrations from about 14,000 µg/L in 1979 to less than 5,000 µg/L during 1980; fluctuating, but generally decreasing, concentrations after 1980; followed by a more rapid general decline in concentrations after 1989. The rapid decrease in concentration to 1980 and the more gradual decrease through 1988 seem to be related to remediation activities and the discontinued use of the old unlined tailings ponds beginning in 1979. Remediation activities consisted of (1) operation of pumpback systems from the SCS reservoir and from ground-water-collection trenches immediately upgradient from the SCS reservoir and immediately downgradient from the old tailings ponds (1979) and (2) transfer of tailings from the old unlined tailings pond to the lined impoundment (1981–83). The general decrease in concentration after 1989 seems to be related to operation of a ground-water injection-withdrawal system north of the primary impoundment that began in September 1989.

The historical plot of dissolved-uranium concentrations for well 330 (fig. 7), located about 250 ft downgradient from the north toe of the SCS dam (fig. 3, inset), indicates generally decreasing concentrations from 1980 through 1989. Remediation activities that began in 1979 (described in the preceding paragraph) possibly explain this trend. The cyclic dilution evident in the data collected since 1989 was caused by the annual injection of fresh municipal water into injection trenches constructed in the alluvium about 100 ft northeast of wells 329, 330, and 331 (fig. 3, inset), which commenced in March 1990. This injection also seems to have masked possible decreases in dissolved-uranium concentrations at well 330 that were caused by installation in September 1988 of the clay barrier on the upgradient side of the SCS dam.

The historical plot of dissolved-uranium concentrations for well 138 (fig. 8), located near the DeWeese Dye Ditch about 0.45 mi northeast of the SCS dam (fig. 3), shows that uranium concentrations generally decreased from a decade peak of 3,570 µg/L in May 1979 to less than 600 µg/L in 1994. This decrease seems to be the result of the remediation activities initiated in 1979. Annual fluctuations in dissolved-uranium concentrations are discussed in the "Water Types" section.

Flow and Chemical Flux through Sand Creek Gap

Modeling of ground-water flow and solute transport requires an estimate of the amount and quality of ground water migrating through the Sand Creek gap. This estimate was made using data obtained by installation of six monitoring wells and drilling of four test holes near the downgradient (north) toe of the SCS dam, measurement of water levels in the vicinity, measurement of hydraulic conductivity at the newly installed monitoring wells, and water-quality sampling. Locations of the monitoring wells and test holes drilled for this evaluation are shown in figure 3 (inset). Information on the monitoring wells (wells 373, 374, 375, 376, 377, and 378) is listed in Banta (1997).

Evaluation of the magnitude of ground-water flow rates through the alluvium at the Sand Creek gap is made according to Darcy's law (Freeze and Cherry, 1979):

$$Q = KIA, \tag{1}$$

where Q = volumetric rate of water flowing through alluvium,
K = hydraulic conductivity of alluvium,
I = hydraulic gradient in alluvium, and
A = cross-sectional area of saturated alluvium.

Estimates of mass fluxes of dissolved uranium and dissolved molybdenum are made according to the relation:

$$M = QC, \tag{2}$$

where M = mass flux of constituent,
Q = volumetric rate of water flowing through alluvium (eq. 1), and
C = concentration of constituent.

A schematic cross section showing the three subareas contributing to the total area of saturated alluvium, A, is shown in figure 9. Depths to bedrock were determined from drillers' logs. Water levels were measured at the wells shown in the inset of figure 3 on March 5, 1996. Straight-line interpolations of the alluvium/bedrock contact were made to minimize bias in determining saturated thickness. A bedrock high in the Vermejo Formation that separates the saturated alluvium into two channels also is shown in figure 9.

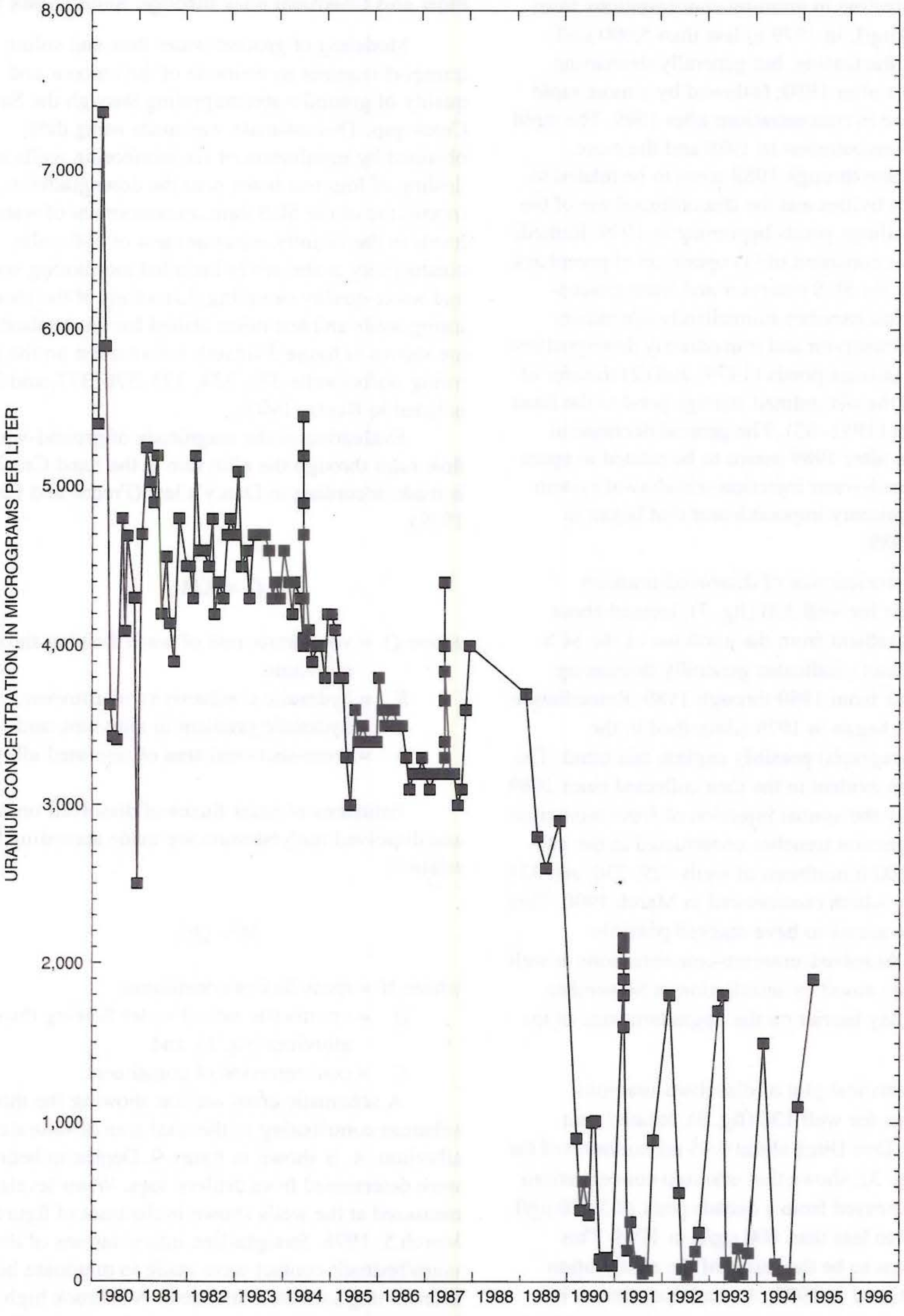


Figure 7. Temporal distribution of concentrations of dissolved uranium for well 330.

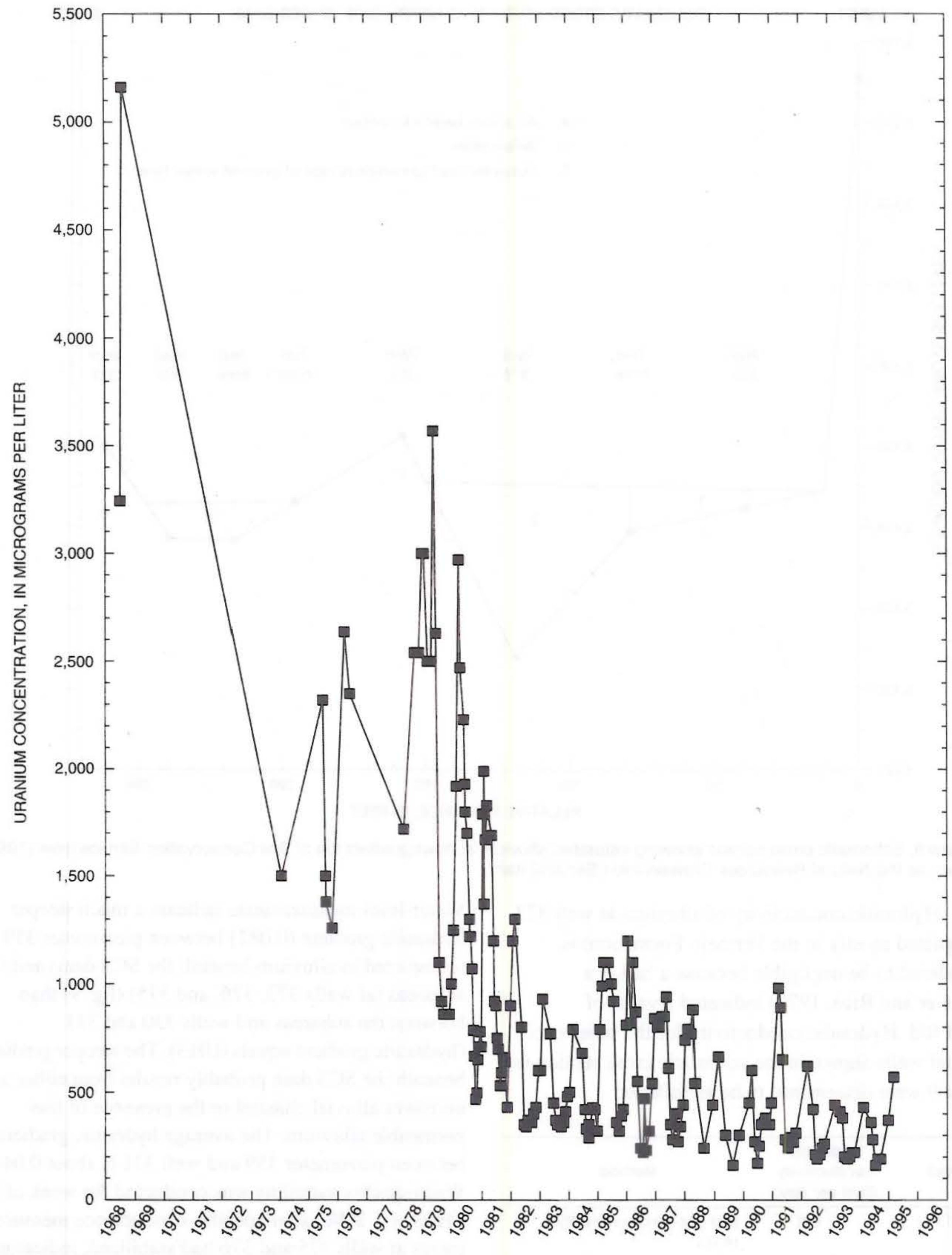


Figure 8. Temporal distribution of concentrations of dissolved uranium for well 138.

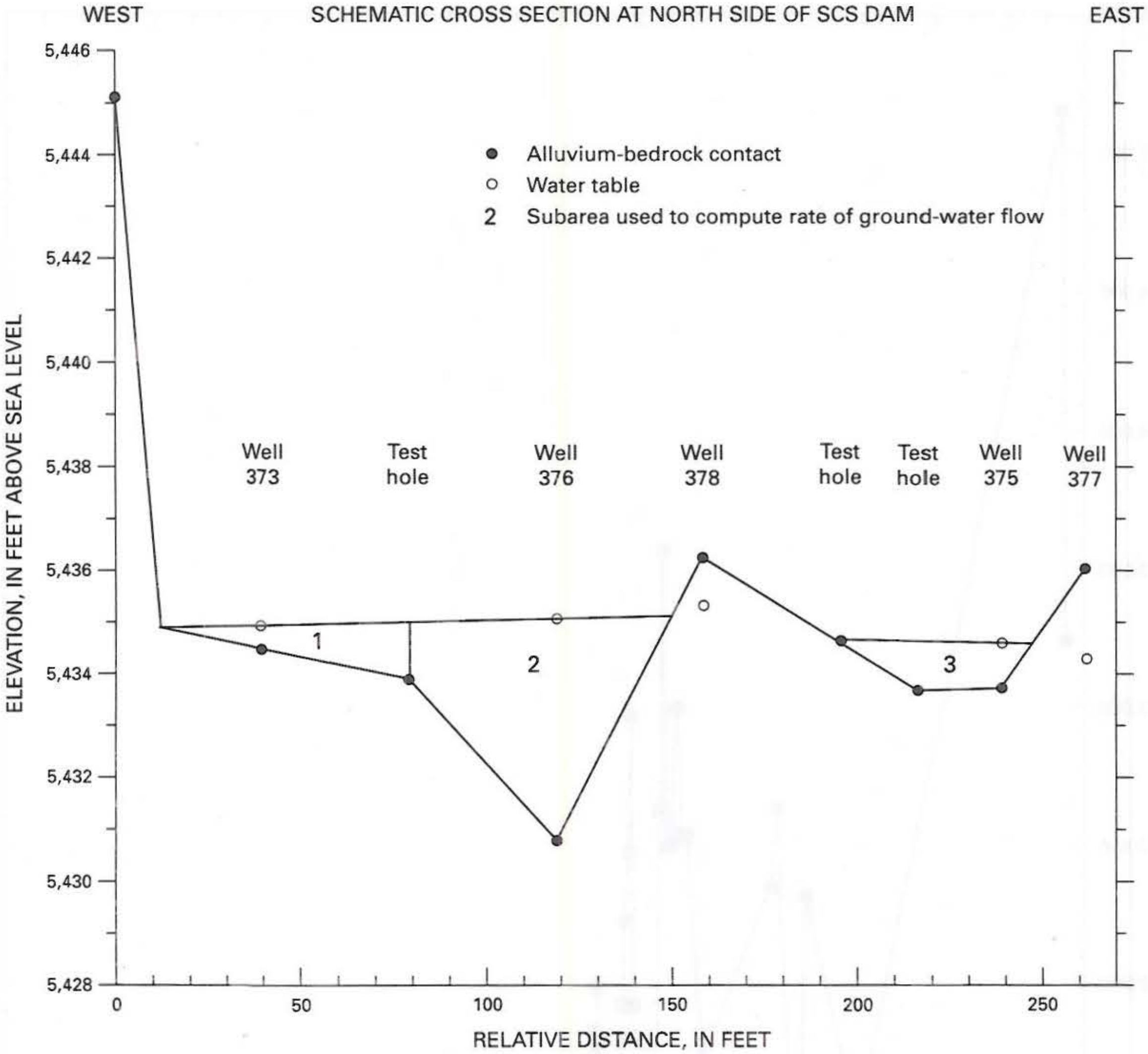


Figure 9. Schematic cross section showing saturated alluvium at downgradient toe of Soil Conservation Service [now (1999) known as the Natural Resources Conservation Service] dam.

Hydraulic conductivity of alluvium at well 373 (completed mostly in the Vermejo Formation) is considered to be negligible because a bail test (Bouwer and Rice, 1976) indicated a value of 0.004 ft/d. Hydraulic conductivity for the other two alluvial wells shown in the schematic cross section in figure 9 were determined to be as follows:

Well	Hydraulic conductivity (feet per day)	Method
375	0.8	Bail test (Bouwer and Rice, 1976)
376	29	Pump test (Cooper and Jacob, 1946)

Water-level measurements indicate a much steeper hydraulic gradient (0.082) between piezometer 359 (completed in alluvium beneath the SCS dam) and the subareas (at wells 373, 376, and 375) (fig. 9) than between the subareas and wells 330 and 331 (hydraulic gradient equals 0.013). The steeper gradient beneath the SCS dam probably results from either a narrower alluvial channel or the presence of less permeable alluvium. The average hydraulic gradient between piezometer 359 and well 331 is about 0.044. Water-quality sampling was conducted the week of March 11, 1996, after specific-conductance measurements at wells 375 and 376 had stabilized, indicating drainage of fresh municipal water that had been injected for dam-to-ditch flushing the previous fall.

(The resulting water-quality data are reported in table 7 in the "Supplemental Information" section.) The parameters necessary to estimate mass-flux subtotals for the three subareas shown in the schematic cross section (fig. 9) are listed in the following table.

Subarea (well)	Hydraulic conductivity (feet per day)	Area (square feet)	Uranium concentration (micrograms per liter)	Molybdenum concentration (micrograms per liter)
1 (373)	--	27	<0.1	42
2 (376)	29	180	4,300	25,000
3 (375)	.8	33	3,300	22,000

The small concentrations of uranium and molybdenum and the small (but unknown) hydraulic conductivity of alluvium at well 373 justify ignoring mass fluxes through subarea 1.

Use of equations 1 and 2, summation for the subareas (excluding subarea 1), and appropriate conversions produced the following estimates of total mass flux through the area shown in the schematic cross section in figure 9, according to the three estimates of hydraulic gradient in the preceding paragraph:

Hydraulic gradient	Water (liters per day)	Uranium (grams per day)	Molybdenum (grams per day)
0.013	1,900	8.3	48
.044	6,500	28	160
.082	12,000	52	300

Because of the large hydraulic conductivity and large area in subarea 2 (fig. 9), almost all flux of ground water through the alluvium occurs in that subarea. Despite the uncertainty in hydraulic gradient, the greatest uncertainty in the accuracy of mass-flux estimates is in the distribution of hydraulic conductivity and area. On the basis of regional flow modeling, Adrian Brown Consultants (1993) estimated that 1 to 3 gal/min of ground water flowed through the Sand Creek gap after installation of the clay barrier at the SCS dam. Because deep migration pathways are unlikely (as discussed in the "Deep Pathways" section), leakage beneath or lateral to the clay barrier at the south toe of the SCS dam probably is the pathway by which raffinate-affected ground water enters Lincoln Park.

West Near-Surface Pathway

A small (about 1 mi^2), unnamed drainage basin west of Sand Creek drains the terrain northwest of the uranium-mill site. Most of this area is occupied by a golf course. The west SCS dam is located in the drainage at the Raton ridge.

Water-quality data for the monitoring wells located in this drainage basin and in the vicinity of the uranium mill (fig. 3) indicate that relatively small quantities of raffinate-affected ground water probably have migrated from the mill site through this basin. Water-quality data (table 7 in the "Supplemental Information" section) for well 15, which is located near the downgradient toe of the west SCS dam, indicate a dissolved-uranium concentration of 420 µg/L and a dissolved-molybdenum concentration of 59 µg/L on January 19, 1996. Well 15 was drilled to a depth of 47 ft in 1988 and was completed in the Vermejo Formation. Subsequent infilling with sediment has decreased the depth to 39.5 ft. Because the water table seldom has been above this depth, no additional water-quality data are available for this well.

At well 9 (fig. 3), which was completed in the near-surface Poison Canyon Formation to a depth of 50 ft in 1988, dissolved-molybdenum concentrations increased from <5 µg/L in 1990 to 47 µg/L in January 1991, whereas dissolved-uranium concentrations remained relatively constant at about 25 µg/L (fig. 10). However, subsequent molybdenum concentrations decreased to <5 to 8 µg/L (except for brief increases to 19 µg/L in August 1992 and January 1993). These data indicate smaller background concentrations of dissolved uranium and dissolved molybdenum than the maximum background concentrations used to approximate the 1987–89 distribution of raffinate-affected ground water along the middle near-surface pathway (figs. 4 and 5).

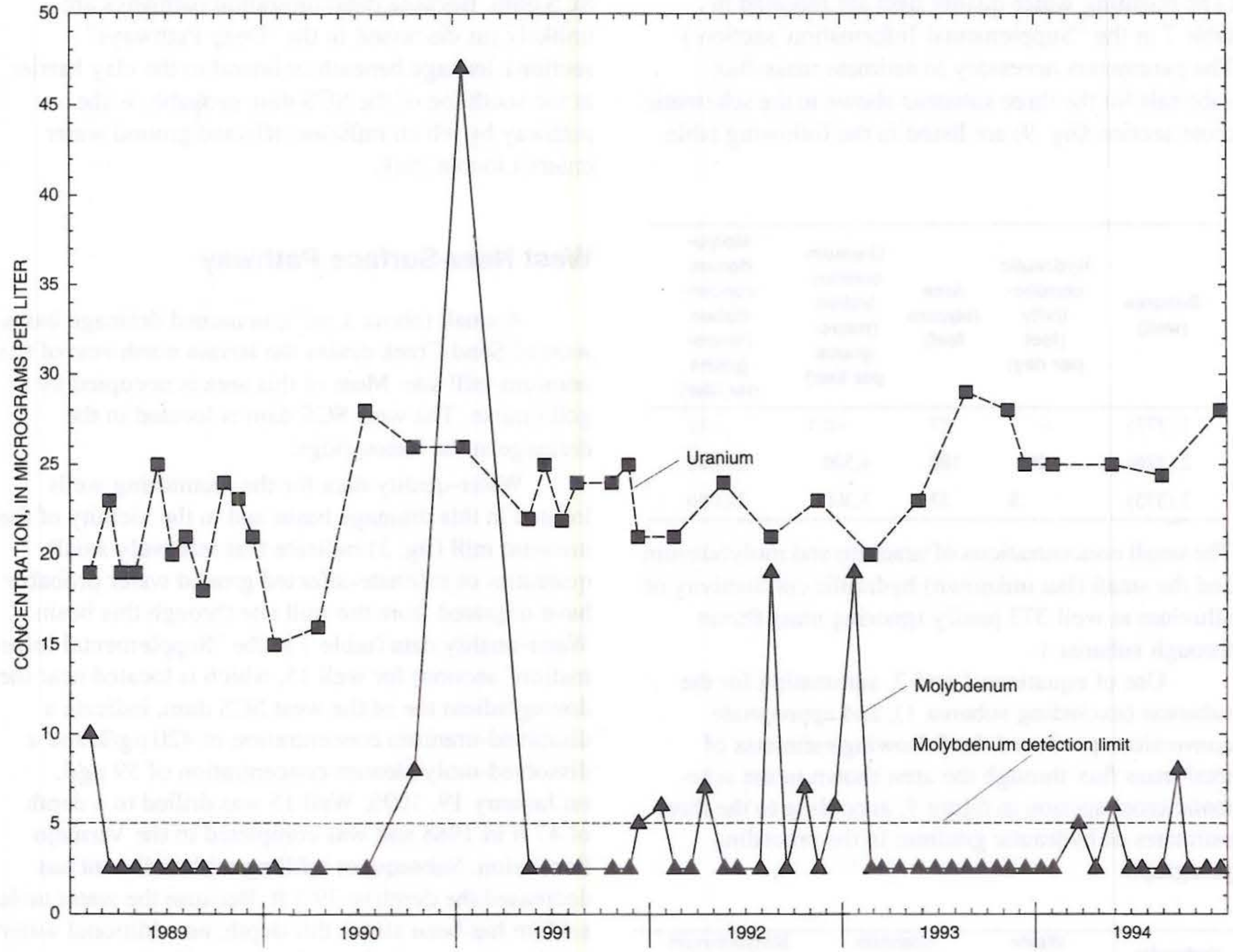


Figure 10. Temporal distribution of concentrations of dissolved uranium and dissolved molybdenum for well 9.

Two wells completed in the near-surface Poison Canyon Formation in the vicinity of the uranium mill yielded raffinate-affected ground water that indicates likely sources for the elevated concentrations of uranium at well 15 and molybdenum at well 9. Well 804 (about 0.35 mi north of the mill; fig. 3) was completed to a depth of 45 ft in 1988, and water-quality samples collected from January 1992 through October 1994 contained dissolved-uranium concentrations between 2,100 and 3,100 µg/L and dissolved-molybdenum concentrations between 210 and 700 µg/L (fig. 11). The anomalously large uranium-to-molybdenum ratios of these data are similar to the ratio for the sample collected from well 15 on January 19, 1996. Furthermore, the water table at well 15 was at an elevation of 5,444.9 ft on that date, whereas the water table was at elevations within 1.0 ft of 5,530 ft in well 804 from 1989 through 1994, indicating a potential hydraulic gradient from the vicinity of well 804 to well 15.

In 1988, well 802 (about 0.25 mi west of the uranium-mill site; fig. 3) was completed to a depth of 70 ft in sandstone and shale of the Poison Canyon Formation. Water-quality samples collected from this well from December 1992 through November 1994 contained dissolved-uranium concentrations between about 190 and 270 µg/L and dissolved-molybdenum concentrations between 1,200 and 1,800 µg/L (fig. 12), indicating that raffinate-affected ground water has migrated northwest of Sand Creek. Dilution of water of this composition by water in the vicinity of well 9, coupled with minor sorption of uranium, is

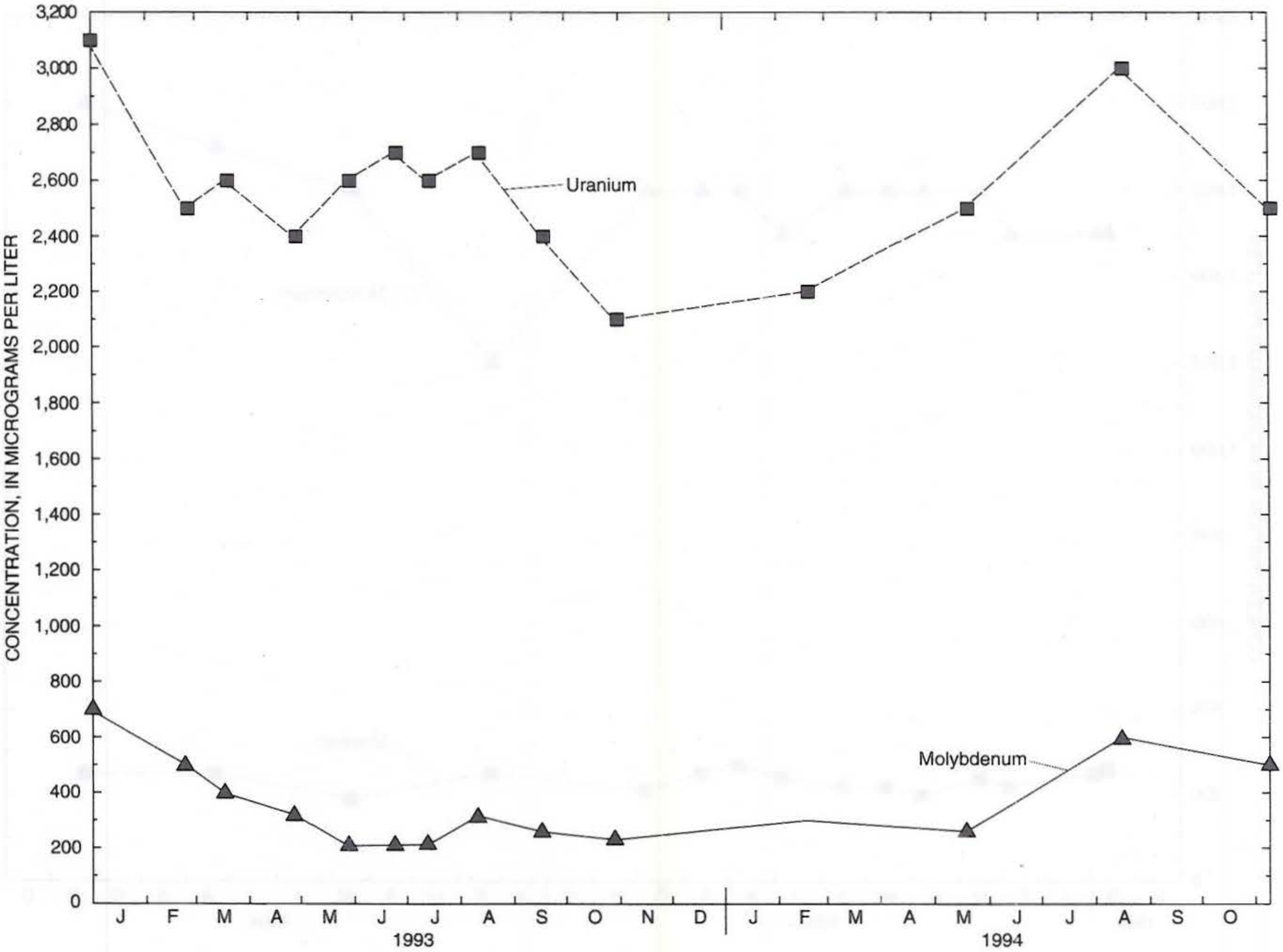


Figure 11. Temporal distribution of concentrations of dissolved uranium and dissolved molybdenum for well 804.

consistent with the increase in molybdenum concentrations at well 9 in late 1990 and early 1991. Furthermore, water levels indicate a potential hydraulic gradient from the vicinity of well 802 to well 9; from 1989 through 1994, water levels ranged in elevation from 5,581.6 to 5,582.7 ft at well 802 and ranged in elevation from 5,514.4 to 5,520.1 ft at well 9.

Because of the limited number of wells in the west basin, the configuration of the water table and the flow directions are poorly defined. However, the relatively small concentrations of dissolved uranium and dissolved molybdenum in samples collected from wells 9 and 15 in the west basin indicate that the west near-surface migration pathway probably is much less important than the middle near-surface migration pathway.

East Near-Surface Pathway

East of the Sand Creek drainage near the uranium-mill site and south of the Raton Ridge are two small (totaling about 1.3 mi^2), unnamed drainages that drain into Lincoln Park (fig. 3). Monitoring wells 16, 17, and 808 (fig. 3) are located in the eastern Sand Creek drainage near the drainage divide separating the Sand Creek drainage from the smaller, unnamed drainage to the east. These wells are completed in the near-surface Poison Canyon Formation to depths of 140 ft or less. A review of historical water-quality data from these wells indicates small background concentrations of dissolved uranium (≤ 5 µg/L) and dissolved molybdenum (≤ 10 µg/L) since August 1989. These small concentrations indicate that raffinate-affected ground water probably never flowed through the near-

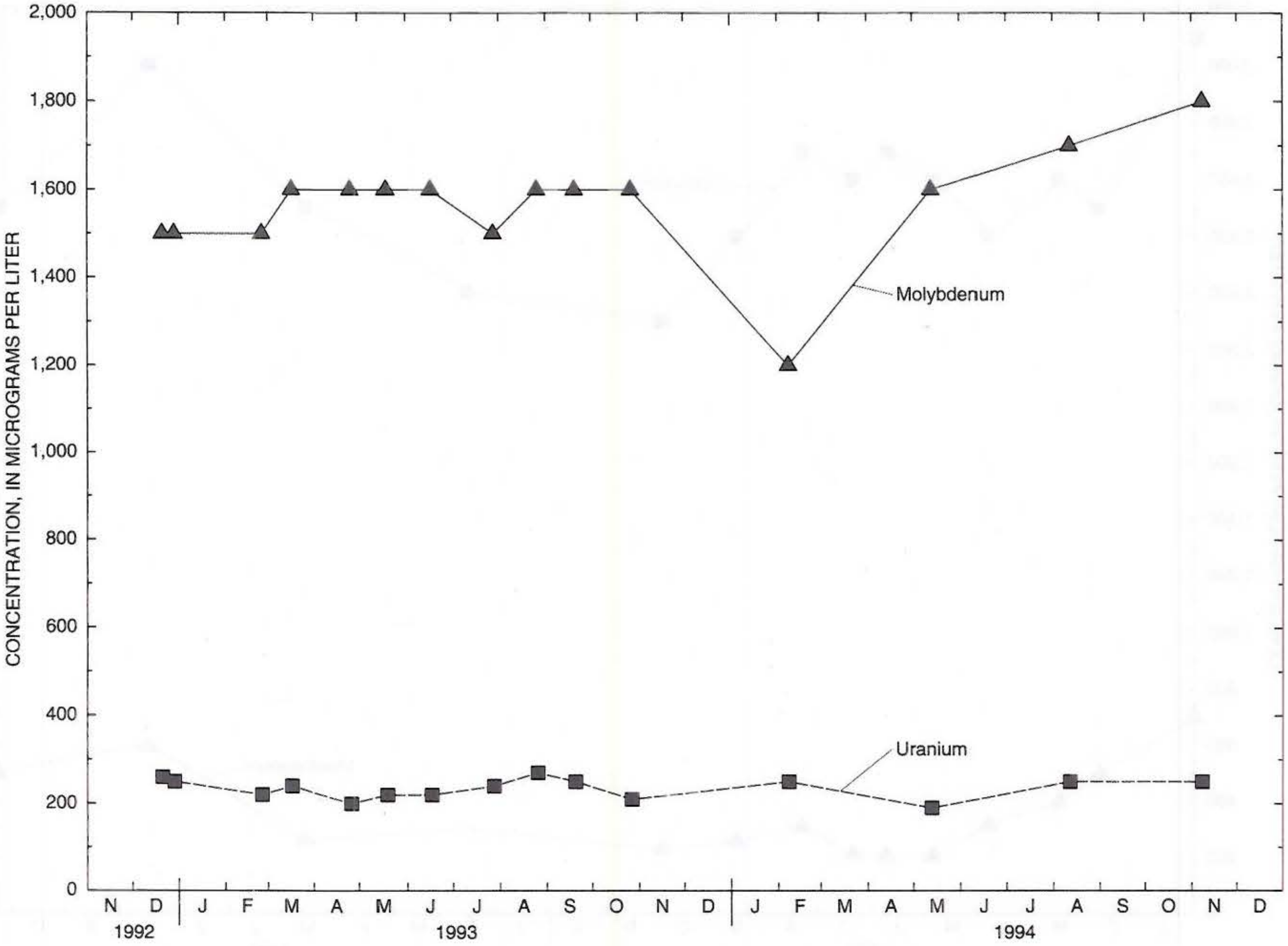


Figure 12. Temporal distribution of concentrations of dissolved uranium and dissolved molybdenum for well 802.

surface Poison Canyon Formation into the area of these three wells; if raffinate-affected ground water had flowed through this area, subsequent desorption from the formation matrix probably would have caused higher concentrations of dissolved uranium and dissolved molybdenum. Flow of raffinate-affected ground water through the Poison Canyon Formation into the potential east near-surface migration pathway is unlikely, given the lack of flow into the vicinity of these three wells. This conclusion is supported by the distribution of electrical conductivity (specific conductance) of ground water south of the Raton ridge in 1976–77 (W.A. Wahler and Associates, 1978a).

Deep Pathways

Hearne and Litke (1987) hypothesized two potential deep migration pathways for raffinate-affected ground water from the uranium-mill site to Lincoln Park (fig. 2): (1) Downward migration through the Poison Canyon and Raton Formations with bedding-plane migration through the Vermejo Formation and discharge into Quaternary alluvium in Lincoln Park, and (2) downward migration along the Littell shaft into the Vermejo Formation with subsequent migration along bedding planes through the Vermejo Formation and discharge into Quaternary alluvium in Lincoln Park. Hearne and Litke (1987) did not evaluate these pathways.

Geohydrologic conditions do not favor downward migration of raffinate through the Poison Canyon and Raton Formations in the vicinity of the old tailings ponds. ENVIRON Corporation and others (1991, p. 87–88) cited the relatively small capability of rocks beneath the Poison Canyon Formation to transmit water downward and the small concentrations of dissolved uranium and dissolved molybdenum in samples from well 339 (fig. 3) as factors minimizing the probability of a deep migration pathway. A review of historical water-quality data for wells 314, 315, 316, and 317 (Banta, 1997) supports this position. These wells are completed at varying depths in a small area located about 0.65 mi downgradient from the uranium mill (fig. 3). Wells 314 (screened from 77 to 97 ft) and 315 (screened from 260 to 270 ft) had substantial molybdenum concentrations (as large as 1,900 and 6,900 µg/L for 1979 through 1987), which were indicative of raffinate contamination; small uranium concentrations indicated selective retardation or precipitation of uranium. However, after discounting large concentrations of molybdenum early in the periods of record, wells 316 (screened from 370 to 650 ft) and 317 (screened in the Wolf Park coals of the Vermejo Formation from 675 to 751 ft) had small uranium and molybdenum concentrations that indicated no raffinate contamination. The data are from September 1979 through January 1984 for well 316 and from September 1979 through March 1986 for well 317. Elevated concentrations of molybdenum early in the periods of record probably were caused by contamination with tailings fluid used for drilling (Runnels and others, 1983). Overall, the data indicate that raffinate migration had not penetrated through the matrix of the Poison Canyon Formation to depths below about 300 ft and that dissolved uranium and dissolved molybdenum are unlikely to have migrated far into the Work Park Mine.

A more plausible deep migration pathway for raffinate is down the Littell shaft, through the coal-mine workings, along unmined coal and sandstone beds in the Vermejo Formation, and into alluvial deposits north of the Raton ridge (fig. 2). The areal distribution of coal mines in the vicinity of the study area is shown in figure 3. The Wolf Park Mine partly overlaps the Chandler Mine to the east; no reliable records indicate whether the two mines were connected. The air shaft into the Chandler Mine (site 153, fig. 3) was discharging water at an elevation of about 5,596 ft at a rate of 8 to 10 gal/min in 1981 (Geotrans, Inc., and others, 1986). Discharge continued until at least April 1988, the last date of water-quality sampling by the Cotter Corporation. Therefore, the hydraulic head in the Chandler Mine would have been greater than 5,596 ft from 1981 to 1988. W.A. Wahler and Associates (1978a) reported that the Littell shaft into the Wolf Park Mine was still open to a depth of 1,067 ft and that the depth to water in the shaft was 150 ft (water-table elevation equaled about 5,410 ft). Geotrans, Inc., and others (1986) reported that the depth to water in well 339 (completed in the Wolf Park Mine at a depth of 1,058 ft near the Littell shaft) (fig. 3) was about 135 ft below land surface (water-table elevation equaled about 5,425 ft) in May 1985. If the mine workings were hydraulically connected, the potentiometric surfaces in the open or collapsed workings of the Chandler and Wolf Park Mines would be approximately the same. The substantially lower water level in the Wolf Park Mine (5,410–5,425 ft) compared to the water level in the Chandler Mine (greater than or equal to 5,596 ft) implies that these two mines are not hydraulically connected and that any raffinate-affected ground water that entered the Littell shaft would not flow eastward into the Chandler Mine.

Geohydrologic factors indicate that ground water could not flow from the Wolf Park Mine into the Rockvale Mine No. 3 to the north (fig. 3). A water-table elevation of about 5,380 ft was measured in May 1961 for well 111 (completed in the Vermejo Formation near the adit at the northwestern corner of the Rockvale Mine No. 3) (fig. 3). Assuming this elevation was reasonably representative in May 1985, when the elevation of the potentiometric surface was about 5,425 ft at well 339, a hydraulic-head difference of about 45 ft would have existed between the Wolf Park and Rockvale No. 3 Mines, indicating that the mines were not connected with tunnels or shafts. Because the Wolf Park Mine was developed in the upper Vermejo Formation (fig. 2), whereas the Rockvale Mine No. 3 was developed near the base of the Vermejo Formation, the substantial (several hundred feet) vertical offset of the coal seams mined in these two mines would limit flow between the mines through unmined strata.

Geochemical evidence indicates that substantial concentrations of dissolved uranium and dissolved molybdenum are unlikely to have migrated far into the Wolf Park Mine via the Littell shaft. The concentrations of dissolved uranium and dissolved molybdenum in samples from well 339 (fig. 3) are shown in figure 13. For a few months following well completion, molybdenum concentrations were as large as 320 µg/L. Data collected by the Cotter Corporation indicate that these concentrations were associated with small dissolved-solids concentrations and pH values ranging from 11.3 to 12.3, indicating that the

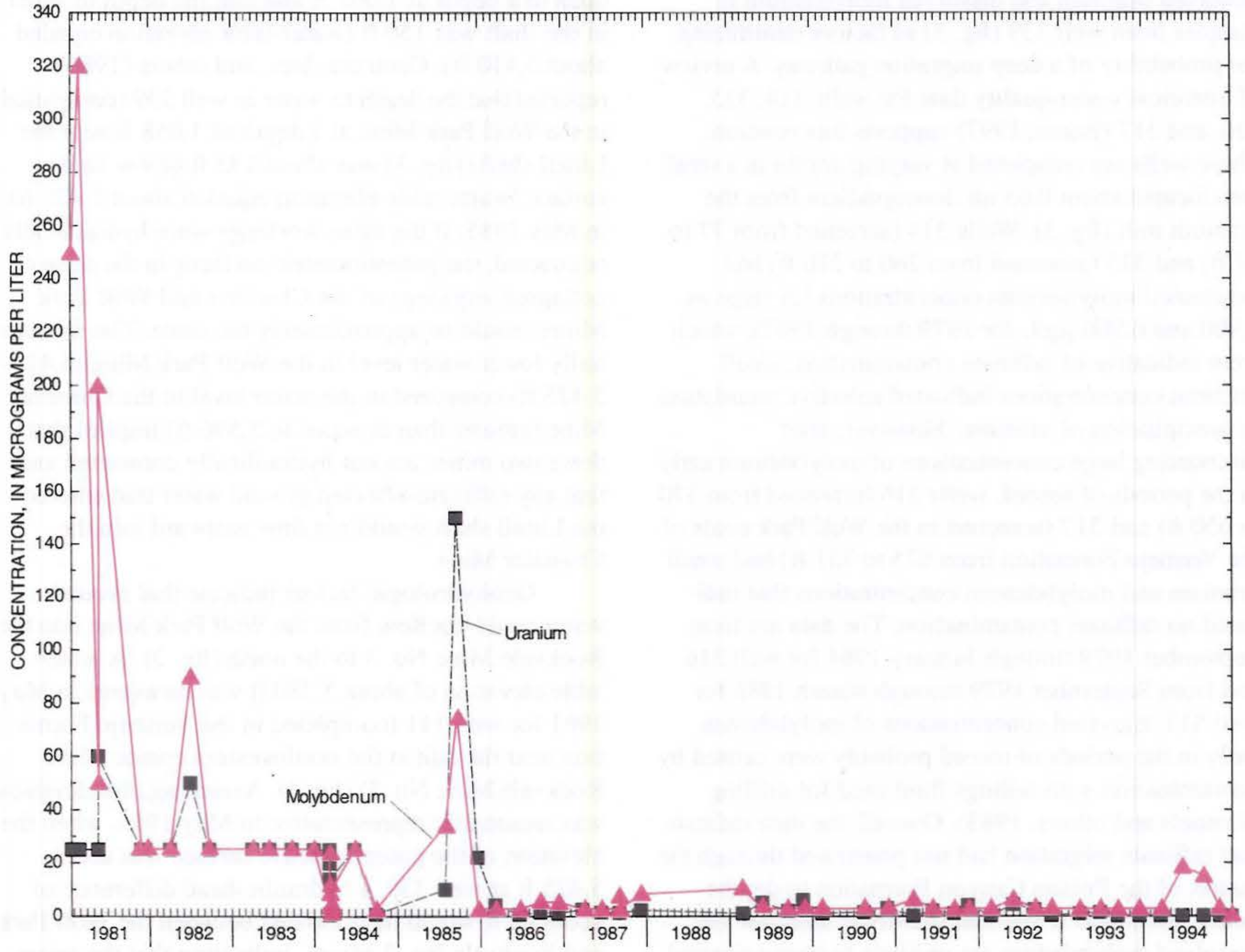


Figure 13. Temporal distribution of concentrations of dissolved uranium and dissolved molybdenum for well 339.

moderately elevated molybdenum concentrations probably were caused by alkaline leaching by cement-affected water introduced during well completion. Uranium and molybdenum concentrations subsequently stabilized to minimal concentrations (except for briefly in late 1985, when uranium concentrations apparently increased to 150 µg/L and molybdenum concentrations apparently increased to 75 µg/L).

When sampled on January 26, 1995, water from well 339 had a strong odor of H_2S, which indicates reducing conditions. Such conditions are expected in the mine because of the presence of coal and pyrite. The reducing conditions in the Wolf Park Mine are not conducive to transport of either dissolved uranium or dissolved molybdenum.

GEOCHEMICAL EVOLUTION OF RAFFINATE-AFFECTED GROUND WATER ALONG MIDDLE PATHWAY

This section examines the chemical evolution of raffinate-affected ground water from the vicinity of the old unlined ponds, through Sand Creek gap, and into Lincoln Park. Downgradient trends in water types and stable isotopes at selected sites and wells are used in development of a conceptual framework for mass-balance reaction modeling. After discussion of modeling for selected pathway segments, an overview of processes affecting the chemical evolution of raffinate-affected ground water is presented.

Water Types

Examination of chemical water types along the middle (primary) near-surface pathway provides preliminary insights into water/matrix and water/water (mixing) interactions. More detailed analyses of these interactions can be made with mass-balance reaction modeling (presented in the "Mass-Balance Reaction Modeling" section). Water types are herein illustrated by trilinear Piper diagrams (Piper, 1944). Briel (1993) reported on the usefulness of Piper diagrams to test linear binary- and ternary-mixing hypotheses.

Site 701, a subdrain collection sump downgradient from the old tailings ponds (fig. 3), has yielded the most highly concentrated raffinate-affected ground water in the study area. A Piper plot of water analyses from this site (fig. 14) shows a sodium sulfate water type. Well 312, about 0.42 mi downgradient from site 701 (fig. 3), had a very similar sodium sulfate water type (fig. 14). Well 333, about halfway between these two sites (fig. 3), has a water type that ranges between sodium sulfate and sodium calcium sulfate and that has a greater proportion of calcium than does water from site 701 and well 312 (fig. 14). Water from well 333 presumably represents a modified mixture of raffinate-affected ground water and Sand Creek alluvial water like the water from well 24 (fig. 14), an alluvial well located adjacent to Sand Creek near the hogback (fig. 3). Accordingly, well 333 cannot be considered to be directly in the flow path between site 701 and well 312.

As ground water flows to the SCS reservoir (site 5) and to well 330 near the northern toe of the SCS dam (inset, fig. 3), it retains its sodium sulfate water type (fig. 15). Municipal water from site 997 has a mixed water type that is dominated by calcium and bicarbonate ions (fig. 15). Since 1990, mixing of this water with raffinate-affected ground water at well 330 during dam-to-ditch flushing has not appreciably affected the water type at well 330 because water from site 997 is too slightly mineralized, in accordance with the two-component mixing effects described by Briel (1993).

Water types (fig. 16) from well 138 (fig. 3) vary considerably and seem to be the result of mixing of two end-member water types. The proximity of well 138 to the DeWeese Dye Ditch makes ditch water (site 526) (fig. 3) an obvious candidate for mixing with raffinate-affected ground water, and historical data (Banta, 1997) indicate an annual cycle of about tenfold dilution of sulfate concentrations during summer months when the ditch is flowing. However, the composite plot of water types (upper part of fig. 16) does not seem to indicate a substantial mixing of water from site 526 with water from well 138 because of the much smaller concentrations of major ions in water from the ditch.

Plots of water analyses (fig. 17) from selected wells completed in the Vermejo Formation to the south of well 138 indicate that alluvial ground water at well 138 trends toward a composition resembling water from the Vermejo Formation during July through September, when the DeWeese Dye Ditch is flowing. During December through March, alluvial ground water at well 138 assumes a type that more closely resembles raffinate-affected alluvial ground water from well 330 (fig. 15). The seasonal variation in water types at well 138 indicates that brackish ground water of a sodium bicarbonate type mixes with raffinate-affected ground water from the middle (primary) near-surface pathway during months of ditch flow. Information discussed in the "Stable-Isotope Trends" section indicates that this water probably does not discharge directly from the Vermejo Formation. Instead, this water probably has recharged the near-surface fracture system of the Vermejo Formation at and north of the Raton ridge and east of the saturated alluvium near Sand Creek. Mixing of this water with raffinate-affected ground water produces a water type during the summer that more closely resembles water from wells completed deeper in the Vermejo Formation (fig. 17).

The water type of samples from alluvial wells 124 and 129 (fig. 16; well locations in fig. 3) consists of calcium magnesium bicarbonate water that is almost identical to the water type of samples from site 526 (fig. 3) on the DeWeese Dye Ditch. This similarity indicates that alluvial water in the vicinity of wells 124 and 129 is mostly water from this ditch and lateral ditches. The water type of well 144 (fig. 17) [downgradient from well 138 (fig. 3)], which is very similar to the water type at site 526 (fig. 16), indicates minor mixing of raffinate-affected ground water that has a water type like the water type from well 330 (fig. 15). Other alluvial wells in Lincoln Park had the same water type (Hearne and Litke, 1987, their fig. 16) as site 526, indicating that alluvial water in Lincoln Park downgradient from the DeWeese Dye Ditch is largely derived from ditch water. This conclusion is consistent with findings described in Banta (1994) that

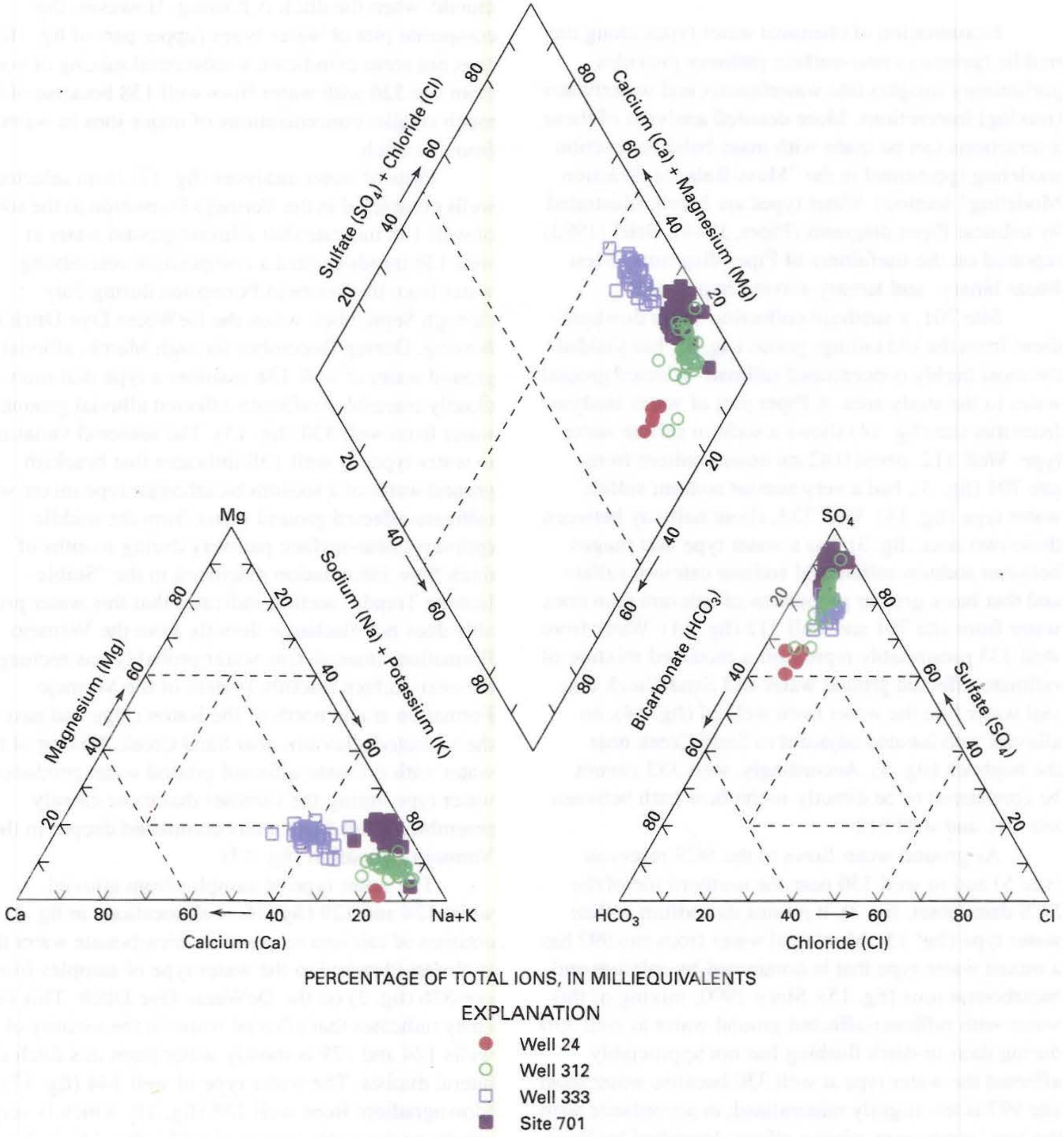


Figure 14. Water types for wells and sites in the vicinity of the old tailings ponds.

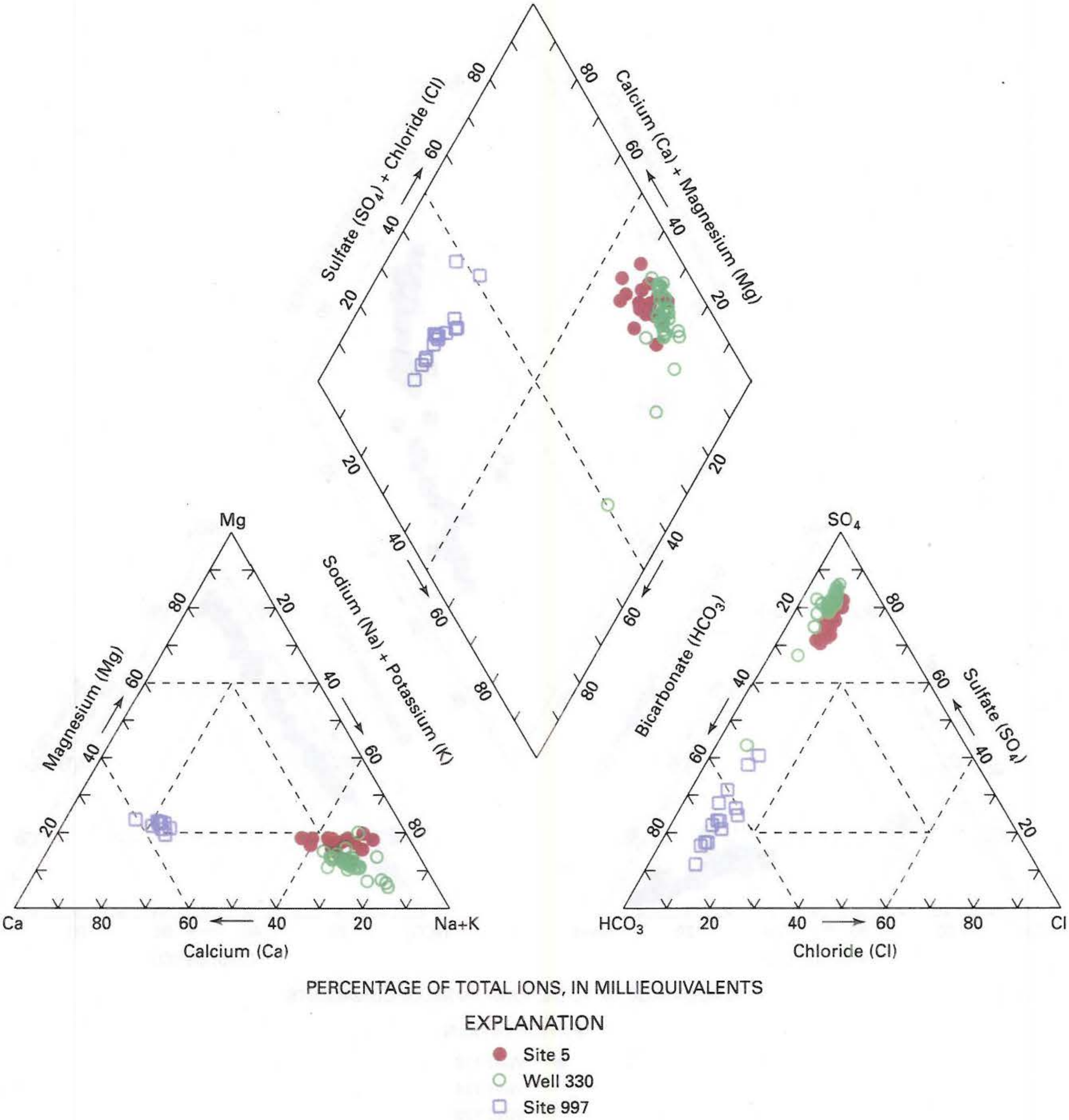
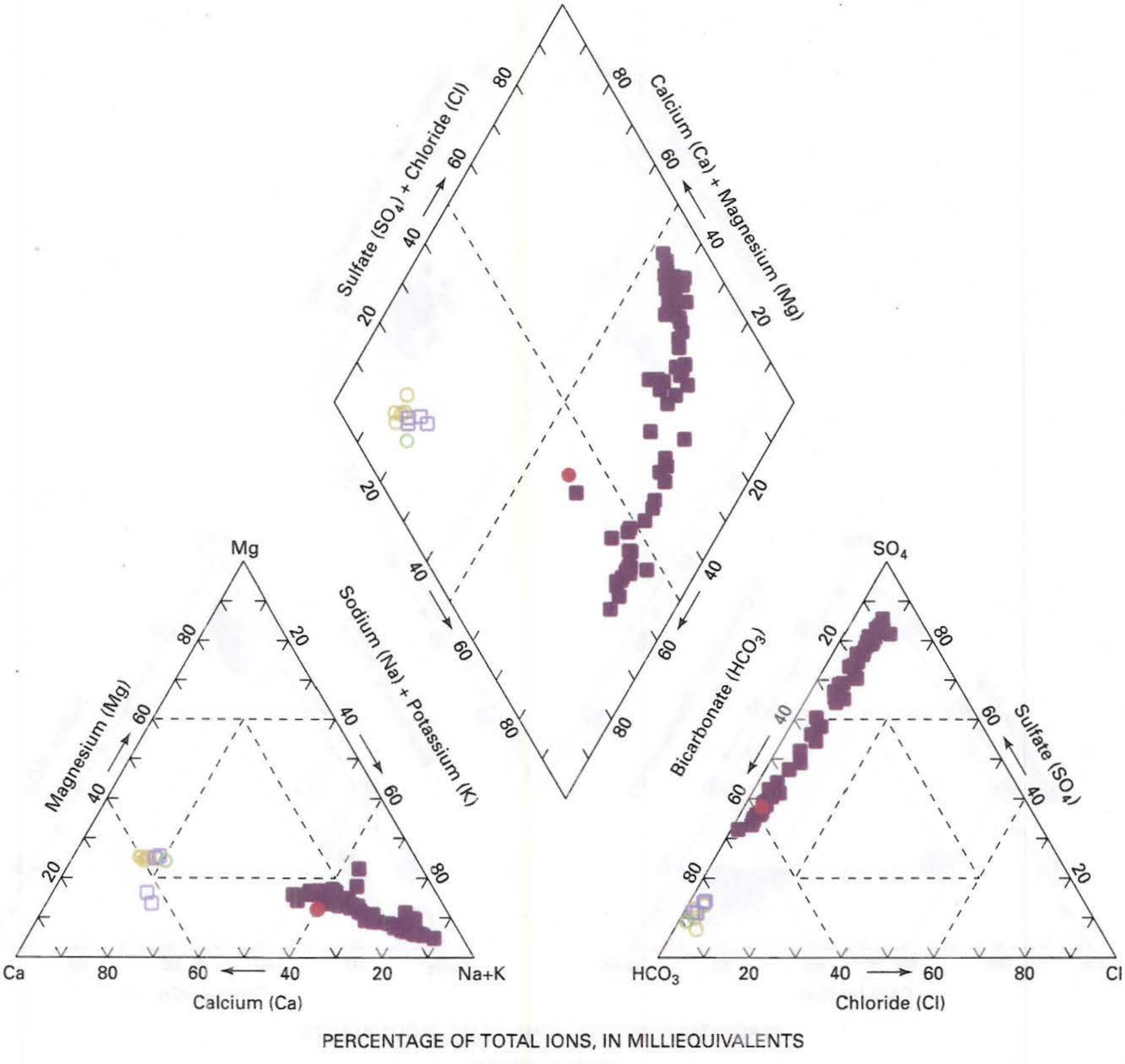


Figure 15. Water types for wells and sites in the vicinity of the Raton ridge.



EXPLANATION

- ● Well 119
- ○ Well 124
- □ Well 129
- ■ Well 138
- ○ Site 526

Figure 16. Water types for wells and sites in the vicinity of Lincoln Park.

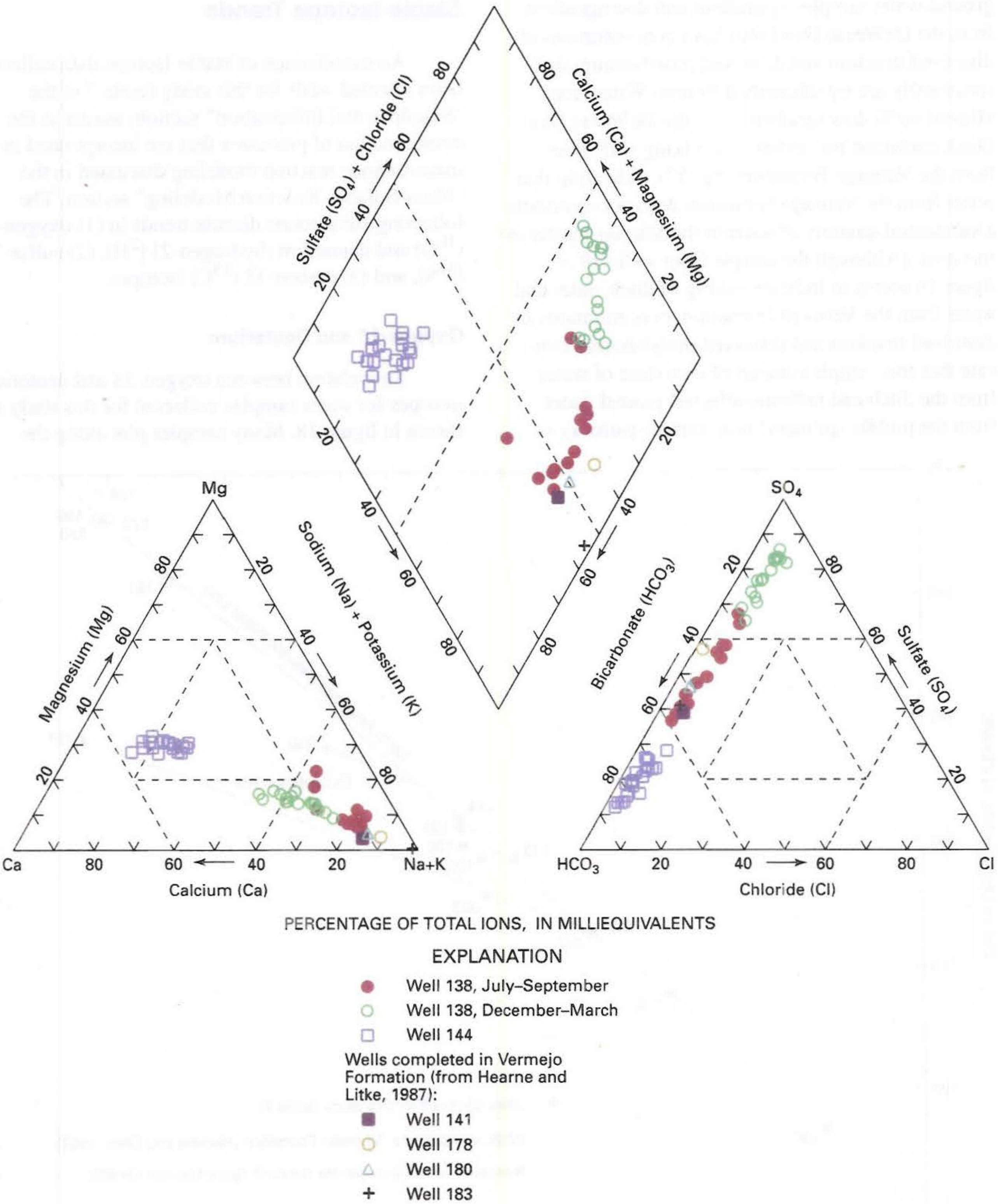


Figure 17. Water types for wells 138 and 144 and for selected wells completed in the Vermejo Formation.

ground-water samples upgradient and downgradient from the DeWeese Dye Ditch have concentrations of dissolved uranium and dissolved molybdenum that statistically are significantly different. Water from alluvial wells downgradient from the DeWeese Dye Ditch contained no evidence of mixing with water from the Vermejo Formation (fig. 17), indicating that water from the Vermejo Formation does not contribute a substantial quantity of water to the alluvial aquifer in this area. [Although the sample from well 119 in figure 16 seems to indicate mixing of ditch water and water from the Vermejo Formation, concentrations of dissolved uranium and dissolved molybdenum indicate that this sample consists of a mixture of water from the ditch and raffinate-affected ground water from the middle (primary) near-surface pathway.]

Stable-Isotope Trends

An examination of stable-isotope data collected from selected wells for this study (table 7 in the "Supplemental Information" section) assists in the determination of processes that are incorporated in mass-balance reaction modeling discussed in the "Mass-Balance Reaction Modeling" section. The following subsections discuss trends in (1) oxygen-18 (^{18}O) and deuterium (hydrogen-2) (^{2}H), (2) sulfur-34 (^{34}S), and (3) carbon-13 (^{13}C) isotopes.

Oxygen-18 and Deuterium

The relation between oxygen-18 and deuterium isotopes for water samples collected for this study is shown in figure 18. Many samples plot along the

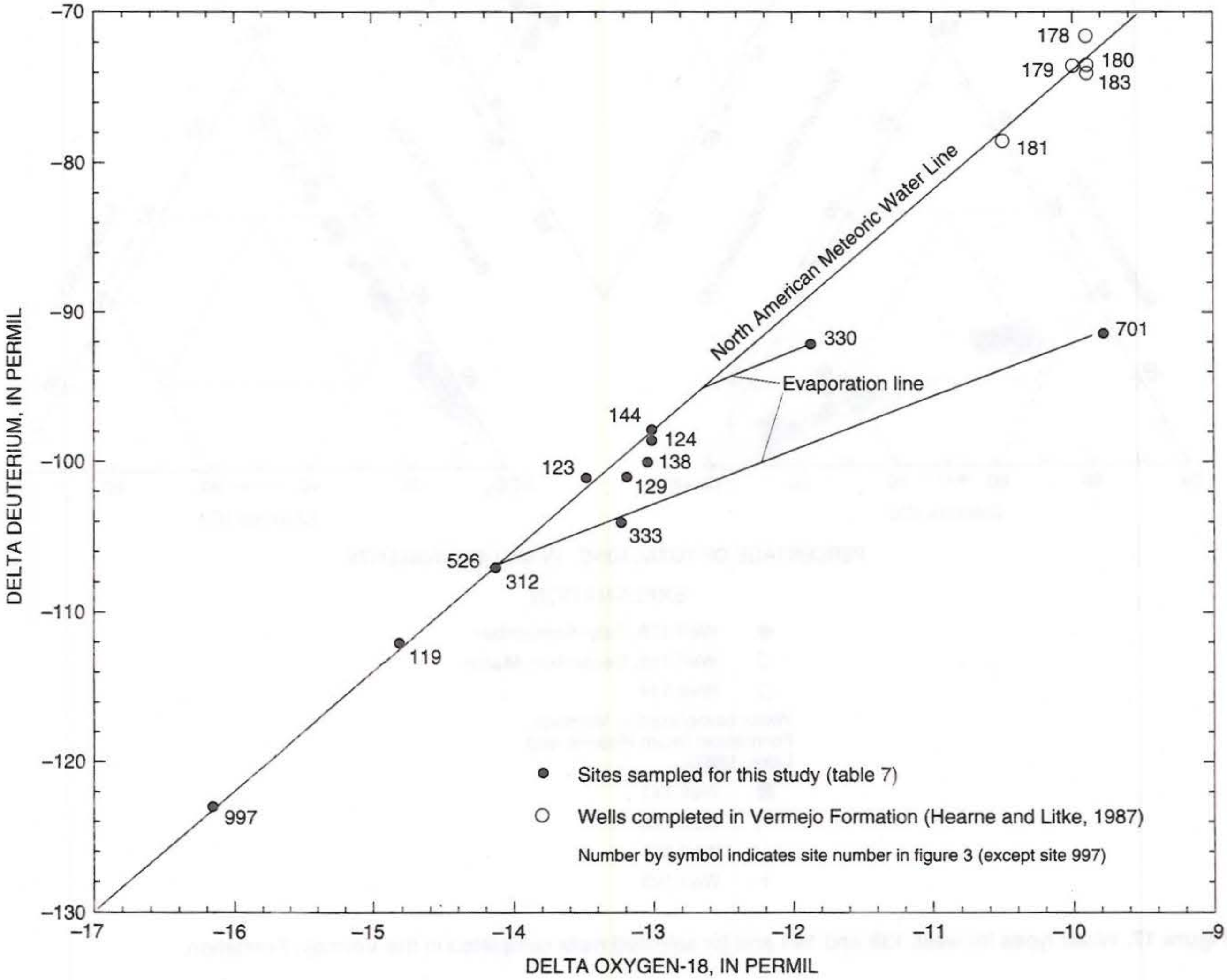


Figure 18. Relation of delta oxygen-18 to delta deuterium for water.

North American meteoric water line defined by the relation $\delta D = 8\delta^{18}O + 6$ (Coplen, 1993). Samples collected from the DeWeese Dye Ditch (site 526) and from the municipal-water supply at the uranium mill (site 997, which was treated water from the Arkansas River) conform to the meteoric water line because they represent composite water from their respective drainages. However, water from these two sites could plot at different locations along the meteroric water line at varying times. Alluvial ground-water samples from Lincoln Park that conform to the water line (wells 119, 123, 124, and 144) are located downgradient from the DeWeese Dye Ditch and are largely derived from water from that ditch (as discussed in the "Water Types" section), except that the sample from well 119 also seems to contain an appreciable fraction of municipal water from site 997 that was injected during the dam-to-ditch flush in late 1994 and that came from a nearby cistern sewage-disposal facility.

Samples that are substantially offset to the right of the meteoric water line are affected by evaporation and plot along lines that have slopes less than 8 (Coplen, 1993). Two evaporation lines shown in figure 18 are plotted with a slope of 3.5. Site 701 has the greatest amount of evaporation. Samples from wells 312 and 333 plot along an evaporation line with site 701, indicating downgradient dilution of evaporated water with fresh recharge water. The sample from well 330, downgradient from wells 312 and 333, plots along an evaporation line that indicates a similar degree of dilution of evaporated water as in well 333. Samples from wells 129 and 138 have a minor component of evaporated water. Because well 129 is downgradient from well 124 and has a water type indicative of ditch water, the slight evaporation of water upgradient from that well probably results from evaporation of ditch and ground water used for irrigation in Lincoln Park.

The sample from well 138, which was postulated in the "Water Types" section to result from mixing of raffinate-affected ground water similar to ground water at well 330 and water recharging the near-surface fracture system of the Vermejo Formation, does not plot in figure 18 between the sample for well 330 and samples from wells completed deeper in the Vermejo Formation. Therefore, water from well 138 cannot be a mixture of these two water types. Based on ^2H and ^{18}O content, water from well 138 is a mixture of water from the vicinity of well 330 and a water similar to ditch water (site 526) or dam-to-ditch injection water (site 997). This conclusion is consistent with the hypothesis that modern precipitation is recharging the near-surface fracture system of the Vermejo Formation to the south of well 138 and that this fracture water mixes with raffinate-affected ground water in the vicinity of well 138, resulting in a water type similar to the type of water deeper in the Vermejo Formation.

Sulfur-34

The relation of dissolved-sulfate concentration to sulfate sulfur-34 isotopic composition ($\delta^{34}S$) (fig. 19) indicates downgradient trends. Samples from sites 701, 333, 330, and 312 have $\delta^{34}S$ values near –2 permil and predominantly contain sulfate originating in the uranium-milling process; although $\delta^{34}S$ is essentially invariant among these sites, sulfate concentrations generally are diluted downgradient by water containing small sulfate concentrations. Wells 119 and 138, both downgradient from well 330, have divergent $\delta^{34}S$. These two sites are along divergent flow paths, as indicated by the split of the raffinate plume (fig. 4). Well 119 is on the northern branch of the raffinate plume and has a slight increase in $\delta^{34}S$, caused by mixing of raffinate-affected ground water with either water recharged from the DeWeese Dye Ditch or water injected for the dam-to-ditch flush, or both; wells 124 and 129 had a more advanced stage of this downgradient mixing trend.

Well 138 (fig. 3) is along the eastern branch of the raffinate plume (fig. 4) and has substantially smaller $\delta^{34}S$ than does well 330 (fig. 19). This difference is consistent with mixing of raffinate-affected ground water with near-surface water from the Vermejo Formation that has lighter $\delta^{34}S$ and that flowed from the south toward the vicinity of well 138. Wells 180 and 183, although yielding water from deeper in the Vermejo Formation, have smaller $\delta^{34}S$ than does well 138. Well 178, which produces water from the near-surface Vermejo Formation (between about 30 to 55 ft in depth) about 0.25 mi southwest of well 138 (fig. 3), has a $\delta^{34}S$ of –9.1 permil. The smaller $\delta^{34}S$ values of dissolved sulfate in the Vermejo Formation probably are caused by dissolution of isotopically lighter pyritic and organic sulfur from the rock matrix. Wells 123 and 144 (fig. 3), which are located sequentially downgradient from well 138 along the eastern raffinate plume branch (fig. 4), have

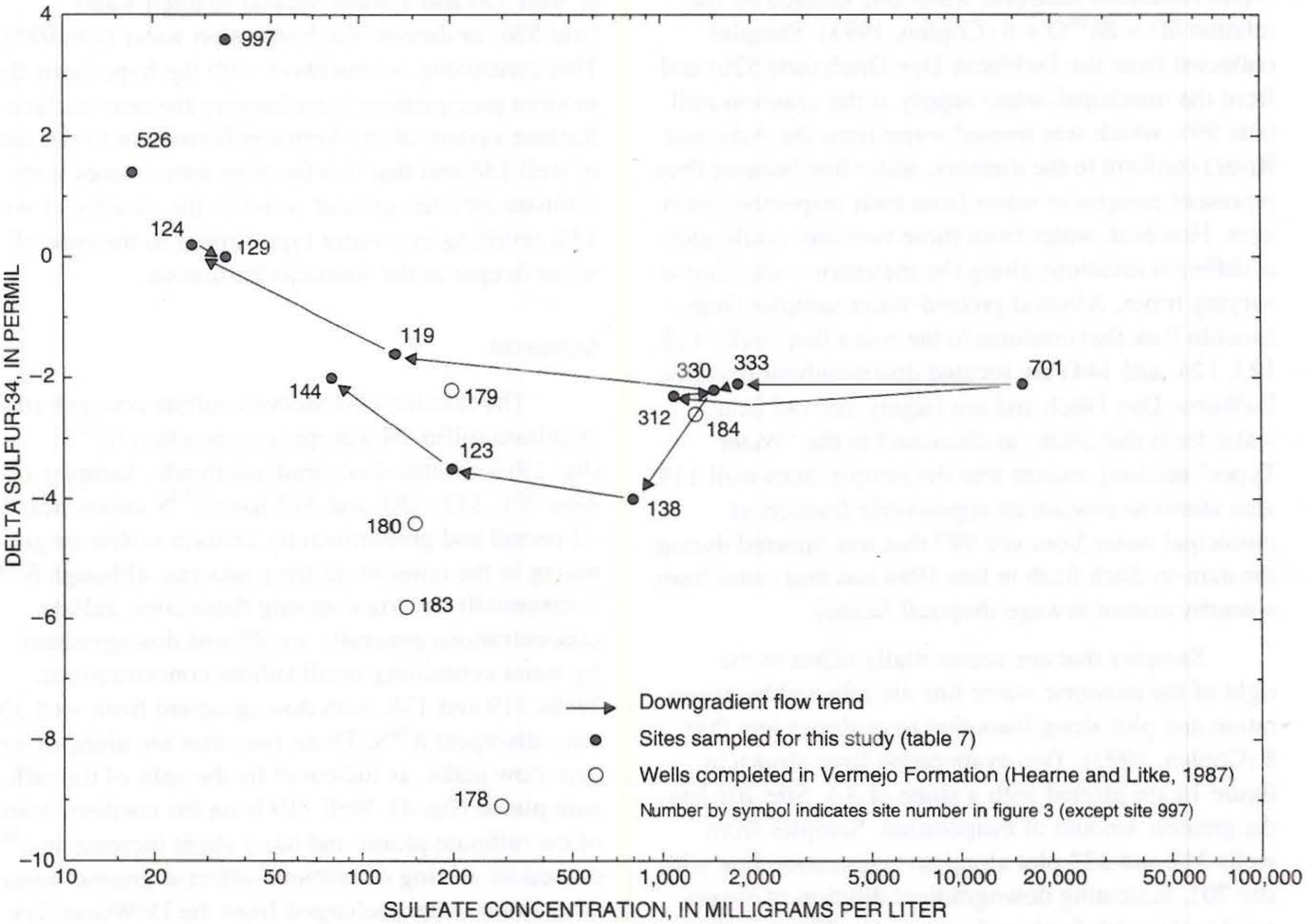


Figure 19. Relation of concentration of dissolved sulfate to delta sulfur-34.

sulfate $\delta^{34}S$ trending toward the ratio of DeWeese Dye Ditch water (site 526), consistent with progressive mixing of ditch water with raffinate-affected ground water and near-surface water from the Vermejo Formation.

Carbon-13

The relation of carbon-13 isotopic composition of inorganic carbon ($\delta^{13}C$) to alkalinity concentration (fig. 20) indicates a general downgradient decrease in $\delta^{13}C$. Generally, this decrease can be attributed to (1) dissolution of isotopically light carbon dioxide from the unsaturated zone and (2) isotopic exchange of dissolved inorganic carbon with dissolved carbon dioxide in the unsaturated zone in the near-surface ground-water environment of the study area. Soil carbon dioxide gas generally has $\delta^{13}C$ between −20 and −25 permil (Plummer and others, 1983). According to relations presented by Mook (1986), bicarbonate resulting from dissolution of soil carbon dioxide gas at 15°C would be 9.0 permil heavier than carbon dioxide at equilibrium. The $\delta^{13}C$ of this bicarbonate, therefore, would be about −11 to −16 permil. However, rapid dissolution of carbon dioxide gas from the unsaturated zone, as occurs during the rapid recharge of flood water or injected water, can cause partial or complete disequilibrium between carbon dioxide gas and bicarbonate. Dissolving bicarbonate can have a $\delta^{13}C$ between −11 and −25 permil. Isotopic exchange (which does not involve net dissolution of carbon dioxide) between bicarbonate and carbon dioxide gas would tend to produce bicarbonate with $\delta^{13}C$ between about −11 and −16 permil at 15°C.

Mass-Balance Reaction Modeling

Mass-balance reaction modeling is a procedure used to quantitatively describe hydrogeochemical

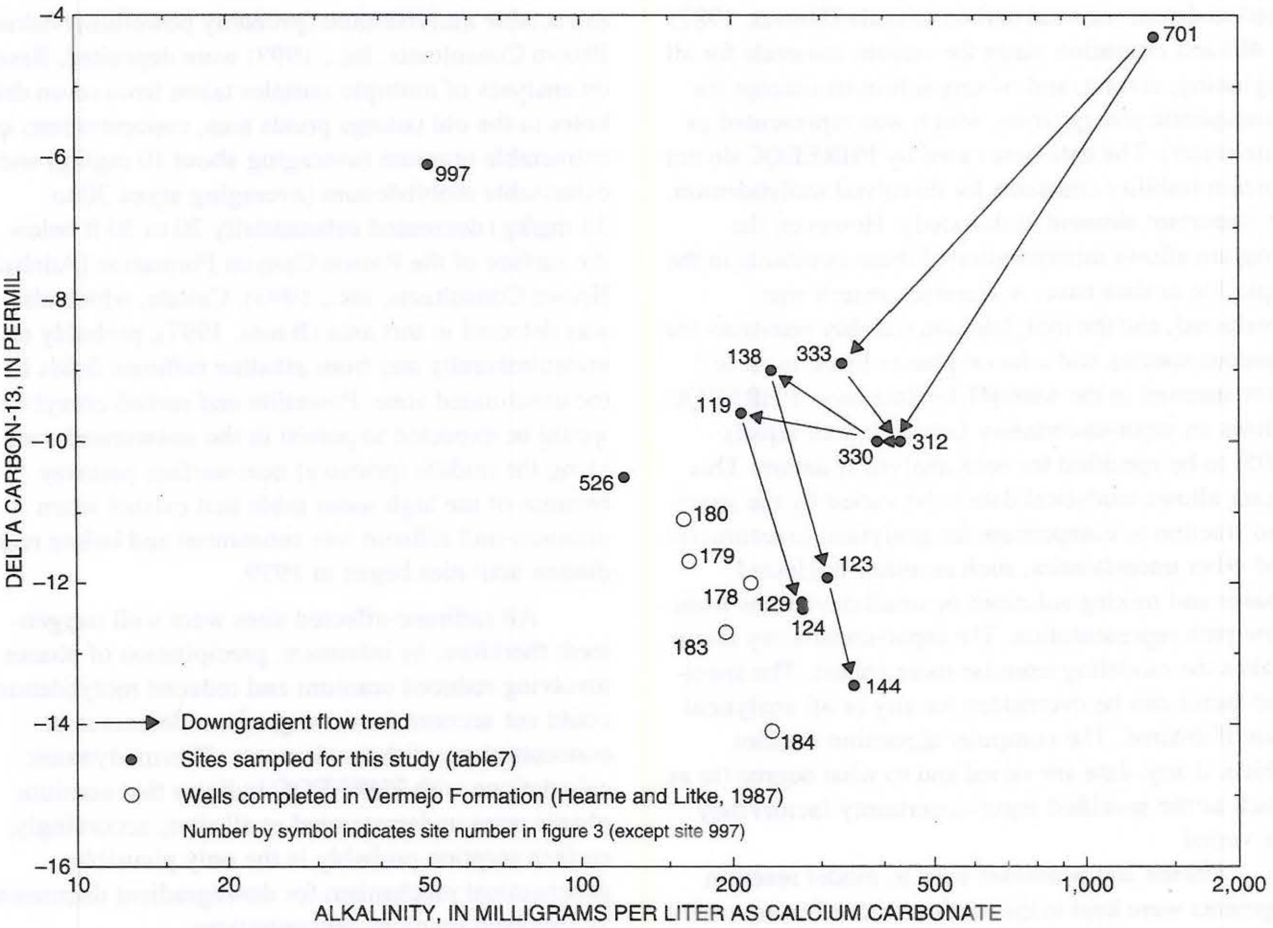


Figure 20. Relation of alkalinity to delta carbon-13.

processes that occur along a hydrogeologic flow path (Plummer and Back, 1980; Parkhurst and others, 1982; Plummer and others, 1994; Parkhurst, 1995). This type of modeling requires two or more water analyses that represent water along a flow path. Processes that can be modeled are (1) dissolution and exsolution of gases, (2) dissolution and precipitation of solid phases, (3) mixing of waters, (4) evaporation and dilution, (5) oxidation-reduction reactions, and (6) sorption and ion-exchange reactions. Mass-balance reaction modeling requires water-quality analyses of beginning, ending, and mixing solutions; selection of a plausible set of reacting and produced phases that can account for the evolution of water chemistry; and thermodynamic constraints to assist in the selection of models. The product of mass-balance reaction modeling is one or more balanced reactions of the form:

Initial solution(s) + reactant phases =
final solution + product phases. (3)

For a given model input, mass-balance reaction modeling usually produces several to numerous alternative geochemical models. The most acceptable model, if any, is the one that is consistent with the hydrogeologic system, saturation states of selected phases, and any isotopic constraints. For example, if calcite is saturated or oversaturated in beginning and ending solutions, then calcite probably is not dissolving in that segment unless it is doing so in a mixing solution (such as recharging atmospheric precipitation). Similarly, calcite is unlikely to be precipitating if it is undersaturated in all solutions in a given model.

Plausible geochemical reactions along selected ground-water pathway segments were investigated using the thermodynamic, inverse-modeling capabilities of PHREEQC (Parkhurst, 1995). PHREEQC was used to determine total carbon dioxide (Drever, 1982, p. 40) and saturation states for various minerals for all beginning, ending, and mixing solutions (except for atmospheric precipitation, which was represented as pure water). The data bases used by PHREEQC do not contain stability constants for dissolved molybdenum, an important element in this study. However, the program allows incorporation of these constants in the input file or data base. A literature search was conducted, and the molybdenum stability constants for aqueous species and mineral phases listed in table 3 were inserted in the wateq4f.dat data base. PHREEQC allows an input-uncertainty factor (default equals 0.05) to be specified for each analytical datum. This factor allows analytical data to be varied by the specified fraction to compensate for analytical inaccuracies and other uncertainties, such as minor neglected phases and mixing solutions or small deviations from flow-path representation. The input-uncertainty factor makes the modeling exercise more robust. The specified factor can be overridden for any or all analytical data, if desired. The computer algorithm decides which, if any, data are varied and to what degree (to as much as the specified input-uncertainty factor) they are varied.

Phases and processes used to model reaction segments were kept to the minimum number necessary to produce realistic models. Silicate phases were ignored because reaction kinetics for silicates are too slow to account for appreciable mass transfers during the relatively short flow times between modeled sites. Calcite and carbon dioxide gas were ubiquitous and, therefore, were included as phases in all models. Ion exchange of major cations (calcium, magnesium, and sodium) was included as a potential process in all model inputs. Fourteen solid-phase analyses (Banta, 1997) indicate whole-sample cation-exchange capacities between 0.2 and 14 (median 1.3) meq/100g and indicate that exchangeable cations generally predominate in the relative order Ca>Mg>Na>K.

Minerals were deposited in the unsaturated zone in the vicinity of the old tailings ponds by raffinate solutions during plant operation before produced tailings were placed in the lined impoundment (beginning in late 1979). To a lesser extent, this process may have continued until the tailings were dredged from the old tailings ponds and placed in the lined impoundment during 1981–83. Solid-phase analyses indicate that gypsum and powellite (Banta, 1997)—possibly introduced in surficial trash—and extractable uranium and extractable molybdenum (probably powellite) (Adrian Brown Consultants, Inc., 1993) were deposited. Based on analyses of multiple samples taken from seven drill holes in the old tailings ponds area, concentrations of extractable uranium (averaging about 10 mg/kg) and extractable molybdenum (averaging about 30 to 35 mg/kg) decreased substantially 20 to 30 ft below the surface of the Poison Canyon Formation (Adrian Brown Consultants, Inc., 1993). Calcite, which also was detected in this area (Banta, 1997), probably originated naturally and from alkaline raffinate fluids in the unsaturated zone. Powellite and sorbed uranyl ions would be expected to persist in the unsaturated zone along the middle (primary) near-surface pathway because of the high water table that existed when uranium-mill effluent was substantial and before remediation activities began in 1979.

All raffinate-affected sites were well oxygenated; therefore, by inference, precipitation of phases involving reduced uranium and reduced molybdenum could not account for downgradient decreases in concentrations of these elements. Thermodynamic calculations with PHREEQC indicate that uranium phases were undersaturated at all sites; accordingly, surface sorption probably is the only plausible geochemical mechanism for downgradient decreases in dissolved uranium concentrations.

Vlek and Lindsay (1977, p. 42) concluded that, in the absence of lead minerals, powellite ($CaMoO_4$) and ferrimolybdite $[Fe_2O_3(MoO_3)_{3.52}{:}10.4H_2O]$ (Kaback and Runnels, 1980) control the solubility of molybdenum in soils. Calculations using PHREEQC indicated that powellite was oversaturated in all samples from sites upgradient from the DeWeese Dye Ditch (except well 24). Therefore, powellite was included as a solid phase for all modeled reaction segments.

Denitrification of dissolved nitrite plus nitrate is a minor process that may occur along some reaction segments, especially in the vicinity of the old tailings ponds. However, nitrogen was not included as an element in reaction models because of (1) the lack of data for concentrations of dissolved nitrite plus nitrate in recharging precipitation and for concentrations of product nitrogen species and (2) the small concentrations of nitrite plus nitrate at beginning and ending sites of most reaction segments (table 4). Instead, processes affecting concentrations of dissolved nitrite plus nitrate are discussed with the model results from

Table 3. Molybdenum speciation and solubility constants added to the wateq4f.dat data base for PHREEQC

[K, speciation or solubility constant at 298 Kelvin]

Reaction	log K	Source
	Aqueous Species	
$MoO_4^{-2} + H^+ = HMoO_4^-$	4.24	Smith and Martell, 1976
$MoO_4^{-2} + 2H^+ = H_2MoO_4$	[1]6.85	Kaback and Runnels, 1980
$MoO_4^{-2} + 3H^+ = MoO_2OH^+ + H_2O$	[1]7.89	Kaback and Runnels, 1980
$MoO_4^{-2} + 4H^+ = MoO_2^{+2} + 2H_2O$	[1]8.34	Kaback and Runnels, 1980
$Ca^{+2} + MoO_4^{-2} = CaMoO_4(aq)$	2.57	Essington, 1990
$Mg^{+2} + MoO_4^{-2} = MgMoO_4(aq)$	3.03	Essington, 1990
$Na^+ + MoO_4^{-2} = NaMoO_4^-$	1.66	Essington, 1990
$K^+ + MoO_4^{-2} = KMoO_4^-$	1.29	Essington, 1990
$MoO_4^{-2} + e^- + 4H^+ = MoO_2^+ + 2H_2O$	[1]20.95	Kaback and Runnels, 1980
$MoO_4^{-2} + 3e^- + 8H^+ = Mo^{+3} + 4H_2O$	[1]29.52	Kaback and Runnels, 1980
$7MoO_4^{-2} + 8H^+ = Mo_7O_{24}^{-6} +4\ H_2O$	[2]57.63	Arnek and Szilard, 1968
$Mo_7O_{24}^{-6} + H^+ = Mo_7O_{23}OH^{-5}$	[2]4.43	Arnek and Szilard, 1968
$Mo_7O_{23}OH^{-5} + H^+ = Mo_7O_{22}(OH)_2^{-4}$	[2]3.56	Arnek and Szilard, 1968
$Mo_7O_{22}(OH)_2^{-4} + H^+ = Mo_7O_{21}(OH)_3^{-3}$	[2]2.62	Arnek and Szilard, 1968
$2Ag^+ + MoO_4^{-2} = Ag_2MoO_4(aq)$	-0.05	Reddy and Drever, 1987
$2Na^+ + MoO_4^{-2} = Na_2MoO_4(aq)$	0.02	Reddy and Drever, 1987
$2K^+ + MoO_4^{-2} = K_2MoO_4(aq)$	0.27	Reddy and Drever, 1987
	Solid Phases	
$CaMoO_4$ (powellite) $= Ca^{+2} + MoO_4^{-2}$	[1]-8.45	Kaback and Runnels, 1980
MoS_2 (molybdenite) $+ 4H_2O = MoO_4^{-2} + 6H^+ + 2e^- + 2HS^-$	[1]-63.44	Kaback and Runnels, 1980
Mo_3O_8 (illsemannite) $+ 4H_2O = 3MoO_4^{-2} + 8H^+ + 2e^-$	[1]-62.90	Kaback and Runnels, 1980
$Fe_2O_3(MoO_3)_{3.52}{:}10.4H_2O$ (ferrimolybdite) $= 2Fe^{+3} + 3.52MoO_4^{-2} + 9.88H_2O + 1.04H^+$	[1]-34.9	Kaback and Runnels, 1980
$Fe_2(MoO_4)_3$ (ferric molybdate) $+ 3H^+ = 2Fe^{+3} + 3HMoO_4^-$	-26.10	Vlek and Lindsay, 1977
$FeMoO_4$ (ferrous molybdate) $= Fe^{+2} + MoO_4^{-2}$	-7.70	Reddy and Drever, 1987
$MgMoO_4$ (magnesium molybdate) $= Mg^{+2} + MoO_4^{-2}$	-0.57	Reddy and Drever, 1987
$MnMoO_4$ (manganous molybdate) $= Mn^{+2} + MoO_4^{-2}$	-4.12	Reddy and Drever, 1987
Mo_3O_8 (molybdenum oxide) $+ 4H^+ + e^- = 3MoO_2^+ + 2H_2O$	-0.45	Vlek and Lindsay, 1977
MoO_3 (molybdite) $+ H_2O = MoO_4^{-2} + 2H^+$	-12.05	Reddy and Drever, 1987
Ag_2MoO_4 (silver molybdate) $= 2Ag^+ + MoO_4^{-2}$	-11.54	Reddy and Drever, 1987
$BaMoO_4$ (barium molybdate) $= Ba^{+2} + MoO_4^{-2}$	-7.45	Reddy and Drever, 1987
$CuMoO_4$ (copper molybdate) $= Cu^{+2} + MoO_4^{-2}$	-6.81	Reddy and Drever, 1987
Li_2MoO_4 (lithium molybdate) $= 2Li^+ + MoO_4^{-2}$	2.35	Reddy and Drever, 1987
Na_2MoO_4 (sodium molybdate) $= 2Na^+ + MoO_4^{-2}$	1.00	Reddy and Drever, 1987
$PbMoO_4$ (lead molybdate) $= Pb^{+2} + MoO_4^{-2}$	-16.01	Reddy and Drever, 1987
$ZnMoO_4$ (zinc molybdate) $= Zn^{+2} + MoO_4^{-2}$	-4.48	Reddy and Drever, 1987

[1] Calculated from Gibbs free energies at 298 Kelvin and 1 atmosphere total pressure.

[2] Calculated from enthalphy and entrophy data at 298 Kelvin

Table 4. Water-quality data for sites used in mass-balance reaction modeling

[mg/L, milligrams per liter; total carbon dioxide was calculated by PHREEQC (Parkhurst, 1995); mmol/L, millimoles per liter; sum, sum of constituents; μg/L, micrograms per liter; --, no data; all sites were sampled by the U.S. Geological Survey, except for wells 24 and 313, which were sampled by the Cotter Corporation on December 28, 1994, and December 9, 1993]

Property or constituent	Well or site											
	24	119	124	138	144	312	313	330	333	526	701	997
pH, standard units	7.91	7.43	7.17	7.80	6.99	7.89	7.71	7.37	7.23	8.49	7.37	7.38
Alkalinity, mg/L as $CaCO_3$	260	208	271	239	350	429	440	388	330	155	1,370	61
Total carbon dioxide, mmol/L	5.31	4.50	6.24	4.90	8.64	8.76	9.08	8.41	7.33	2.37	28.0	1.33
Dissolved solids, sum, mg/L	1,220	445	337	1,520	518	2,280	3,980	2,750	3,300	194	26,400	126
Calcium, mg/L	57	41	67	86	96	41	78	150	230	44	350	26
Magnesium, mg/L	3	11	18	32	32	22	44	59	110	11	970	6.1
Sodium, mg/L	350	100	27	370	36	700	1,300	660	650	10	6,800	7.4
Potassium, mg/L	2.1	2.8	3.3	2.6	2.4	0.9	2.0	3.7	5.2	1.2	15	0.9
Chloride, mg/L	63	10	4.0	43	6.4	85	170	97	140	2.1	770	6.7
Sulfate, mg/L	590	130	27	800	80	1,100	2,100	1,500	1,800	17	16,000	35
Nitrite plus nitrate, mg/L as N	--	0.5	1.0	2.5	1.0	7.7	--	5.4	30	<0.05	150	0.07
Molybdenum, μg/L	16	1,800	250	5,200	150	9,600	18,000	9,600	6,900	1	84,000	2
Uranium, μg/L	4.6	140	47	570	40	2,000	3,000	1,900	3,700	2.5	89,000	1.2

selected reaction segments in the following subsections.

The locations of sites used for reaction modeling are shown in figure 21. Models were generated for the following eight reaction segments:

1. Well 24 and site 701 to well 333;
2. Site 701 to well 312;
3. Site 701 to well 313;
4. Wells 313 and 333 to well 330;
5. Well 330 to well 138;
6. Well 138 to well 144;
7. Well 330 to well 119; and
8. Well 119 to well 124.

Site 701 (fig. 21), which is a 20-ft-deep sump that collects raffinate-affected ground water from a buried trench that stretches to the west from the sump toward the uranium mill, yields saline water (tables 5 and 7) that represents the most concentrated leachate detected in the study area. Therefore, water from site 701 is used in reaction modeling to represent the general type of water generated from leaching of the unsaturated zone in the area of the old tailings ponds. Water from the vicinity of site 701 has migrated northeastward toward wells 312, 313, and 333 (as discussed in the "Middle Near-Surface Pathway" section) and westward, affecting water quality in the vicinity of well 802, which is located west of Sand Creek (fig. 3) (as discussed in the "West Near-Surface Pathway" section). Water from well 24 represents water flowing into the Chandler Syncline via Sand Creek alluvium upgradient from well 333, which originates from permeable sandstones in the Poison Canyon Formation adjacent to the Sand Creek alluvium. Well 333, part of a raffinate-pumpback system, yielded an average of 14.5 gal/min from January 1988 through October 1994 (Richard Wooten, Cotter Corporation, written commun., 1995). Therefore, water from site 701 and well 24 represents reasonable source-water types for water from well 333. (The term "source-water type" hereinafter is used to indicate that water from a given site is representative of a water type in that area but is not the actual source of downgradient water.) Furthermore, as indicated in the "Water Types" section, well 333 is not located directly upgradient from well 312, which is consistent with divergent $\delta^{13}C$ trends between site 701 and well 333 and between site 701 and well 312 (fig. 20). Accordingly, separate reaction segments were modeled from site 701 to well 333 and from site 701 to well 312.

Wells 312 and 313 are located near the confluence of the channels of Sand Creek and a small, unnamed tributary draining the area east and southeast of the old tailings ponds (fig. 21). Water from wells 312 and 313 originates near the old tailings ponds and the unnamed tributary. Both wells are completed in the Poison Canyon Formation; well 312 is completed from a 10- to 18-ft depth, and well 313 (about 41 ft east of well 312) is completed from a 17- to 37-ft depth. Historical data (Banta, 1997) indicate that dissolved-solids and dissolved-molybdenum concentrations were generally greater in water from well 313, a relation consistent with greater recharge of freshwater into the shallow horizon in which well 312 is completed. Both wells are located about 700 ft downgradient from an injection-withdrawal system (fig. 21), where municipal water (site 997) has been injected and water has been withdrawn since September 1989. In 1992, municipal water (site 997) was injected into this system at an average rate of about 10 gal/min, whereas only about 5 gal/min was withdrawn by this system, creating an average recharge of about 5 gal/min (Adrian Brown Consultants, Inc., 1993). Because of the stratification of water at wells 312 and 313, separate mass-balance reaction models are presented for flow paths from the vicinity of site 701 to each well.

Water in the Sand Creek alluvium and in the Poison Canyon Formation north of the area of the old tailings ponds converges toward Sand Creek gap, where most of it is intercepted by the ground-water-collection trenches immediately upgradient from the SCS reservoir and from a sump in the SCS reservoir (site 5) (fig. 3). The SCS reservoir also collects surface water during flow events in Sand Creek. Most of the ground and surface water flowing to the SCS reservoir is pumped into the lined impoundment. However, some of the raffinate-affected ground water flows under or around the SCS dam and through the Sand Creek alluvium on the north side of the dam, as discussed in the "Flow and Chemical Fluxes through Sand Creek Gap" section. Samples collected from well 330 historically represent the most raffinate-affected ground water flowing in the alluvium near the downgradient toe of the dam. Water from wells 313 and 333 and precipitation were modeled as source-water types for well 330.

Modeled end-water wells downgradient from well 330 (wells 119, 124, 138, and 144) were selected

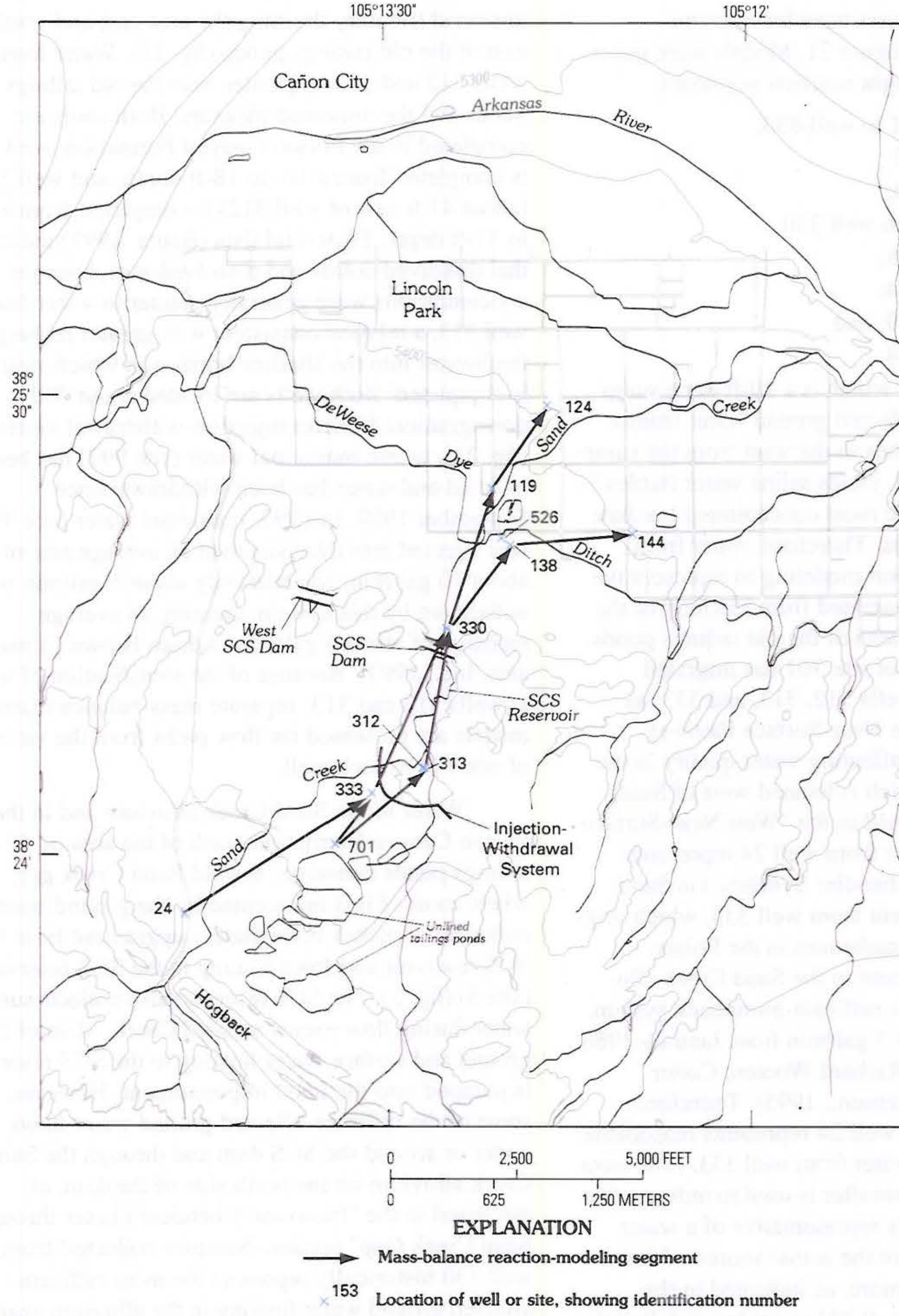


Figure 21. Locations of reaction segments used for mass-balance reaction modeling.

Table 5. Saturation states of selected minerals in water-quality samples collected from sites used in mass-balance reaction modeling

[Saturation states were determined with the thermodynamic computer program PHREEQC (Parkhurst, 1995); a phase was undersaturated (under) if the saturation index was less than –0.10, saturated (sat) if the saturation index was –0.10 to 0.10, or oversaturated (over) if the saturation index was greater than 0.10; --, water-quality analysis insufficient for determination]

Well or site	Sample date	Saturation states						
		Calcite	Dolomite	Gypsum	K-feldspar	Powellite	Quartz	Silica gel
24	12-28-94	over	under	under	--	under	--	--
119	3-15-95	under	under	under	sat	over	over	under
124	3-15-95	sat	under	under	over	under	over	under
138	3- 9-95	over	over	under	sat	over	over	under
144	3- 8-95	sat	under	under	over	under	over	sat
312	3- 8-95	over	over	under	under	over	over	under
313	12- 9-93	over	over	under	--	over	--	--
330	3- 9-95	over	over	under	under	over	over	under
333	3- 1-95	over	over	under	over	over	over	under
526	6-14-95	over	over	under	under	under	over	under
701	3- 2-95	over	over	sat	over	over	over	under
997	6-12-95	under	under	under	under	under	over	under

for mass-balance reaction modeling on the basis of historical data (Banta, 1997), which indicated that these wells are located along the axes of plume migration, a conclusion in agreement with contours of dissolved-uranium and dissolved-molybdenum concentrations in 1988 (ENVIRON Corporation and others, 1991). Wells 119 and 138 are in the vicinity of the DeWeese-Dye Ditch, where the plume divides. Well 119 is about 600 ft downgradient from the ditch; well 138 is about 400 ft upgradient from the ditch. Water from well 330, the dam-to-ditch injection (site 997), and the DeWeese Dye Ditch (site 526) were modeled as source-water types for well 119. Well 330, site 997, and precipitation recharging fractures in the Vermejo Formation south of well 138 (as discussed in the "Water Types" section) were modeled as source-water types for well 138; ditch water was not modeled as a potential source for the sample for well 138, which was collected a few weeks before the ditch was opened to flow. Well 124 is a substantial distance downgradient from well 119 (the source-water type for raffinate-affected ground water) and the ditch, whereas well 144 is a substantial distance downgradient from well 138 (the source-water type for raffinate-affected ground water) and the ditch. Therefore, water from the DeWeese Dye Ditch was modeled as a source-water type for wells 124 and 144, in accordance with analysis of water types (as discussed in the "Water Types" section).

Water-quality data used for reaction models are listed in table 4. Saturation states of selected phases for the sites in reaction segments are listed in table 5. The following subsections describe the results for each of the reaction segments, followed by an overview discussion of all segments. Most of the models in the following discussion incorporate an input-uncertainty factor of 0.05 for constituent concentrations, but a factor of 0.10 was necessary in some models to obtain acceptable model results. Input-uncertainty factors are listed in table 6.

Well 24 and Site 701 to Well 333

Results of mass-balance reaction modeling (table 6) indicate that water from well 333 can be represented as a mixture of water from well 24 (91.4 percent) and from site 701 (8.6 percent). Calcite is oversaturated at sites 24, 701, and 333 (table 5), indicating precipitation of calcite at those sites. The model indicates net precipitation of calcite and powellite and net dissolution of carbon dioxide gas. A small quantity of uranyl (UO_2^{++}) ions were sorbed. Cation exchange is the most important reaction affecting water in this segment, with sodium ions exchanging for calcium and magnesium ions.

Table 6. Results of mass-balance reaction modeling

[Positive reaction coefficient indicates dissolution of phase or desorption of uranyl (UO_2^{++}) ion or exchanged cation; negative reaction coefficient indicates precipitation of phase or sorption of uranyl ion or exchanged cation; Ca^{++}, calcium ion; Mg^{++}, magnesium ion; Na^+, sodium ion; K^+ potassium ion; --, reaction coefficient not generated by model; precip, water from atmospheric precipitation]

End-water well or site	Source-water-type sites	Input-uncertainty factor	Source-water mixing fractions	Reaction coefficients (millimole per liter)							
				Phases			Sorption	Cation exchange			
				Calcite ($CaCO_3$)	Carbon dioxide (CO_2)	Powellite ($CaMoO_4$)	UO_2^{++}	Ca^{++}	Mg^{++}	Na^+	K^+
333	24	[1]0.05	0.914	-0.258	0.326	-0.0041	-0.0169	3.98	1.12	-10.2	--
	701		.086								
312	701	.05	.066	2.79	2.81	.0417	-.0166	-2.97	-1.97	9.91	-0.0241
	997		.934								
313	701	.10	.130	2.51	2.63	.0741	-.0361	-2.47	-3.63	12.21	-.0188
	997		.870								
330	313	.10	.087	1.26	1.38	.0350	-.0037	-1.61	-.801	4.84	--
	333		.678								
	Precip		.235								
138	330	.10	.492	.240	--	.0049	-.0015	-.197	.023	.339	.011
	997		.394								
	Precip		.114								
144	138	[2].05	.083	1.88	3.58	-.0030	-4.1×10^{-5}	-.751	.7923	-.109	.0277
	526		.917								
119	330	[3].05	.067	1.00	1.28	.0121	4.9×10^{-5}	-.968	--	1.90	.0411
	526		.356								
	997		.577								
124	119	.05	.084	1.11	1.97	.0010	.00014	-.529	.288	.430	.0503
	526		.916								

[1] Factor for chloride is 0.06.

[2] Factor for alkalinity and chloride is 0.10.

[3] Factor for chloride is 0.10.

Concentrations of dissolved nitrite plus nitrate decreased from 150 mg/L as N at site 701 to 30 mg/L at well 333 (table 4). Given the mixing fractions for this reaction segment (table 6), if concentrations of dissolved nitrite plus nitrate mixed conservatively, then water from well 24 would have had a concentration of about 19 mg/L as N, probably too large a quantity for ground water entering the Chandler Syncline. Other possible explanations for the large concentration of dissolved nitrite plus nitrate at well 333 include: (1) Mixing of irrigation water that has acquired large concentrations of dissolved nitrate from fertilizer from the Shadow Hills Golf Course, adjacent to Sand Creek; (2) a larger concentration of dissolved nitrite plus nitrate in the actual source water from site 701; and (3) uncertainty in the mixing fractions for well 24 and site 701. If well 333 consisted of 20 percent water from site 701, then no dissolved nitrite plus nitrate would be required in water from well 24.

Site 701 to Well 312

Results of mass-balance reaction modeling from site 701 to well 312 (table 6) indicate that water at well 312 was 6.6 percent like water from site 701 and 93.4 percent like water from site 997, which is injected at the injection-withdrawal system. Although calcite and powellite are oversaturated at site 701 and well 312 (table 5), injection of fresh municipal water (site 997) caused substantial dissolution of calcite and carbon dioxide gas and minor dissolution of powellite from the unsaturated zone. The model also simulated sorption of uranyl ions and exchange of calcium, magnesium, and potassium ions for sodium ions as a major process affecting water chemistry.

Recharge of precipitation—mostly in the small, unnamed tributary during periods of flow—could account for a small fraction of the dilution of raffinate-affected ground water. Because of the small concentrations of dissolved constituents in precipitation and water from site 997, compared to raffinate-affected ground water at site 701 and well 312, model results would not vary substantially if pure water were substituted for municipal water (site 997) in the model input.

Concentrations of dissolved nitrite plus nitrate decreased from 150 mg/L as N at site 701 to 7.7 mg/L as N at well 312 (table 4). Given the mixing fractions for this reaction segment (table 6), if concentrations of dissolved nitrite plus nitrate mixed conservatively, then water at well 312 would have had a concentration of 9.9 mg/L as N, indicating that dilution by water from site 997 accounted for most of the decrease in concentration. Other possible explanations for the apparently small concentration of dissolved nitrite plus nitrate at well 312 include: (1) Slight uncertainty in the mixing fractions for water from sites 701 and 997, (2) a smaller concentration of dissolved nitrite plus nitrate in the actual source water from site 701, and (3) denitrification of nitrite plus nitrate by organic matter. Evidence indicates that minor denitrification is occurring; samples collected for CFC analysis from nearby well 313 contained substantial concentrations of nitrous oxide (N_2O) (Edward Busenberg, U.S. Geological Survey, written commun., 1995), one of the products of denitrification (Freeze and Cherry, 1979). However, because this process is anaerobic and because water from wells 312 and 313 and site 997 had considerable dissolved oxygen (table 7 in the "Supplemental Information" section), if denitrification occurred between site 701 and well 312, it probably occurred near site 701 in pores and fractures that had small-scale, localized reducing conditions. Adding denitrification to the model for this reaction segment produced essentially the same results listed in table 6 (with coefficients within 4.7 percent of the coefficients listed), with consumption of 0.213 mmol/L of organic carbon (as CH_2O) and production of 0.090 mmol/L of N_2 gas.

Site 701 to Well 313

Results of mass-balance reaction modeling from site 701 to well 313 (table 6) are very similar to the results for the reaction segment from site 701 to well 312 (table 6). Source-water types from site 701 (13.0 percent) and site 997 (87.0 percent) were modeled to evolve into water from well 313. Injected water from site 997 dissolved calcite, carbon dioxide gas, and powellite. Sorption of uranyl ions and cation exchange of magnesium, calcium, and potassium ions for sodium ions were modeled as important processes affecting water quality at well 313, as with water from well 312.

Wells 313 and 333 to Well 330

Results of mass-balance reaction modeling from wells 313 and 333 to well 330 (table 6) indicate that most (67.8 percent) of the precursor water comes from alluvial deposits along Sand Creek (represented by water from well 333). The remaining source-water-type fraction comes from precipitation (23.5 percent) and the Poison Canyon Formation (represented by well 313, 8.7 percent). The large fraction of source-water type from well 333, when compared to well 313, is consistent with the greater hydraulic conductivity expected in alluvial deposits along Sand Creek compared to the conductivity in the Poison Canyon Formation and is consistent with the relatively large quantity of water entering the basin from the foothills. Surface water episodically flows down Sand Creek and infiltrates in the stream channel or enters the SCS reservoir, or both.

Model results indicate that calcite, carbon dioxide gas, and powellite dissolved upgradient from well 330. Because calcite and powellite were oversaturated at wells 313, 333, and 330 (table 5) and, thereby, could not dissolve at those wells, dissolution of these phases occurred in the unsaturated zone during infiltration of precipitation or where infiltrating water mixed with ground water, causing localized undersaturation of calcite and powellite. Sorption of uranyl ions and cation exchange of calcium and magnesium ions for sodium are other important processes modeled as affecting water quality at well 330.

The concentration of dissolved nitrite plus nitrate for water from well 333 (table 4) and the mixing fractions for this reaction segment (table 6) indicate that the source-water type from well 330 would have at least 20 mg/L as N of dissolved nitrite plus nitrate if that constituent had mixed conservatively. A feasible mechanism for decreasing concentrations of this nutrient upgradient from well 330 is uptake by vegetation in and around the SCS reservoir. Other factors that may partly affect the small concentration of dissolved nitrite plus nitrate at well 330 are: (1) Uncertainty in the source-water mixing fractions, (2) a smaller concentration of dissolved nitrite plus nitrate in the actual source water from the vicinity of well 333, and (3) denitrification of nitrite plus nitrate by organic matter. Because water from wells 333 and 330, site 997, and presumably, precipitation contained considerable dissolved oxygen, if denitrification occurred in this reaction segment, it occurred in pores and fractures that had locally anaerobic conditions. Organic-rich muds in the SCS reservoir could provide such an environment.

Well 330 to Well 138

Results of mass-balance reaction modeling from well 330 to well 138 (table 6) indicate mixing of a source-water type from well 330 (49.2 percent), water from the dam-to-ditch injection (site 997, 39.4 percent), and recharging precipitation (11.4 percent) from the south and southeast. The modeled sources are consistent with the discussion in the "Water Types" section, which described water from well 138 as consisting of a seasonally varying mixture between raffinate-affected ground water from the vicinity of well 330 and water recharging near-surface fractures in the Vermejo Formation. Although calcite was oversaturated at wells 138 and 330 (table 5), indicating precipitation of that phase, recharging precipitation or injected water could account for the small net dissolution of calcite. Model results also indicate net dissolution (presumably by injected water) of a small quantity of powellite, which was oversaturated at wells 138 and 330 (table 5). Sorption of uranyl ions and cation exchange of calcium ions for sodium, magnesium, and potassium ions are indicated by modeling as being involved in evolution of water at well 138. Dissolution of calcite coupled with this ion-exchange reaction accounts for the sodium bicarbonate composition of precipitation water that recharged the near-surface fracture system of the Vermejo Formation (as was postulated in the "Water Types" section).

Well 138 to Well 144

Results of mass-balance reaction modeling from well 138 to well 144 (table 6) indicate that water from well 144 consists of source-water type from well 138 diluted 11 times with water from the DeWeese Dye Ditch (site 526). Water from the ditch dissolves substantial quantities of calcite and carbon dioxide gas, and raffinate-affected ground water precipitates a small quantity of powellite. Model results also indicate cation exchange of calcium and sodium ions for magnesium and potassium ions and sorption of a very small quantity of uranyl ions.

Well 330 to Well 119

Results of mass-balance reaction modeling from well 330 to well 119 (table 6) indicate mixing of source-water types from well 330 (6.7 percent), the DeWeese Dye Ditch (site 526, 35.6 percent), and municipal water (site 997, 57.7 percent) that was injected for the dam-to-ditch flush and that probably also came from a cistern sewage-disposal facility near well 119. These quantities indicate that raffinate-affected ground water from well 330 was diluted 15 times before it reached well 119. The relative fractions of source-water types from sites 526 and 997 could vary considerably from the fractions listed in table 6, with little effect on overall model results because of similarity in water types (figs. 14 and 15) and because of the small concentrations of dissolved solids, uranium, and molybdenum in water from those two sites compared to water from site 330 (table 4). Results also indicate dissolution of moderate quantities of calcite and carbon dioxide gas and a small quantity of powellite. Model results also indicate sorption of a small quantity of uranyl ions and cation exchange of calcium ions for sodium and potassium ions.

Because the injection trench for the dam-to-ditch flush is only about 100 ft from well 330, oversaturation of calcite at well 330 (table 5) would cause little precipitation of calcite over the approximately 2,900-ft distance between wells 330 and 119. Dissolution of calcite and carbon dioxide gas was caused by injection of water from site 997 and infiltration of water from the DeWeese Dye Ditch. Water from the DeWeese Dye Ditch (site 526), although oversaturated with calcite (table 5), on infiltration could dissolve carbon dioxide from the unsaturated zone (which would lower pH) and become undersaturated with calcite.

Well 119 to Well 124

Results for mass-balance reaction modeling from well 119 to well 124 (table 6) indicate mixing of source-water types from well 119 (8.4 percent) and the DeWeese Dye Ditch (site 526, 91.6 percent). The results also indicate dissolution of moderate quantities of calcite and carbon dioxide gas and a small quantity of powellite. Sorption of uranyl ions and cation exchange of calcium ions for sodium, magnesium, and potassium ions are other important processes modeled to account for the evolution of water along this reaction segment. Results indicate that recharge of water from the DeWeese Dye Ditch flushed traces of uranium and molybdenum from the near-surface alluvial aquifer.

Processes Affecting Evolution

The final results of mass-balance reaction modeling need to be interpreted with caution. Modeled mass-transfer phase coefficients, although mathematically valid, cannot be regarded as precise quantifiers of real-world processes. Ending sites may not be situated exactly downgradient from beginning sites, and samples from beginning sites may not exactly represent precursor water because of temporal variations in water quality. The omission of minor phases and minor sources of mixing water also adds uncertainty to the final results. Despite these caveats, results for the preceding model segments assist in the understanding of the evolution of raffinate-affected ground water from the old tailings ponds area to Lincoln Park, especially for processes affecting migration of dissolved uranium and dissolved molybdenum.

Raffinate-deposited and natural minerals in the vicinity of the old tailings ponds are leached by infiltrating precipitation, producing raffinate-affected ground water. This leachate is oversaturated with calcite, dolomite, K-feldspar, quartz, and powellite and is saturated with gypsum. Water of this type moves primarily northeastward toward the SCS dam, although water-quality analyses from wells 802 and 804 in the vicinity of the uranium mill (fig. 3) indicate that a small fraction of this water has migrated northwestward and northward toward the west migration pathway, as discussed in the "West Near-Surface Pathway" section. The results of mass-balance reaction modeling indicate that raffinate-affected ground water from the old tailings ponds area is modified by several processes as it migrates northward: (1) Dilution, (2) dissolution of calcite and carbon dioxide, (3) cation exchange of major ions and sorption of uranyl ions, and (4) dissolution of powellite.

Dilution

Dilution is a major process affecting evolution of raffinate-affected ground water from the old tailings ponds area to Lincoln Park. Model results (table 6) indicate that water from the vicinity of site 701 is diluted about 12 times with fresher water from Sand Creek alluvium (site 24) before it reaches well 333 and about 8 times with freshwater from the injection-withdrawal system (site 997) before it reaches well 313 (water from adjacent well 312, being shallower, is diluted about 15 times by this system). Assuming that

Sand Creek alluvium brings water through Alkali Gap into the Chandler Syncline at about 25 gal/min (Adrian Brown Consultants, Inc., 1993), raffinate-affected ground water would flow into the Sand Creek alluvium at about 2.4 gal/min upgradient from well 333. On average, about one-half of the resulting mixture is withdrawn from well 333 and pumped back to the lined impoundments (Richard Wooten, Cotter Corporation, written commun., 1995).

Model results (table 6) indicate that water from the vicinity of well 330 consisted of water that was about seven parts water from well 333, one part water from well 313, and about two parts recharge from precipitation. The greater proportion of source-water type from well 333 compared to well 313 is consistent with the much greater permeability and recharge of alluvial deposits along Sand Creek compared to the permeability and recharge of the Poison Canyon Formation. Most of the recharge of precipitation downgradient from well 333 probably occurs along the channel of Sand Creek and in the vicinity of the SCS reservoir. On average, dilution by recharge from precipitation would be more prevalent than concentration by evaporation between wells 333 and 330 because of the large catchment area draining upstream from the SCS reservoir compared to the area of the reservoir—where most evaporation occurs.

The greatest dilution of raffinate-affected ground water occurs as a result of recharge of irrigation water from the DeWeese Dye Ditch. This greater dilution is facilitated by pumpback of most of the raffinate-affected ground water flowing to the Sand Creek gap. Model results (table 6) indicate that water from the vicinity of well 330 was diluted about twofold by dam-to-ditch injection water plus precipitation by the time the water reached well 138, and water from the vicinity of well 138 was diluted 11 times by water from the DeWeese Dye Ditch (site 526) by the time it reached well 144 on the eastern branch of the plume. Because the modeled samples from wells 138 and 144 were collected only a few weeks before activation of the ditch in the spring, dilution factors at these wells can be assumed to be greater during ditch flow and for months after deactivation of the ditch in October. Model results (table 6) indicated that water from well 330 was diluted 15 times by municipal water (site 997) from the dam-to-ditch flush and a nearby cistern sewage-disposal facility, and water from the DeWeese Dye Ditch (site 526) by the time it reached well 119 (which, unlike well 138, is located downgradient from the ditch) on the western branch of the plume. As with well 144, the sample from well 119 was collected a few weeks before the activation of the ditch in the spring; greater dilution would be expected during and shortly after ditch flow. Model results from the vicinity of well 119 to well 124 indicate another twelvefold dilution of raffinate-affected ground water by water from the DeWeese Dye Ditch. The cumulative dilution of raffinate-affected water from the vicinity of well 330 was 24-fold at well 144 and 180-fold at well 124. Based on dissolved-chloride concentrations (table 4), water from the vicinity of site 701 was diluted 120 times (pure-water equivalent) by the time it reached well 144 and 190 times by the time it reached well 124; only an eightfold dilution had occurred at well 330, indicating the much greater ability of the DeWeese Dye Ditch to dilute compared to the ability of precipitation and of injection south of the Raton ridge to dilute. Dilution by ditch water probably increased downgradient from wells 119 and 144, although evaporative concentration of major water-quality constituents and flushing of uranium and molybdenum from solid phases offset some of the immediate water-quality benefits of dilution.

Dissolution of Calcite and Carbon Dioxide Gas

Dissolution of calcite and carbon dioxide gas are other important processes that affect ground-water chemistry between the old tailings ponds and Lincoln Park. Although calcite was oversaturated at all modeled ground-water sites upgradient from the DeWeese Dye Ditch (preventing dissolution in the saturated zone), recharge by precipitation and injected water probably caused dissolution of calcite and carbon dioxide gas from the unsaturated zone. Recharge from precipitation runoff in Sand Creek caused dissolution downgradient to the SCS reservoir, according to the reaction:

$$CaCO_3(\text{calcite}) + CO_2(\text{gas}) + 2H_2O = Ca^{++} + 2HCO_3^{-}. \qquad (4)$$

Model results (table 6) indicate that recharge of precipitation did not appreciably affect evolution of ground water between wells 24 and 333. However, water chemistry in the vicinity of well 24 resulted from dissolution processes (including that in eq. 4) associated with recharge of precipitation in the Sand

Creek drainage. During episodic surface-water flow, recharge extends along Sand Creek to the SCS reservoir. Injection of municipal water (site 997) in the injection-withdrawal system also caused dissolution (eq. 4) that affects the water chemistry in the vicinity of wells 312 and 313. Model results indicate that additional dissolution occurred between wells 313, 333, and 330 and between wells 330 and 138 as a result of recharge of precipitation. Between wells 138 and 144, wells 330 and 119, and wells 119 and 124, recharge of injected municipal water and ditch water caused additional dissolution of calcite and carbon dioxide gas from the unsaturated zone.

Cation Exchange and Sorption of Uranyl Ions

Model results (table 6) indicate that cation exchange is a much more important process affecting the evolution of ground-water chemistry in the Chandler Syncline than it is north of the Raton ridge. Total exchanged cations (the sum of the products of reaction coefficient times cation charge for either sorbed or desorbed cations, but not both) ranged from 4.84 to 12.21 (average 9.3) meq/L for the four reaction segments upgradient from well 330 and from 0.396 to 1.94 (average 1.25) meq/L for the four segments downgradient from well 330. This relation is consistent with the more clay-rich lithology of the near-surface Poison Canyon Formation in the Chandler Syncline compared to the largely sand and gravel alluvium that constitutes the alluvial aquifer north of the Raton ridge. Cation-exchange-capacity data for <2-µm size fractions (Banta, 1997) indicate bulk-corrected values between 0.9 and 14 (average 5.2) meq/100g for eight samples from the near-surface Poison Canyon Formation and between 0.5 to 1.4 (average 0.7) meq/100g for five samples from the near-surface Vermejo Formation (two samples) and terrace alluvium (three samples) north of the Raton ridge. X-ray-diffraction analysis of these <2-µm fractions (Banta, 1997) indicate that smectite is the major clay mineral causing these cation-exchange capacities.

Model results (table 6) indicate net exchange of sodium ions for calcium and magnesium ions only between site 701, well 24, and well 333, the only modeled reaction segment not appreciably affected by recharge of water or dissolution of calcite (which would favor greater sorption of calcium). Other reaction segments generally exchanged calcium (and sometimes magnesium and potassium) ions for sodium ions.

Model results (table 6) indicate that uranyl (UO_2^{++}) ions were sorbed along all reaction segments, except between wells 330 and 119 and between wells 119 and 124, where uranyl ions were flushed by large quantities of calcium-rich water injected for the dam-to-ditch flush (site 997) and infiltrating from the DeWeese Dye Ditch (site 526) and associated feeder ditches and irrigation. However, between wells 330 and 138 and between wells 138 and 144, model results indicate continued sorption of uranyl ions, probably because of larger concentrations of dissolved uranium between wells 330 and 138 and a short distance downgradient from well 138; some desorption of uranium probably occurred between wells 138 and 144 as a result of infiltration of water from the DeWeese Dye Ditch, but not enough to cause net desorption in the model. Similarly, recharge of injected water (site 997) upgradient from wells 312 and 313 and recharge of precipitation upgradient from well 330 probably desorbed uranyl ions from the unsaturated zone, but in smaller quantities than were sorbed in the saturated zone, causing net sorption in those reaction segments.

Dissolution of Powellite

Model results (table 6) indicate that powellite ($CaMoO_4$) dissolved along most reaction segments where recharge of freshwater was caused by infiltration of precipitation or injection of municipal water. In segments where powellite dissolved, beginning and ending solutions from wells (except ending solutions at wells 124 and 144) were oversaturated with powellite. This oversaturation at wells implies that powellite dissolution occurred in the unsaturated zone (and possibly where recharge water mixed with ground water) and that powellite precipitation occurred in the saturated zone, but in insufficient quantities to result in net precipitation (except between wells 138 and 144 and between site 701 and well 333). Uranyl ions probably were desorbed from the unsaturated (or mixing) zones where powellite was dissolved, but this desorption was insufficient to cause net desorption in those model segments. Powellite was precipitated and uranyl ions were sorbed between site 701 and well 333 in the vicinity of the old tailings ponds; these processes probably occurred in the part of the reaction segments upgradient from the injection-withdrawal system between site 701 and well 312 and between site 701 and well 313. Powellite was dissolved, and dissolved molybdenum was flushed where uranyl ions were desorbed because of the dam-to-ditch flush between wells 330 and 119 and by infiltration of irrigation water between wells 119 and 124. Flushing of powellite also occurred between wells 330 and 138, but because less flush water was involved in this reaction segment, net sorption of uranyl ions occurred.

Dissolved molybdenum is generally more mobile than dissolved uranium in the study area, resulting in a general downgradient increase in the ratio of dissolved molybdenum to dissolved uranium to the vicinity of the DeWeese Dye Ditch. This ratio increased from 0.94 to 1.9 between site 701 and well 333, where no surface recharge was modeled. Between site 701 and well 312, the ratio increased from 0.94 to 4.8, and at well 313, it increased to 6.0, presumably because recharge with injected water dissolved molybdenum faster than it dissolved uranium. Between wells 333 and 330, recharge of precipitation increased the ratio from 1.9 to 5.1. Concentration ratios peaked at wells 138 (9.1) and 119 (13) but decreased at downgradient wells 144 (3.8) and 124 (5.3), possibly because of greater concentrations of leachable uranium than leachable molybdenum in the alluvial-aquifer matrix. Small dissolved concentrations of both elements north of the DeWeese Dye Ditch would allow such differential leaching to substantially decrease the ratio of dissolved molybdenum to dissolved uranium.

SUMMARY

A uranium-ore processing mill began operating near Cañon City, Colorado, in 1958 and remained active until January 1986. Data collected in 1968 indicated ground-water contamination by dissolved uranium and dissolved molybdenum in Lincoln Park, an unincorporated neighborhood immediately south of Cañon City. This report presents information related to migration pathways of ground water affected by mill activities and geochemical processes that affect ground-water quality.

Previous investigations determined that the primary near-surface pathway of raffinate migration was from the vicinity of old unlined tailings ponds on the uranium-mill site, down the Sand Creek drainage, and through the Sand Creek gap in the Raton ridge. Plots of maximum dissolved-uranium and dissolved-molybdenum concentrations for 1987 through 1989 confirm this pathway and indicate that the raffinate plume split about 0.33 mi north-northeast of the SCS dam; the main uranium plume continued north-northeast for about 1.2 mi and then turned eastward for about 0.5 mi, and another uranium plume extended eastward about 0.5 mi. The molybdenum plumes formed similar pathways, but extended farther downgradient. The near-surface pathway is in alluvium and fractured bedrock immediately underlying the alluvium, generally extending no deeper than 100 ft.

Historical trends in ground-water chemistry at several wells along the primary raffinate-migration pathway indicate that use of a new lined tailings impoundment, beginning in 1979, and other remediation activities that began in about 1979 have substantially decreased concentrations of dissolved uranium and dissolved molybdenum. The remediation activities consisted of (1) transfer of tailings from the old tailings ponds to a lined impoundment (1981–83); (2) operation of ground-water pumpback systems a short distance upgradient from the SCS reservoir and immediately downgradient from the old unlined ponds, beginning in about 1979; (3) installation of a clay barrier against the upgradient toe of the SCS dam in 1988; and (4) operation of a ground-water injection-withdrawal system downgradient from the area of the old tailings ponds, beginning in 1989. For example, dissolved-uranium concentrations at well 138 in Lincoln Park decreased from 3,570 µg/L in 1979 to less than 600 µg/L in 1994.

To evaluate the amount and quality of ground water migrating through the Sand Creek gap, six monitoring wells were installed and four test holes were drilled near the north toe of the SCS dam in 1995. Hydraulic conductivity was measured, and water-quality samples were taken from the six monitoring wells early in 1996; the flow rate of water and flux of dissolved uranium and dissolved molybdenum through the gap were estimated to be 1,900 to 12,000 L/d for water flow, 8.3 to 52 g/d uranium flux, and 48 to 300 g/d molybdenum flux.

Historical water-quality and water-level data indicate that raffinate-affected ground water probably has migrated from the vicinity of the uranium mill northward into a small, unnamed drainage west of Sand Creek and through a gap in the Raton ridge. Available information does not allow evaluation of the timing or the extent of possible raffinate migration into this basin, although such migration has probably been small compared to migration via Sand Creek. Data for wells near drainage basins east of and adjacent to the Sand Creek drainage indicate that raffinate-affected ground water probably did not flow into these basins.

Previous investigators have hypothesized that raffinate-affected ground water might have flowed into Lincoln Park along deep migration pathways. Interbedded shales in the Poison Canyon Formation probably limit downward flow of water through that formation, a conclusion supported by historical water-quality data from several clustered wells that are downgradient from the old tailings ponds and that are screened at varying depths. Another possible deep migration pathway for raffinate is via the Littell shaft, a shaft for the Wolf Park coal mine in the Vermejo Formation about 1,060 ft beneath the vicinity of the old tailings ponds. Previous investigators have hypothesized that raffinate-affected ground water might have migrated down this shaft, through mined voids and unmined coal and sandstone in the Vermejo Formation, and then into alluvial ground water at Lincoln Park. Water levels in the coal mines in the vicinity of the uranium-mill site indicate that the Wolf Park Mine is not connected to the Chandler Mine to the east or to the Rockvale Mine to the north and that raffinate-affected ground water would not flow in the direction of the Chandler Mine. Water-quality data for two wells completed in coals of the Vermejo Formation beneath the uranium-mill property indicate that reducing conditions in the Wolf Park Mine are not conducive to transport of dissolved uranium and dissolved molybdenum; therefore, this deep migration pathway is unlikely.

Mass-balance reaction modeling was completed for eight reaction segments to assist in characterization of hydrogeochemical processes that evolved raffinate-affected ground water from the area of the old tailings ponds to Lincoln Park. Results indicate that dilution is a major process affecting downgradient ground-water chemistry. South of the Raton ridge, most dilution is accomplished by ground-water flow into the basin where the uranium mill is located, injection of water at the injection-withdrawal system downgradient from the old tailings ponds, and infiltration of precipitation along the channel of Sand Creek during surface-water flow. North of the Raton ridge, infiltration of fresh irrigation water from the DeWeese Dye Ditch causes much greater dilution of raffinate components.

Model results indicate that dissolution of calcite and carbon dioxide gas is an important geochemical process between the area of the old tailings ponds and Lincoln Park. Because calcite was oversaturated at all modeled ground-water sites upgradient from the DeWeese Dye Ditch, recharge by fresh atmospheric precipitation and injected water caused dissolution of calcite and carbon dioxide gas from the unsaturated zone or where fresh recharging water mixed with ground water.

Model results indicate that cation exchange was much greater in the Chandler Syncline (the structural basin where the uranium mill is located) than it was in alluvium downgradient (north) from the Raton ridge. Most reaction segments had exchange of calcium (and sometimes magnesium and potassium) for sodium. Results indicate that uranyl (UO_2^{++}) ions generally were sorbed. Along two reaction segments in alluvium north of the Raton ridge, UO_2^{++} ions were desorbed (flushed) by calcium-rich water that was injected and by water that infiltrated from the DeWeese Dye Ditch and associated irrigation.

Model results indicate that powellite ($CaMoO_4$) generally dissolved in reaction segments where recharge of fresh precipitation or municipal water occurred, although beginning and ending solutions were oversaturated with this mineral. This relation implies that powellite was dissolved in unsaturated or mixing zones by fresh recharge water, but was precipitated in the saturated zone. Powellite also was flushed (dissolved) in the same two reaction segments in alluvium north of the Raton ridge where uranyl ions were desorbed by fresh injection and irrigation water. Dissolved molybdenum generally is more mobile than dissolved uranium in the study area; the difference in mobility causes a general downgradient increase in the ratio of dissolved molybdenum to dissolved uranium to the DeWeese Dye Ditch.

REFERENCES CITED

Adrian Brown Consultants, Inc., 1993, Old pond area remediation final report, pilot phase study: Denver, several loose-leaf volumes.

Arnek, R., and Szilard, I., 1968, Thermochemical studies of hydrolytic reactions, IX—The reactions of H^+ and molybdate ions in 3M sodium perchlorate: Acta Chemica Scandinavica, v. 22, p. 1134–1138.

Banta, E.R., 1994, Statistical analysis of uranium-mill raffinate contamination in water wells in Lincoln Park, south-central Colorado: U.S. Geological Survey Water-Resources Investigations Report 93–4211, 11 p.

Banta, E.R., 1997, Water-level, water-quality, lithology, solid-phase concentration, and surface-water discharge data for the vicinity of Lincoln Park, Colorado, 1961 through 1996: U.S. Geological Survey Open-File Report 97–361, 16 p.

Banta, E.R., and Chafin, D.T., in press, Ground-water hydrology and simulation of five remediation alternatives for an area affected by uranium-mill effluent near Cañon City, Colorado: U.S. Geological Survey Water-Resources Investigations Report 98–4229.

Bouwer, Herman, and Rice, R.C., 1976, A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells: Water Resources Research, v. 12, p. 423–428.

Briel, L.I., 1993, Documentation of a multiple-technique computer program for plotting major-ion composition of natural waters: U.S. Geological Survey Open-File Report 93–74, 88 p.

Busenberg, Eurybiades, and Plummer, L.N., 1992, Use of chlorofluorocarbons (CCl_3 and CCl_2F_2) as hydrologic tracers and age-dating tools—The alluvium and terrace system of central Oklahoma: Water Resources Research, v. 28, no. 9, p. 2257–2283.

Cooper, H.H., and Jacob, C.E., 1946, A generalized graphical method for generalizing formation constants and summarizing well field history: American Geophysical Union Transactions, v. 27, p. 526–534.

Coplen, T.B., 1993, Use of environmental isotopes, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 227–254.

Drever, J.I., 1982, The geochemistry of natural waters: Englewood Cliffs, N.J., Prentice-Hall, Inc., 388 p.

Dunkle, S.A., Plummer, L.N., Busenberg, Eurybiades, Phillips, P.J., Denver, J.M., Hamilton, P.A., Michel, R.L., and Coplen, T.B., 1993, Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tools and hydrologic tracers in shallow groundwater of the Delmarva Peninsula, Atlantic Coastal Plain, United States: Water Resources Research, v. 29, no. 12, p. 3837–3860.

ENVIRON Corporation, Radiation Surveillance Associates, Radiant Energy Management, and Western Radiation Consultants, 1991, Health risk assessment of the Cotter uranium mill site, Cañon City, Colorado: Arlington, Va., 336 p.

Essington, M.E., 1990, Calcium molybdate solubility in spent oil shale and a preliminary evaluation of the association constants for the formation of $CaMoO_4{}^\circ(aq)$, $KMoO_4{}^-(aq)$, $NaMoO_4{}^-(aq)$: Environmental Science and Technology, v. 24, p. 214–220.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice-Hall, Inc., 604 p.

Geotrans, Inc., Rocky Mountain Consultants, Inc., and ERI Logan, Inc., 1986, Remedial investigation, Cotter Corporation uranium mill site: 1 loose-leaf volume.

Hearne, G.A., and Litke, D.W., 1987, Ground-water flow and quality near Cañon City, Colorado: U.S. Geological Survey Water-Resources Investigations Report 87–4014, 72 p.

Hershey, L.A., 1977, Geohydrology of the Cotter mill environment: Cañon City, Colo., Hershey-Wooderson Associates, Inc., 62 p.

Kaback, D.S., and Runnells, D.D., 1980, Geochemistry of molybdenum in some stream sediments and waters: Geochemica Cosmochemica Acta, v. 44, p. 447–456.

Mook, W.G., 1986, ^{13}C in atmospheric CO_2: Netherlands Journal of Sea Research, v. 20, p. 211–223.

Parkhurst, D.L., 1995, User's guide to PHREEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 95–4227, 143 p.

Parkhurst, D.L., Plummer, L.N., and Thorstenson, D.C., 1982, BALANCE—A computer program for calculating mass transfer for geochemical reactions in ground water: U.S. Geological Survey Water-Resources Investigations Report 82–14, 29 p.

Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses: American Geophysical Union Transactions, v. 25, p. 914–923.

Plummer, L.N., and Back, W.W., 1980, The mass-balance approach—Application to interpreting the chemical evolution of hydrologic systems: American Journal of Science, v. 280, p. 130–142.

Plummer, L.N., Parkhurst, D.L., and Thorstenson, D.C., 1983, Development of reaction models for groundwater systems: Geochemica et Cosmochemica Acta, v. 47, p. 665–686.

Plummer, L.N., Prestemon, E.C., and Parkhurst, D.L., 1994, An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, version 2.0: U.S. Geological Survey Water-Resources Investigations Report 94–4169, 130 p.

Reddy, K.J. and Drever, J.I., 1987, Geochemical modeling research related to the surface disposal of processed oil shale solid waste: Laramie, Wyo., Western Research Institute, 109 p.

Reilly, T.E., Plummer, L.N., Phillips, P.J., and Busenberg, Eurybiades, 1994, The use of simulation and multiple environmental tracers to quantify groundwater flow in a shallow aquifer: Water Resources Research, v. 30, no. 2, p. 421–433.

Reynolds, G.W., Hoff, J.T., and Gillham, R.W., 1990, Sampling bias caused by materials used to monitor halocarbons in groundwater: Environmental Science and Technology, v. 24, p. 135–142.

Runnells, D.D., Gerlitz, C.N., Davis, A., Lindberg, R.D., Maglen, R., Swanson, G., Taylor, L., Sistko, R., and McNelly, R., 1983, Contamination of ground and surface water due to uranium mining and milling—v. 3, Experimental studies and analytical techniques: Washington, D.C., U.S. Bureau of Mines contract no. J0295033, 229 p.

Scott, G.R., 1977, Reconnaissance geologic map of the Cañon City quadrangle, Fremont County, Colorado: U.S. Geological Survey Miscellaneous Field Studies Map MF–892, scale 1:24,000.

Smith, R.M., and Martell, A.E., 1976, Critical stability constants—v. 4, Inorganic complexes: New York, Plenum Press, 257 p.

U.S. Environmental Protection Agency, 1984, Amendment to national oil and hazardous substance contingency plan; national priorities list, final rule: Federal Register, v. 49, no. 185, September 21, 1984, p. 37070–37090.

Vlek, P.L.G., and Lindsay, W.L., 1977, Thermodynamic stability and solubility of molybdenum minerals in soils: Soil Science Society of America Journal, v. 41, p. 42–46.

W.A. Wahler and Associates, 1978a, Investigations related to seepage from the existing Cotter tailings impoundments: Palo Alto, Calif., variously paginated.

W.A. Wahler and Associates, 1978b, Site and laboratory investigation and definitive design report, Cotter Corporation uranium-vanadium tailings impoundment, Cañon City, Colorado: Palo Alto, Calif., variously paginated.

Washburne, C.W., 1910, The Cañon City coal field, Colorado: U.S. Geological Survey Bulletin 381–C, p. 341–378.

Zielinski, R.A., Chafin, D.T., Banta, E.R., and Szabo, B.J., 1997, Use of ^{234}U and ^{238}U isotopes to evaluate contamination of near-surface ground water with uranium-mill effluent—A case study in south-central Colorado, U.S.A.: Environmental Geology, v. 32, p. 124–136.

SUPPLEMENTAL INFORMATION

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96

[Site locations are shown on pl. 1 in Banta (1997); ft, feet; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; --, no data; IT, incremental titration; mg/L, milligrams per liter; <, less than; µg/L, micrograms per liter; $\delta^{34}S$, $^{34}S/^{32}S$ isotopic ratio expressed compared to the Canyon Diablo meteorite standard; $\delta^{13}C$, $^{13}C/^{12}C$ isotopic ratio expressed compared to the PeeDee belemnite marine-carbonate standard; $\delta^{2}H$, $^{2}H/^{1}H$ isotopic ratio; $\delta^{18}O$, $^{18}O/^{16}O$ isotopic ratio; $\delta^{2}H$ and $\delta^{18}O$ are expressed compared to the Standard Mean Ocean Water standard]

Site number	Station number	Station name	Date	Water level, depth below land surface (ft)	Temperature, water (°C)	Specific conductance (µS/cm)	pH (standard units)
1	382317105133101	SC01907016DCCD1	03-08-95	43.40	11.0	3,000	5.8
10	382552105133101	SC01907004ABBD1	03-16-95	37.19	17.5	850	7.1
11	382442105111401	SC01907011ACDB1	03-14-95	36.75	20.0	2,260	7.4
14	382424105135401	SC01907009CCA2	02-06-95	40.81	14.0	2,820	8.0
15	382455105134401	SC01907005BAC1	01-19-96	37.37	12.5	2,940	7.3
17	382412105130201	SC01907009DDDDD1	02-01-95	77.69	14.0	978	8.3
19	382504105125101	SC01907003CCDC1	03-14-95	33.32	15.0	931	7.4
20	382510105124701	SC01907003CCD1	03-14-95	29.62	15.5	685	7.3
22	382418105132201	SC019070009DCDA1	01-26-95	13.11	12.0	1,080	9.5
114	382536105131901	SC01907004ADBC1	03-21-95	53.10	16.0	537	7.3
117	382516105130901	SC01907004DADC1	07-21-95	30.11	15.5	585	7.2
119	382505105130501	SC01907004DDD2	03-15-95	29.42	16.0	723	7.4
120	382514105125501	SC01907003CCBAD1	07-20-95	13.70	16.0	621	7.4
122	382521105125201	SC01907003CBDBB1	07-19-95	31.97	15.5	616	7.3
123	382502105125301	SC01907003CCDCC1	03-14-95	--	17.5	1,010	7.1
124	382527105125001	SC01907003CBA2	03-15-95	56.47	16.5	569	7.2
129	382531105122201	SC01907003ACDD1	03-15-95	34.25	16.0	612	7.1

Site number	Oxygen, dissolved (mg/L)	Alkalinity, dissolved, onsite, IT (mg/L as $CaCO_3$)	Dissolved solids, sum of constituents (mg/L)	Dissolved solids, residue at 180°C (mg/L)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, $NO_2 + NO_3$, dissolved (mg/L as N)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)
1	2.5	51	--	--	--	--	--	--	--
10	5.6	334	--	--	--	--	--	--	--
11	5.7	365	--	--	--	--	--	--	--
14	<0.1	292	--	--	--	--	--	--	--
15	--	232	2,440	2,550	0.06	3.4	320	110	260
17	<0.1	214	--	--	--	--	--	--	--
19	5.0	283	--	--	--	--	--	--	--
20	4.2	286	--	--	--	--	--	--	--
22	0.3	230	--	--	--	--	--	--	--
114	4.6	251	--	--	--	--	--	--	--
117	9.5	--	--	--	--	--	--	--	--
119	6.3	208	445	454	<0.015	0.50	41	11	100
120	9.0	--	--	--	--	--	--	--	--
122	8.3	--	--	--	--	--	--	--	--
123	4.8	310	641	661	<0.015	2.2	93	35	71
124	5.7	271	337	338	<0.015	1.0	67	18	27
129	7.2	277	367	363	<0.015	1.7	75	20	26

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96 —Continued

Site number	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO_2)	Aluminum, dissolved (µg/L as Al)	Bromide, dissolved (mg/L as Br)	Iron, dissolved (µg/L as Fe)	Manganese, dissolved (µg/L as Mn)
1	--	--	--	--	--	--	--	--	--
10	--	--	--	--	--	--	--	--	--
11	--	--	--	--	--	--	--	--	--
14	--	--	--	--	--	--	--	--	--
15	13	54	1,500	1.2	26	400	0.63	410	27
17	--	--	--	--	--	--	--	--	--
19	--	--	--	--	--	--	--	--	--
20	--	--	--	--	--	--	--	--	--
22	--	--	--	--	--	--	--	--	--
114	--	--	--	--	--	--	--	--	--
117	--	--	--	--	--	--	--	--	--
119	2.8	10	130	1.9	18	10	0.08	11	<1
120	--	--	--	--	--	--	--	--	--
122	--	--	--	--	--	--	--	--	--
123	3.1	18	200	0.70	23	<10	0.17	5	<1
124	3.3	4.0	27	0.60	24	20	0.06	<3	4
129	2.5	7.0	35	0.70	25	20	0.08	<3	<1

Site number	Selenium, dissolved (µg/L as Se)	Molybdenum, dissolved (µg/L as Mo)	Uranium, dissolved (µg/L as U)	$\delta^{34}S$ of sulfate (permil)	$\delta^{13}C$ of dissolved inorganic carbon (permil)	$\delta^{2}H$ of water (permil)	$\delta^{18}O$ of water (permil)
1	--	<1	0.20	--	--	--	--
10	--	9	24	--	--	--	--
11	--	6	31	--	--	--	--
14	--	6	0.39	--	--	--	--
15	150	59	420	--	--	--	--
17	--	2	0.62	--	--	--	--
19	--	550	72	--	--	--	--
20	--	140	35	--	--	--	--
22	--	3	1.4	--	--	--	--
114	--	6	8.7	--	--	--	--
117	--	240	34	--	--	--	--
119	<5	1,800	140	-1.6	-9.6	-112.0	-14.82
120	--	150	14	--	--	--	
122	--	400	57	--	--	--	
123	4	620	83	-3.5	-11.9	-101.0	-13.48
124	<1	250	47	0.2	-12.5	-98.5	-13.01
129	<1	150	55	0.0	-12.3	-101.0	-13.19

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96 —Continued

Site number	Station number	Station name	Date	Water level, depth below land surface (ft)	Temperature, water (°C)	Specific conductance (µS/cm)	pH (standard units)
130	382516105120901	SC01907003DDB1	03-21-95	41.23	15.5	676	7.2
138	382501105125901	SC01907010BBBA1	03-09-95	45.24	14.5	2,200	7.8
144	382502105122901	SC01907010ABB1	03-08-95	32.07	14.5	821	7.0
163	382442105111901	SC01907011ACC1	03-13-95	--	15.0	1,730	7.7
165	382531105113401	SCO1907002BDCD1	07-19-95	--	14.0	382	7.3
166	382526105114101	SC01907002CBADA1	07-19-95	12.05	14.5	495	7.3
167	382502105121101	SC01907010AAB1	07-21-95	13.67	15.5	550	7.4
173	382536105125401	SC01907003BCADC1	07-19-95	--	15.0	630	7.2
174	382521105123201	SC01907003CADA1	07-20-95	38.05	17.0	567	7.2
183	382453105131202	SC01907009AAC3	03-15-96	20.08	15.5	683	7.6
190	382517105130101	SC01907003CBCC1	03-21-95	38.48	16.5	552	7.2
197	382549105132001	SC01907004ABAD1	03-22-95	43.57	15.0	681	7.1
228	382518105131801	SC01907004DACC1	03-16-95	42.30	15.0	824	7.4
230	382529105130401	SC01907004DAAA1	07-20-95	27.81	14.5	602	7.3
312	382404105132001	SC01907009DCA1	03-08-95	9.23	11.0	3,270	7.9
313	382404105132002	SC01907009DCA2	02-03-95	10.07	11.5	5,100	7.7
324	382351105133501	SC01907016ACBD1	02-02-95	103.83	15.5	979	7.5

Site number	Oxygen, dissolved (mg/L)	Alkalinity, dissolved, onsite, IT (mg/L as $CaCO_3$)	Dissolved solids, sum of constituents (mg/L)	Dissolved solids, residue at 180°C (mg/L)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, NO_2 + NO_3, dissolved (mg/L as N)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)
130	5.1	314	--	--	--	--	--	--	--
138	6.8	239	1,520	1,570	<0.015	2.5	86	32	370
144	5.0	350	518	524	<0.015	1.0	96	32	36
163	3.5	--	--	--	--	--	--	--	--
165	4.8	--	--	--	--	--	--	--	--
166	7.0	--	--	--	--	--	--	--	--
167	8.8	--	--	--	--	--	--	--	--
173	7.1	--	--	--	--	--	--	--	--
174	9.0	--	--	--	--	--	--	--	--
183	3.0	147	430	431	0.14	<0.05	29	8.0	110
190	1.0	255	326	324	--	--	59	18	34
197	5.6	319	408	413	--	--	70	32	29
228	4.8	242	502	509	--	--	68	23	74
230	10.0	--	--	--	--	--	--	--	--
312	6.6	429	2,280	2,280	<0.015	7.7	41	22	700
313	4.0	589	--	--	--	--	--	--	--
324	<0.1	299	--	--	--	--	--	--	--

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96 —Continued

Site number	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO_2)	Aluminum, dissolved (µg/L as Al)	Bromide, dissolved (mg/L as Br)	Iron, dissolved (µg/L as Fe)	Manganese, dissolved (µg/L as Mn)
130	--	--	--	--	--	--	--	--	--
138	2.6	43	800	2.6	22	<10	0.40	310	<3
144	2.4	6.4	80	1.0	42	<10	0.11	<3	<1
163	--	--	--	--	--	--	--	--	--
165	--	--	--	--	--	--	--	--	--
166	--	--	--	--	--	--	--	--	--
167	--	--	--	--	--	--	--	--	--
173	--	--	--	--	--	--	--	--	--
174	--	--	--	--	--	--	--	--	--
183	2.6	13	160	1.3	13	<10	0.15	10	97
190	2.4	4.9	27	0.70	23	10	0.07	920	53
197	3.9	5.9	33	1.3	37	20	0.09	<3	<1
228	2.9	9.9	150	1.0	24	10	0.10	10	120
230	--	--	--	--	--	--	--	--	--
312	0.90	85	1,100	2.2	17	<10	0.37	<9	<3
313	--	--	--	--	--	--	--	--	--
324	--	--	--	--	--	--	--	--	--

Site number	Selenium, dissolved (µg/L as Se)	Molybdenum, dissolved (µg/L as Mo)	Uranium, dissolved (µg/L as U)	δ^{34}S of sulfate (permil)	δ^{13}C of dissolved inorganic carbon (permil)	δ^{2}H of water (permil)	δ^{18}O of water (permil)
130	--	45	18	--	--	--	--
138	17	5,200	570	-4.0	-9.0	-100.0	-13.04
144	<1	150	40	-2.0	-13.4	-97.8	-13.01
163	--	2	5.5	--	--	--	--
165	--	22	3.9	--	--	--	--
166	--	66	13	--	--	--	--
167	--	36	9.6	--	--	--	--
173	--	100	25	--	--	--	--
174	--	42	14	--	--	--	--
183	<1	92	76	--	--	--	--
190	<1	420	39	--	--	--	--
197	1	7	16	--	--	--	--
228	3	20	23	--	--	--	--
230	--	13	16	--	--	--	--
312	44	9,600	2,000	-2.3	-10.0	-107.0	-14.12
313	--	20,000	3,600	--	--	--	--
324	--	4	0.46	--	--	--	--

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96 —Continued

Site number	Station number	Station name	Date	Water level, depth below land surface (ft)	Temperature, water (°C)	Specific conductance (µS/cm)	pH (standard units)
325	382317105132301	SC01907016DCD1	03-08-95	55.05	14.0	3,260	7.0
327	382450105130701	SC01907009ADAB1	02-07-95	45.10	14.0	1,480	8.1
328	382450105130702	SC01907009ADAB2	03-20-95	62.37	14.0	1,030	9.4
330	382438105131601	SC01907009ADC1	03-09-95	19.95	15.0	3,980	7.4
333	382412105133401	SC01907009DCC1	03-01-95	--	14.5	4,330	7.2
335	382335105140701	SC01907016CBCC1	02-01-95	88.55	14.0	2,520	6.7
336	382419105133801	SC01907009DCB1	03-07-95	40.82	15.0	2,400	7.3
339	382352105133101	SC01907016ACCA1	01-26-95	--	19.5	11,700	5.5
342	382455105134501	SC01907009BACA1	02-09-95	49.05	15.0	2,570	6.7
350	382358105134001	SC01907016BADC1	02-09-95	5.23	11.5	2,800	7.4
357	382405105133401	SC01907016ABB1	03-17-95	26.52	12.5	2,790	7.2
373	382443105131801	SC01907009ADBC01	03-13-96	25.84	15.5	1,430	7.1
374	382443105131601	SC01907009ADB01	03-13-96	10.00	14.0	3,550	7.8
375	382442105131601	SC01907009ADBD01	03-12-96	20.73	14.0	4,860	7.2
376	382442105131701	SC01907009ADBC02	03-11-96	18.79	13.5	4,550	7.0
377	382442105131602	SC01907009ADBDO2	03-15-96	--	13.0	1,240	7.3
378	382442105131702	SC01907009ADBC03	03-13-96	--	14.5	2,880	7.3

Site number	Oxygen, dissolved (mg/L)	Alkalinity, dissolved, onsite, IT (mg/L as $CaCO_3$)	Dissolved solids, sum of constituents (mg/L)	Dissolved solids, residue at 180°C (mg/L)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, NO_2 + NO_3, dissolved (mg/L as N)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)
325	1.3	248	--	--	--	--	--	--	--
327	<0.1	251	--	--	--	--	--	--	--
328	--	491	--	--	--	--	--	--	--
330	6.2	388	2,750	2,850	<0.015	5.4	150	59	660
333	--	330	3,300	3,480	<0.015	30	230	110	650
335	<0.1	270	--	--	--	--	--	--	--
336	1.7	240	--	--	--	--	--	--	--
339	<0.2	248	--	--	--	--	--	--	--
342	0.5	401	--	--	--	--	--	--	--
350	<0.6	214	--	--	--	--	--	--	--
357	1.1	395	--	--	--	--	--	--	--
373	2.7	193	924	944	0.13	0.09	74	20	200
374	7.5	375	2,490	2,610	0.02	5.4	86	41	700
375	3.0	336	3,730	3,840	0.04	14	250	81	830
376	4.0	487	3,550	3,600	0.05	3.3	230	90	830
377	--	151	823	844	0.04	0.24	55	17	190
378	6.0	202	2,110	2,450	0.05	0.07	210	59	360

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96 —Continued

Site number	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO_2)	Aluminum, dissolved (μg/L as Al)	Bromide, dissolved (mg/L as Br)	Iron, dissolved (μg/L as Fe)	Manganese, dissolved (μg/L as Mn)
325	--	--	--	--	--	--	--	--	--
327	--	--	--	--	--	--	--	--	--
328	--	--	--	--	--	--	--	--	--
330	3.7	97	1,500	1.9	19	<10	0.87	36	<3
333	5.2	140	1,800	2.1	17	20	1.0	18	<3
335	--	--	--	--	--	--	--	--	--
336	--	--	--	--	--	--	--	--	--
339	--	--	--	--	--	--	--	--	--
342	--	--	--	--	--	--	--	--	--
350	--	--	--	--	--	--	--	--	--
357	--	--	--	--	--	--	--	--	--
373	4.1	54	430	2.7	15	20	0.43	83	72
374	3.2	81	1,300	3.1	17	30	0.74	33	<3
375	5.2	140	2,100	2.8	16	20	1.1	<12	71
376	5.2	130	1,900	1.6	22	20	1.3	16	<4
377	2.9	48	380	3.5	20	60	0.35	19	58
378	5.5	130	1,200	1.8	13	20	1.1	<9	240

Site number	Selenium, dissolved (μg/L as Se)	Molybdenum, dissolved (μg/L as Mo)	Uranium, dissolved (μg/L as U)	$\delta^{34}S$ of sulfate (permil)	$\delta^{13}C$ of dissolved inorganic carbon (permil)	$\delta^{2}H$ of water (permil)	$\delta^{18}O$ of water (permil)
325	--	3	3.3	--	--	--	--
327	--	150	1.2	--	--	--	--
328	--	59	1.0	--	--	--	--
330	22	9,600	1,900	-2.2	-10.0	-92.1	-11.87
333	110	6,900	3,700	-2.1	-8.9	-104.0	-13.23
335	--	4	0.89	--	--	--	--
336	--	43	130	--	--	--	--
339	--	<1	<0.10	--	--	--	--
342	--	2	3.9	--	--	--	--
350	--	640	3.1	--	--	--	--
357	--	21	9.1	--	--	--	--
373	<1	42	<0.10	--	--	--	--
374	1	13,000	2,900	--	--	--	--
375	38	22,000	3,300	--	--	--	--
376	11	25,000	4,300	--	--	--	--
377	25	10	1.2	--	--	--	--
378	<1	140	23	--	--	--	--

Table 7. Water-level and water-quality measurements at selected wells, springs, and surface-water sites, 1995–96—Continued

Site number	Station number	Station name	Date	Water level, depth below land surface (ft)	Temperature, water (°C)	Specific conductance (µS/cm)	pH (standard units)
526	382501105131001	SC01907009AAB1	06-14-95	--	16.5	326	8.5
701	382402105134301	SC01907016BAD1	03-02-95	--	12.0	25,400	7.4
710	382401105132201	SC01907016AAC1	03-09-95	--	11.5	6,820	7.0
806	382432105134301	SC01907009CADB1	02-08-95	43.80	15.5	3,850	6.3
997	382358105135301	SC01907016B1	06-12-95	--	15.0	232	7.4
2107	382529105131801	SC01907004DABB1	07-20-95	25.55	16.5	618	7.2

Site number	Oxygen, dissolved (mg/L)	Alkalinity, dissolved, onsite, IT (mg/L as $CaCO_3$)	Dissolved solids, sum of constituents (mg/L)	Dissolved solids, residue at 180°C. (mg/L)	Nitrogen, ammonia, dissolved (mg/L as N)	Nitrogen, $NO_2 + NO_3$, dissolved (mg/L as N)	Calcium, dissolved (mg/L as Ca)	Magnesium, dissolved (mg/L as Mg)	Sodium, dissolved (mg/L as Na)
526	8.5	[1]122	194	203	<0.015	<0.05	44	11	10
701	--	1,370	26,400	27,900	1.3	150	350	970	6,800
710	0.9	349	5,230	5,570	0.03	150	620	190	780
806	4.1	263	--	--	--	--	--	--	--
997	8.3	[1]50	126	131	<0.015	0.07	26	6.1	7.4
2107	5.3	--	--	--	--	--	--	--	--

Site number	Potassium, dissolved (mg/L as K)	Chloride, dissolved (mg/L as Cl)	Sulfate, dissolved (mg/L as SO_4)	Fluoride, dissolved (mg/L as F)	Silica, dissolved (mg/L as SiO_2)	Aluminum, dissolved (µg/L as Al)	Bromide, dissolved (mg/L as Br)	Iron, dissolved (µg/L as Fe)	Manganese, dissolved (µg/L as Mn)
526	1.2	2.1	17	0.30	15	20	<0.01	29	4
701	15	770	16,000	1.3	7.1	80	2.3	<10	170
710	4.7	740	2,000	1.0	15	10	2.7	<10	30
806	--	--	--	--	--	--	--	--	--
997	0.90	6.7	35	0.30	7.1	30	<0.01	8	2
2107	--	--	--	--	--	--	--	--	--

Site number	Selenium, dissolved (µg/L as Se)	Molybdenum, dissolved (µg/L as Mo)	Uranium, dissolved (µg/L as U)	$\delta^{34}S$ of sulfate (permil)	$\delta^{13}C$ of dissolved inorganic carbon (permil)	$\delta^{2}H$ of water (permil)	$\delta^{18}O$ of water (permil)
526	<1	1	2.5	1.4	-10.5	-107.0	-14.14
701	1,200	84,000	89,000	-2.1	-4.3	-91.4	-9.78
710	900	550	890	-3.1	-12.6	-75.4	-8.70
806	--	4	25	--	--	--	--
997	<1	2	1.2	3.6	-6.1	-123.0	-16.16
2107	--	5	11	--	--	--	--

[1] Laboratory alkalinity measurement substituted for onsite measurement to yield better ion balance for solution.

Discussion of Chlorofluorocarbon-Recharge Dates

Several important processes were considered to obtain an estimate of recharge dates for the seven chlorofluorocarbon (CFC) samples (table 8; well locations are shown in fig. 3). Recharge-age date refers to the year that a given sample of ground water became isolated from the atmosphere as it flowed into an aquifer or a formation. The processes that can affect apparent recharge dates are (1) CFC sorption onto plastic casings, (2) anaerobic degradation of CFC's in the aquifer, and (3) sorption of CFC's onto organic matter in the aquifer matrix. Also, intermediate apparent recharge dates can result from mixing of different age waters from multiple ground-water-bearing zones along the screen or gravel pack of a well.

Modern atmospheric CFC's analyzed for recharge-age dating are: trichlorofluoromethane (CFC-11); dichlorodifluoromethane (CFC-12); and trichlorotrifluoroethane (CFC-113). These compounds can sorb onto polyvinyl chloride (or fiberglass) casings during installation or prepurging of wells and can subsequently desorb into sample water, causing apparent recharge dates that are too recent (Reynolds and others, 1990). Although an attempt was made to prevent atmospheric contamination of casings by preventing evacuation of water too close to the depth from which CFC sampling was done, the small yields of wells 17 and 22 caused casings at the sampling depths to be exposed to the atmosphere. In addition, prior prepurging by uranium-mill personnel of most or all of the seven wells sampled for CFC's probably exposed casings (and in some wells, screens) to the atmosphere.

Anaerobic degradation of CFC's in the aquifer can cause apparent recharge dates that are too old (Busenberg and Plummer, 1992). The potential for anaerobic degradation of CFC's is in the order CFC-11>CFC-113>>CFC-12. Five wells (14, 17, 324, 327, and 335) had unmeasurable dissolved-oxygen concentrations, although only well 327 had noticeable H_2S.

Sorption of CFC's onto organic matter in the aquifer matrix can cause apparent recharge dates that are too old (Busenberg and Plummer, 1992). This potential exists in the order CFC-113> CFC-11>>CFC-12. The potential for this problem probably applies only to wells completed in the Vermejo Formation (wells 327 and 342), which has some coal seams. No lithologic log is available for well 327, but the lithologic log for well 342 indicates that no coal was in or near the strata in which the well was screened; therefore, matrix sorption of CFC's probably is not important for well 342.

The relatively late date indicated by CFC-113 compared to CFC-11 and CFC-12 from well 14 (table 8) indicates that exposure of the casing to the atmosphere had occurred. Because of the relatively good agreement between CFC-11 and CFC-12 dates, the latest of these dates, 1956, is judged to be the latest possible recharge date for this well, but the oldest of these CFC dates, 1950.5, is probably a more realistic estimate of the earliest recharge date because of the likelihood that the CFC-12 dates appear younger than they would otherwise because of desorption CFC-12 from the casing. The same reasoning was applied to wells 17 and 22, using dates from replicate 4 (table 8) for both wells because that replicate is the least affected by casing desorption.

Because of relatively good yield and a long water column, casing exposure probably has not occurred at great depth in well 324 since installation. However, the disparately late CFC-113 recharge-age dates indicate probable contamination during sampling. Without any additional information to aid interpretation, 1987.5 needs to be used as the latest possible recharge date for well 324.

The presence of H_2S in the water from well 327 indicates the potential that CFC concentrations have been diminished by anaerobic degradation because the long water column probably has protected the casing from atmospheric exposure near sampling depth. Sorption into the aquifer matrix may have caused additional loss of CFC's from solution. Assuming these processes could not have removed all CFC-113 from solution, the absence of this compound indicates that this ground water had recharged by 1966, the year CFC-113 attained detectable concentrations in recharge water (Eurybiades Busenberg, U.S. Geological Survey, written commun., 1995). The dates for CFC-12 imply that the absence of CFC-11 was caused by degradation and possibly sorption. These removal processes also would cause CFC-12 recharge dates to be minimized; therefore, the earliest of those dates, 1954, would be the earliest possible recharge date. The presence of a relatively large concentration of dissolved molybdenum (150 µg/L) and dissolved uranium (1.2 µg/L) having a $^{234}U/^{238}U$ ratio indicative of a raffinate source (Zielinski and others, 1997), implies that the water from well 327 contains some water that recharged during 1958, when uranium-mill operations commenced, or later.

Well 335 also had an absence of CFC-113. This well has a relatively good yield and a long water column to prevent atmospheric exposure of the casing near the sampling depth. Although the absence of measurable dissolved oxygen (table 7) indicates the possibility of anaerobic degradation, the presence of the more readily degradable CFC-11 indicates that the absence of CFC-113 results from recharge prior to 1966. The oldest CFC-11 date, 1953, sets the earlier limit for the recharge date.

Relatively good yield and a long water column in well 342 probably protected CFC samples from recent casing exposure to the atmosphere. The presence of dissolved oxygen in water from this well (table 7) indicates that anaerobic degradation probably did not affect CFC concentrations, and the absence of coal in the screened strata indicates that sorption of CFC's onto the aquifer matrix probably was not substantial. Using replicate 4 as the sample least contaminated during sampling, a recharge-date range of 1966 to 1971 is rendered.

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Table 8. Results of chlorofluorocarbon analyses and estimated recharge dates

[Well locations are shown in fig. 3; calculated partial pressures and date interpretations assume a mean atmospheric recharge temperature of 12.1 degrees Celsius and a recharge elevation of 5,600 feet above sea level; CFC-11, trichlorofluoromethane; CFC-12, dichlorodifluoromethane; CFC-113, trichlorotrifluoroethane; T_{pc}, Poison Canyon Formation; K_v, Vermejo Formation; TK_r, Raton Formation; ppt, parts per trillion by volume; --, contaminated; ≤, earlier than or equal to; <, earlier than]

Well	Formation	Sample date	Sample replicate	Calculated atmospheric partial pressure (ppt)			Theoretical recharge date			Estimated recharge date
				CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	
14	T_{pc}	2-6-95	2	3.8	14.6	15.0	1955	1954	1974.5	≤1956, probably
			4	5.3	8.4	14.0	1956	1950.5	1974	≤1950.5
			5	3.8	8.4	14.0	1955	1950.5	1974	
17	T_{pc}	2-1-95	2	39.8	148.5	20.7	1967	1971	1978	≤1963, probably
			4	19.2	38.1	10.1	1963	1960.5	1971.5	≤1960.5
			5	20.7	130.5	14.7	1963.5	1970	1974.5	
22	T_{pc}	1-26-95	2	31.0	62.2	75.8	1965.5	1964	1989.5	≤1965, probably
			4	26.9	34.5	60.9	1965	1960	1987.5	≤1960
			5	46.0	95.3	99.5	1968	1967.5	--	
324	T_{pc}	2-2-95	1	297.3	744.0	128.6	--	--	--	≤1987.5
			3	78.0	227.2	63.9	1971.5	1975	1987.5	
			5	80.6	272.4	43.5	1972	1977.5	1984.5	
327	K_v	2-7-95	2	0.0	14.7	0.0	1945	1954	≤1966	[1]1954-1966
			4	0.0	20.6	0.0	≤1945	1956	≤1966	
			5	0.0	17.0	0.0	≤1945	1955	≤1966	
335	TK_r	2-1-95	2	3.7	40.8	0.0	1955	1961	≤1966	1953-1966
			4	3.5	28.9	0.0	1954.5	1958.5	≤1966	
			5	2.0	46.9	0.0	1953	1962	≤1966	
342	K_v	2-9-95	2	230.2	237.1	45.2	--	--	--	Probably
			4	33.9	142.5	9.2	1966	1970.5	1971.0	1966-1971,
			5	60.3	179.5	16.2	1970	1973	1975	Possibly <1966

[1] Uranium isotopes and dissolved-molybdenum concentrations indicate the presence of raffinate (Zielinski and others, 1997), production of which began in 1958.

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