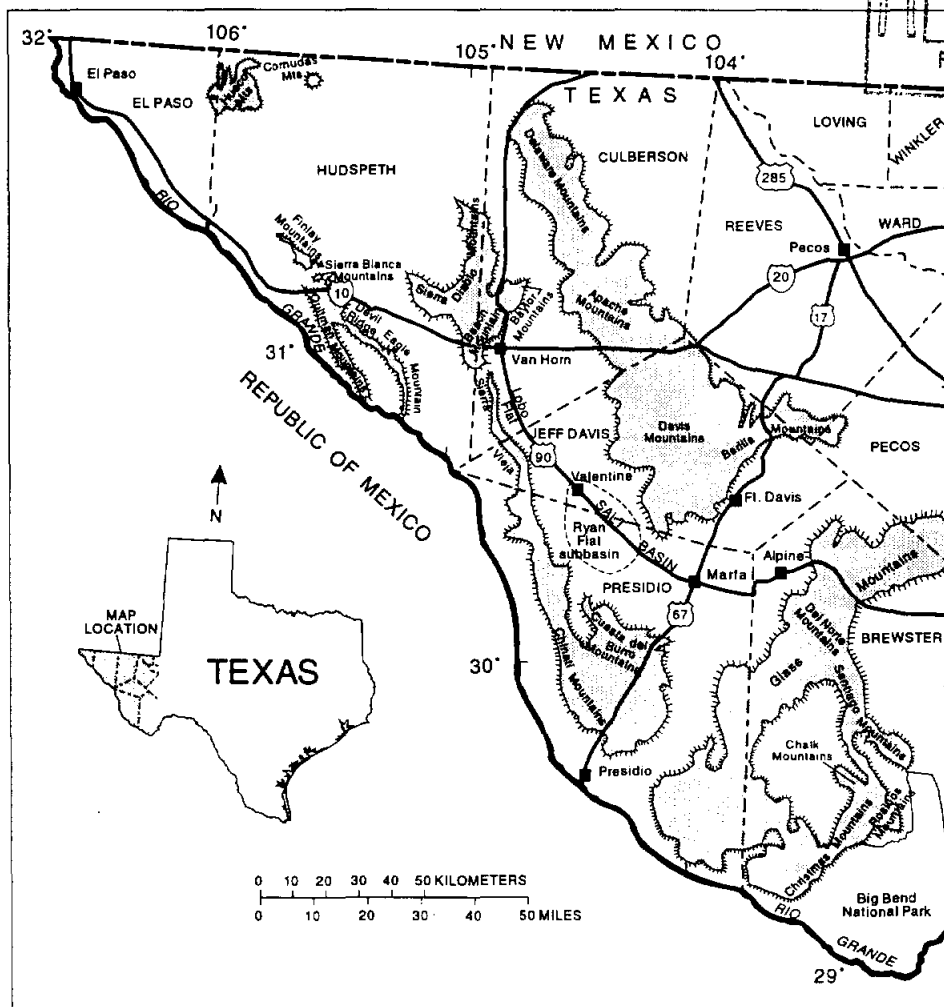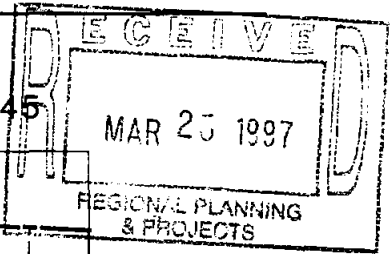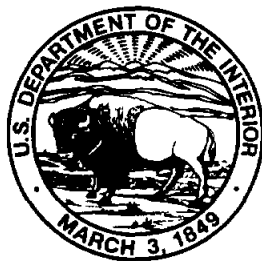# CHLOROFLUOROCARBON AND TRITIUM AGE DETERMINATION OF GROUND-WATER RECHARGE IN THE RYAN FLAT SUBBASIN, TRANS-PECOS TEXAS

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 96-4245

Prepared in cooperation with the
TEXAS WATER DEVELOPMENT BOARD
and the
EL PASO WATER UTILITIES PUBLIC SERVICE BOARD

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U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Gordon P. Eaton, Director

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS, AND VERTICAL DATUM

Multiply	By	To obtain
acre-feet (acre-ft)	1,233	cubic meters (m^3)
feet (ft)	0.3048	meters (m)
gallons per minute (gal/min)	0.06309	liters per second (L/sec)
inches (in.)	2.54	centimeters (cm)
mile (mi)	1.609	kilometer (km)
square miles (mi^2)	2.590	square kilometers (km^2)
tons (tons)	907.2	kilograms (kg)
tons/acre-feet (tons/acre-ft)	0.0007357	megagram/cubic meter (mg/m^3)

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:

$$°F = 1.8 (°C) + 32.$$

Specific conductance is reported in microsiemens per centimeter (µS/cm) at 25 degrees Celsius.

Chemical concentrations in water are reported in milligrams per liter (mg/L), micrograms per liter (µg/L), or picograms per liter (pg/L), which are roughly equivalent to parts per million, parts per billion, and parts per quadrillion, respectively, when concentrations are less than about 7,000 milligrams per liter.

Chlorofluorocarbon concentrations in water are reported in picograms per kilogram (pg/kg), which are equivalent to parts per quadrillion.

Tritium activities in water are reported in tritium units (TU's), which are equivalent to 3.24 picocuries per liter (pCi/L) or 1 tritium atom in 10^{18} atoms of hydrogen.

Gross alpha and gross beta activities in water are reported in picocuries per liter (pCi/L).

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

CHLOROFLUOROCARBON AND TRITIUM AGE DETERMINATION OF GROUND-WATER RECHARGE IN THE RYAN FLAT SUBBASIN, TRANS-PECOS TEXAS

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ABSTRACT

A study was conducted to determine the relative influence of mountain-front infiltration in the Ryan Flat subbasin and to determine whether recent recharge (post-1940), which is of importance to water-use planning, has reached the Salt Basin aquifer, Trans-Pecos Texas. The alluvial and volcanic Salt Basin aquifer lies within a bolson, and the average depth to water in most of the subbasin is approximately 250 feet. Concentrations of the chlorofluorocarbons CFC-11, CFC-12, and CFC-113, as well as tritium, were measured in water from 10 wells in the study area. CFC-model recharge dates ranged from pre-1940 to the early 1970's. Ground water in five wells had CFC-model dates of pre-1940 or pre-1945. Ground water in two wells had dates of the mid- to late 1940's. Ground water from one well had a CFC-model recharge age of the early 1950's. Samples from the remaining two wells were most probably contaminated in some manner and are probably unreliable. CFC-model ages were calculated independently for the three chlorofluorocarbons, though the presence of volatile organic compounds affected agreement among them. Tritium activities in the nine wells for which tritium was analyzed indicated pre-1953 recharge and thus agreed approximately with the CFC-model dates.

Ground water was analyzed for selected water-quality constituents. Water from all wells met U.S. Environmental Protection Agency national primary and secondary drinking water standards for all tested constituents except fluoride in samples from three wells. Silica concentrations in water from six wells exceeded a range considered typical in natural waters.

INTRODUCTION

In 1992, the El Paso Water Utilities purchased land and water rights in the northern portion of the Ryan Flat subbasin of the Salt Basin near Valentine, Texas, approximately 125 mi southeast of El Paso (fig. 1). The Salt Basin aquifer may contain the largest volume of fresh ground water available to the City of El Paso within the Trans-Pecos Texas area (Tom Cliett, Tom Cliett and Associates, written commun., 1991). The part of the Salt Basin aquifer within the Ryan Flat subbasin is composed of basin alluvium and colluvium derived from sediments from the mountains flanking the basin and underlying volcanic flows, tuffs, and pyroclastic debris. Recharge to the aquifer in the Ryan Flat subbasin has been estimated to be 5,800 acre-ft/year as the result of mountain-front recharge in the foothills of the Davis Mountains and Sierra Vieja bordering the subbasin and of infiltration of water from ephemeral-stream channels crossing the subbasin (Gates and others, 1978). However, the accuracy of this recharge estimate is limited by a lack of supporting hydrogeologic and hydrogeochemical data. In 1993 the U.S. Geological Survey (USGS) in cooperation with the Texas Water Development Board and the El Paso Water Utilities Public Service Board began an investigation to determine the relative influence of mountain-front infiltration in the Ryan Flat subbasin and to determine whether recent recharge (post-1940), which is of importance to water-use planning, has reached the Salt Basin aquifer. Chlorofluorocarbon (CFC) analysis and tritium analysis of local ground water were chosen as the most appropriate methods. The report was prepared in cooperation with the Texas Water Development Board and the El Paso Water Utilities Public Service Board.
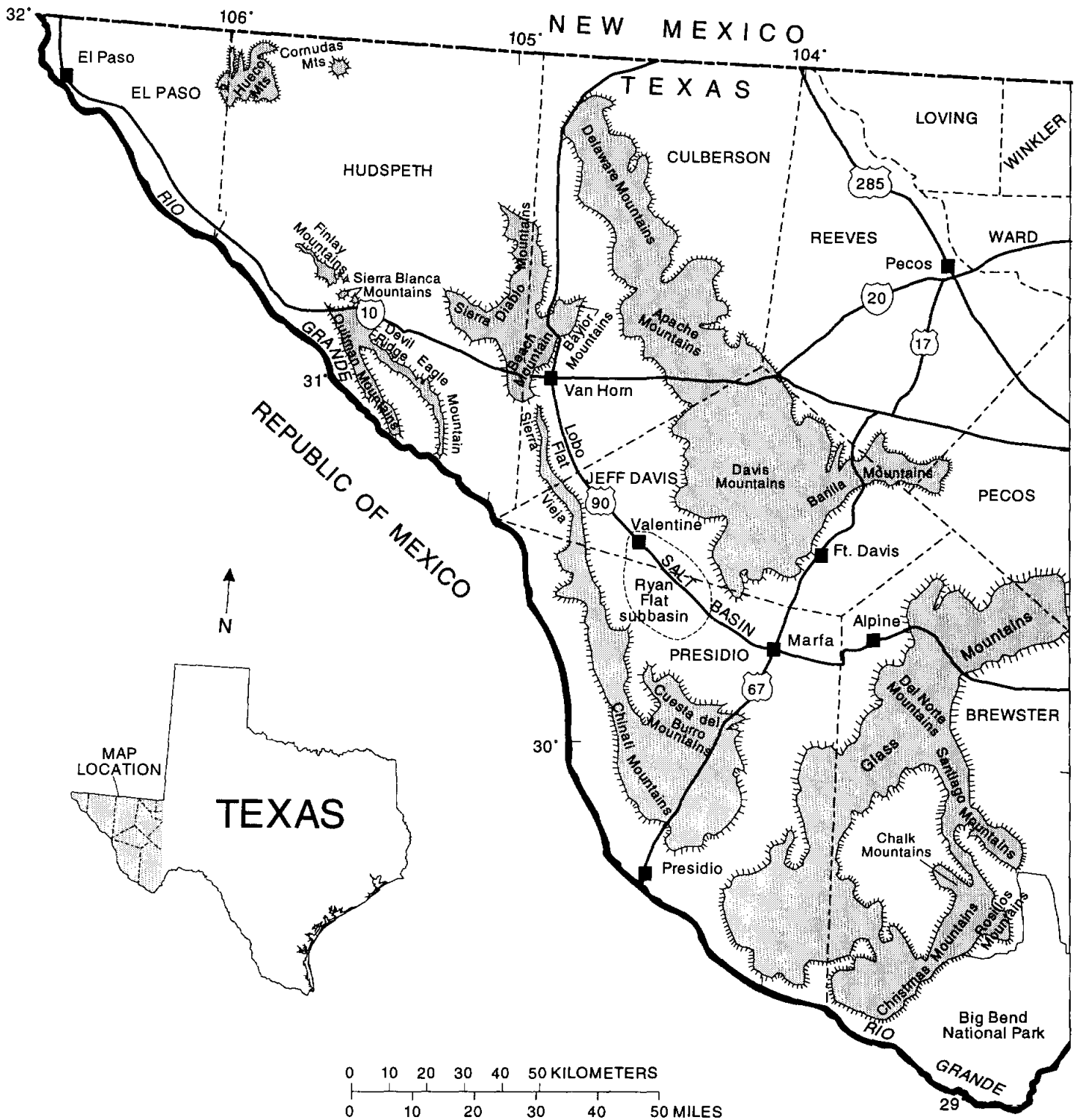
Figure 1.--Location of the Ryan Flat subbasin and major cultural and physiographic features.

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Purpose and Scope

This report presents water-quality data and CFC and tritium age dates of ground-water samples collected from 10 wells in the Ryan Flat subbasin. Age dates of ground water were used to determine the time of ground-water recharge (the time ground water became isolated from the unsaturated zone) in the study area. To this end, CFC concentrations and tritium activities in water from 10 wells in the Ryan Flat subbasin are described. Additionally, other water-quality properties and constituents from these 10 wells are described and discussed. The report also includes the methodology used, presentation and interpretation of the data, and discussion of the results.

Description of the Study Area

The Ryan Flat subbasin of the Salt Basin is in Jeff Davis and Presidio Counties in Trans-Pecos Texas (fig. 1). (Trans-Pecos Texas refers to the portion of Texas west of the Pecos River.) The Ryan Flat subbasin extends southeast from Rubio Dome (fig. 2) to the drainage divide 10 mi northwest of Marfa (Gates and others, 1978) and encompasses approximately 360 mi^2. The study area is the entire Ryan Flat subbasin; however, suitable wells for sampling were found only in the northernmost portion of the subbasin. The only town in the study area is Valentine with a population of 217 (U.S. Department of Commerce, 1991). Agricultural activity in the area is currently (1996) limited to cattle grazing; between 1979 and 1990, however, Antelope Valley Ranch (formerly Antelope Valley Farms) irrigated a variety of grain and vegetable crops. Figure 2 shows major features of the study area.

Geohydrologic Setting

The Ryan Flat subbasin lies on the eastern edge of the Basin and Range physiographic province (Fenneman, 1931). This area of Texas is characterized by a series of isolated, northwest-trending mountain ranges (horsts) separated by broad structural basins (grabens) formed by late Tertiary and Quaternary normal faulting. These basins, or bolsons, are filled with alluvium and volcanic flows from the surrounding mountains and commonly have closed drainage systems, though through-flowing drainage has developed in the basins along the Rio Grande. Local names for these features may be "basin," "bolson," or "flat." The Salt Basin, of which Ryan Flat is a subbasin, is the easternmost basin in the Basin and Range Province (Underwood, 1980).

The Ryan Flat subbasin is underlain by basin-fill alluvium and bordered on the northwest by Rubio Dome, an outcrop of volcanic rock; on the southeast by the drainage divide at the southern end of the Salt Basin; to the northeast by the Davis Mountains, a "Tertiary volcanic field of alkalic igneous rocks"; and on the west by the Sierra Vieja (or Rim Rock Mountains), a "sequence of Tertiary flow and pyroclastic rocks" (Underwood, 1980). The lithology of a well drilled south of Valentine in the Ryan Flat subbasin was described by Gates and White (1976) as basin-fill alluvium from the surface to 385 ft; clay or altered ash-fall tuff to 555 ft; well-sorted, permeable volcanic-clastic sands and thin volcanic flows to 1,250 ft; volcanic flows and tuffs to 1,465 ft; and tuff and altered tuff below this. Gates and others (1978) considered the water-bearing units in the alluvium and volcanic rocks to be part of the Salt Basin aquifer.

For the current study ground-water recharge was assumed to have several possible sources: infiltration of precipitation along the mountain fronts, infiltration of precipitation through the basin floor or ephemeral streams incised into the basin floor, or infiltration of irrigation water. Gates and others (1978) reported that recharge to the Salt Basin aquifer in the Ryan Flat subbasin is along the mountain fronts bordering the basin and probably along the channels of the ephemeral streams crossing the flat. Flow through the aquifer was reported (Gates and others, 1978) to be northwest to Lobo Flat and to the south and west. Ground-water discharge is through springs and wells.
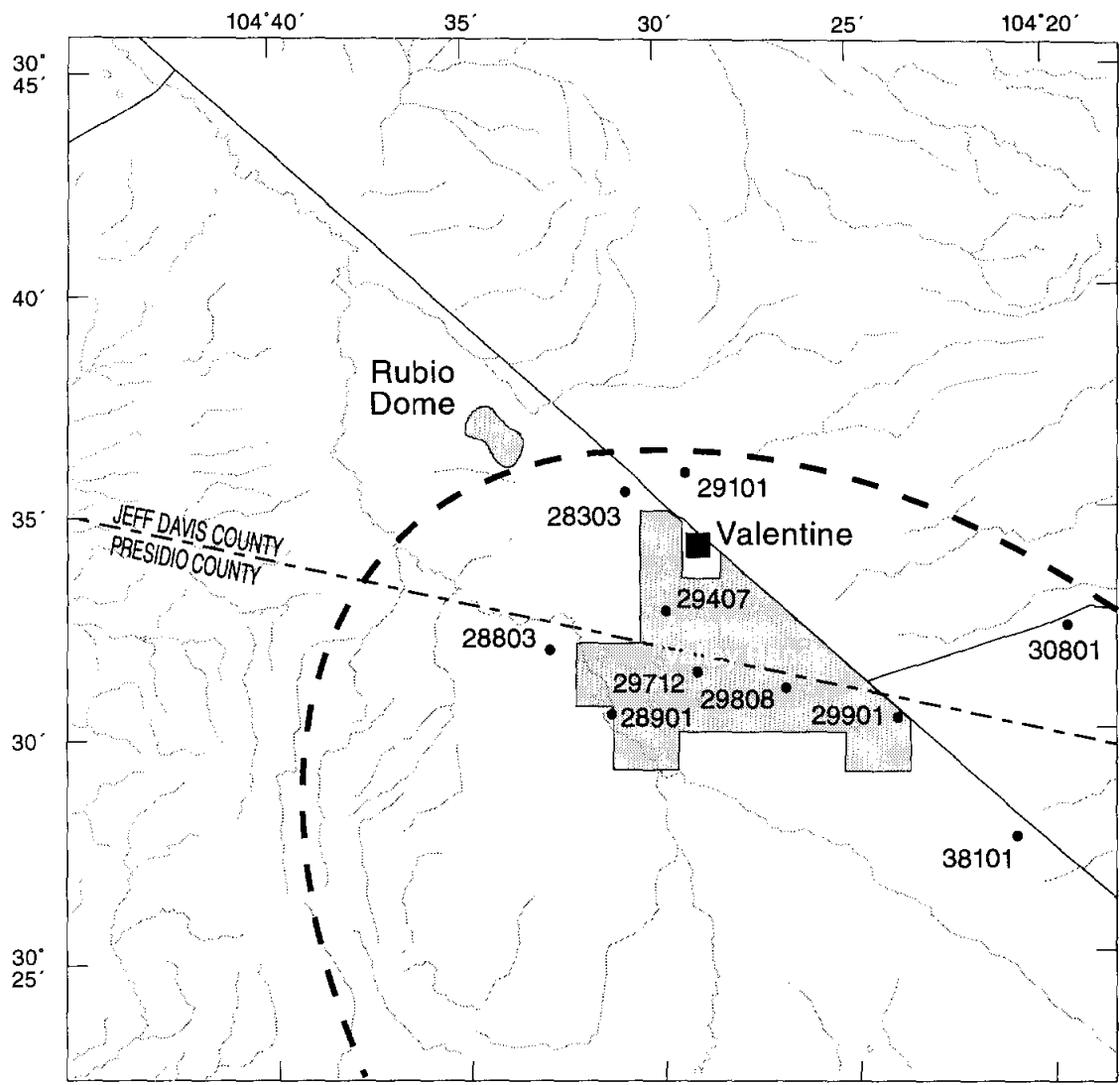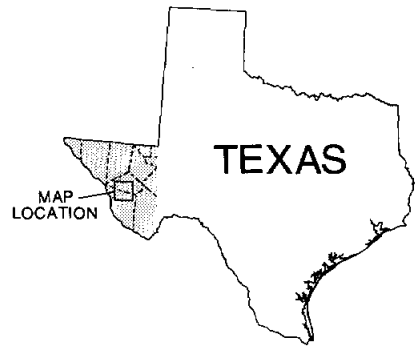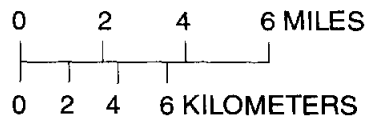
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Figure 2.--Major features of the northern portion of the Ryan Flat subbasin and wells sampled.

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Figure 3 shows ground-water levels in the Salt Basin aquifer from measurements made by the Texas Water Development Board during 1993-94 (Doug Coker, written commun., 1995). Ground-water flow is generally toward the northwest-trending axis of the Ryan Flat subbasin and then to the northwest. The general shape of the water table is similar to that shown in Gates and others (1978) for water levels measured during 1972-74. However, water levels have declined an average of 2.6 ft in 27 wells measured during both time periods. In these 27 wells, the maximum water-level decline was 152 ft in well 36101, and the maximum water-level increase was 25.6 ft in well 19801. Depth to water in the Ryan Flat subbasin ranges from approximately 26 to 750 ft, with an average water-level depth of approximately 250 ft.

The climate of the study area is subtropical arid with hot summers and mild winters (Gates and others, 1978; Larkin and Bomar, 1983). Two meteorological observation sites are within the study area: Valentine, which has recorded temperatures since 1975 and precipitation since 1949, and Valentine 10 SW (approximately 10 miles southwest of Valentine), which does not record temperature but has recorded precipitation since 1930. Annual precipitation for 1993 was 12.9 in. at the Valentine station and 14.6 in. at the Valentine 10 SW station. Average annual precipitation was not calculated for the Valentine station but was 14.8 in. at the Valentine 10 SW station for 1930-93 (U.S. Department of Commerce, 1994). Annual pan evaporation in the study area is approximately 106 in. (Dugas and Ainsworth, 1983).

Previous Investigations

Six reports on the hydrogeology of the Ryan Flat subbasin and surrounding area are most relevant to the present study. The earliest of these is a report by Hood and Scalapino (1951) summarizing development of ground water for irrigation in the late 1940's. Drillers' logs and water levels are included for wells at Valentine. Follet (1954) listed water levels and wells in a three-county area, though none of these wells are within the boundaries of the study area. Gates and White (1976) described the lithology, water quality, and aquifer tests for four test holes drilled by the USGS in Trans-Pecos Texas. One of these test holes was drilled in the study area, approximately 5 mi south of Valentine. White and others (1978) presented water levels and ground-water quality for parts of Trans-Pecos Texas, including wells in the study area.

Gates and others (1978) described nine areas (among them the Ryan Flat subbasin) in Trans-Pecos Texas with regard to general ground-water hydrology, quality, development, and supply. Interpretations in this report were made with borehole data, supplemented by geophysical methods (including electrical, seismic, and gravity surveys). The report includes estimated volumes of stored ground water and estimated recharge.

The most recent report, by Baumgardner and Scanlon (1992), discusses surface fissures in Trans-Pecos Texas. Though elsewhere in the Southwest similar features are caused by subsidence related to ground-water production (Laney and others, 1978), Baumgardner and Scanlon found no correlation between ground-water pumping in Trans-Pecos Texas and the appearance of surface fissures.

Chlorofluorocarbon age dating of ground water is becoming more widely used, and several studies have been published in the literature. Though CFC's in ground water were first studied in the 1970's (Plummer and others, 1993), CFC's were not widely used for age dating because of difficulties associated with analysis in the field. These difficulties were circumvented by isolating the samples in the field for laboratory analysis, as described by Busenberg and Plummer (1992) in their study of the alluvium and terrace system of central Oklahoma. Busenberg and others (1993) described CFC age interpretation and limitations as they apply to the Snake River Plain aquifer. A more generalized discussion of CFC age dating is found in Plummer and others (1993).
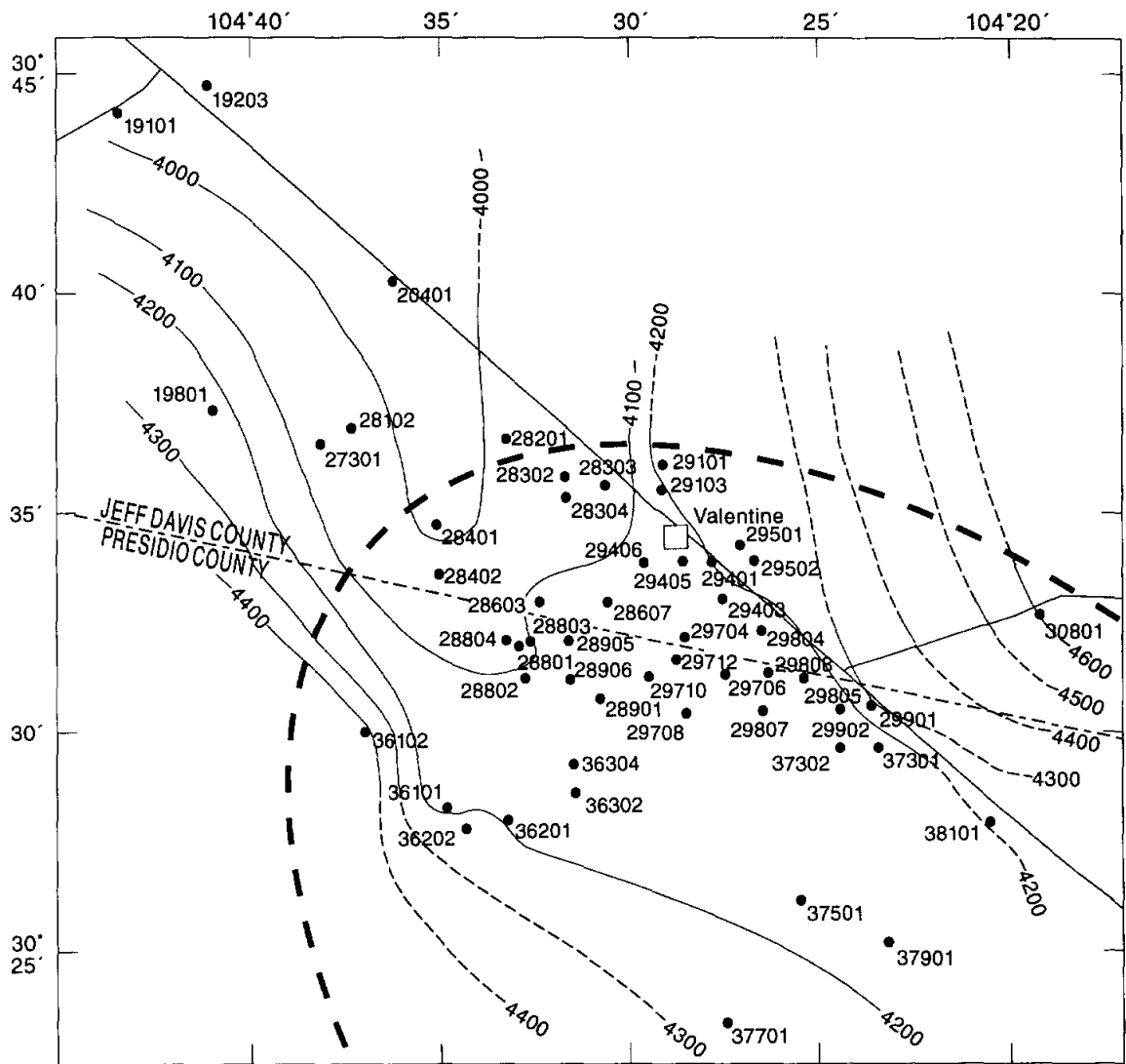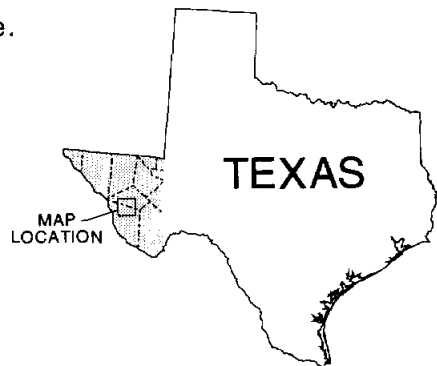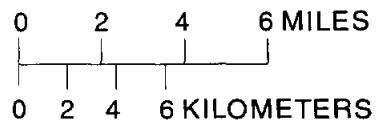
Figure 3.-- Ground-water levels in the northern portion of the Salt Basin aquifer, 1993-94 (water levels from the Texas Water Development Board and this study).

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One of the earliest studies to use tritium age dating of ground water was described by von Buttlar and Wendt (1958). It has since been used in a large number of other studies. Tritium age dating was discussed by Freeze and Cherry (1979), Fontes (1980), Mazor (1991), and Plummer and others (1993).

Well-Numbering System

The well-numbering system used in this report is that of the State of Texas and is based on the division of the State into a series of 1-degree quadrangles. The repeated division of these quadrangles allows placement of the well to the nearest 2.5-minute quadrangle (approximately 12,800 by 14,900 ft (3,900 by 4,540 m) in the study area).

Each 1-degree quadrangle is divided into 64 7.5-minute quadrangles, each of which is then divided into 9 2.5-minute quadrangles. Each of the 1-degree quadrangles has been assigned a two-digit identification number by the State; the 7.5-minute quadrangles are numbered consecutively, beginning in the upper left corner of the 1-minute quad; the 2.5-minute quadrangles are numbered consecutively, beginning in the upper left corner of the 7.5-minute quadrangle. Finally, the Texas Water Development Board assigns a two-digit number to the well to allow identification within the 2.5-minute quadrangle. The result is a unique seven-digit number registered with the Texas Water Development Board.

Prior to 1990, the well identification number was prefixed with a two-letter county code. Though the Texas Water Development Board discontinued the use of this prefix in 1990, the Texas and New Mexico Districts of the USGS have continued its use for consistency in the Ground-Water Site-Inventory data base and with previous publications.

In this report, the two-letter county code (either PS for Jeff Davis County or UW for Presidio County) and the two-digit code for the 1-degree quadrangle (51 for all wells) have been omitted for clarity and space. Thus, well UW-51-28-803 becomes 28803, and the unique State of Texas numbers can be recreated by adding 51 to the beginning of the well numbers in this report.

Acknowledgments

The author acknowledges Eurybiades Busenberg who provided assistance in the interpretation of the CFC and tritium results. Appreciation is extended to Deron Kasparian and Allen Kasparian for allowing free access to the wells on Antelope Valley Ranch and providing miscellaneous field support. The author also thanks the members of the Board of Directors of the Jeff Davis County Underground Water Conservation District for assistance and advice during the course of the study.

METHODS OF STUDY

Well Selection

Ten wells in the Ryan Flat subbasin were sampled for this study (fig. 2). Most wells are located on the basin floor; thus most samples were collected from the basin floor. Because of the small number of wells available for sampling in the study area, sampling was not limited to wells with complete records or logs. Well 29407 was first sampled to determine whether the pump and sampling apparatus were free of CFC contamination. This well is screened 420 ft below the water table and is assumed to yield water older than 50 years--that is, water recharged before 1945--and free of CFC-11 and CFC-113.

Collection and Analysis of Ground Water for Selected Properties and Constituents

Complete field water-quality properties (specific conductance, pH, temperature, dissolved oxygen, and alkalinity) were measured in accordance with procedures outlined in Claassen (1982). Properties and constituents measured are listed in table 1 (all tables are in the back of the report).

Prior to CFC sample collection a series of bottles were filled with discharge from the CFC sampling apparatus (described below). Water samples were collected for analysis of major anions and cations, trace metals, and gross alpha and gross beta radioactivity. The major anion, cation, and trace-metal analyses required 500 milliliters (mL) of unfiltered and unacidified water, 500 mL of filtered unacidified water, and 500 mL of filtered and acidified water. Gross alpha and beta radiation samples required 2 L of filtered and acidified water. Samples requiring filtration were filtered with disposable 0.45-micron-pore-size cartridge-style filters. The filter either was attached directly to the discharge line during sample collection or was used in conjunction with a peristaltic pump. Samples requiring preservation were acidified with HNO_3 to a pH less than 2 in the field and checked with pH paper. Samples were shipped to the USGS National Water Quality Laboratory in Arvada, Colorado, for analysis.

Age Dating Ground Water with Chlorofluorocarbons

CFC's are synthetic organic compounds of the halocarbon group believed to have no natural sources. They are used for refrigeration, aerosol propellants, cleaning solvents, and blowing agents in the production of foams and plastics. Production of CFC's began in the 1930's for refrigeration and has since expanded to more than 1.1 million tons annually (Plummer and others, 1993). For age dating ground water, the primary CFC's of interest are CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 ($C_2Cl_3F_3$). Some of the advantages of CFC dating are its analytical detection limit of 0.3 pg/kg (L.N. Plummer, written commun., 1996) and the ability to determine the presence of as little as 0.01 percent modern water where it has mixed with pre-1940 ground water (Plummer and others, 1993).

Chlorofluorocarbons were first measured in the atmosphere in 1975, and measurements since then, combined with 1940-75 concentration estimates from production records, provide estimates of atmospheric concentrations of CFC's since their production began (Busenberg and Plummer, 1992). Because atmospheric concentrations have increased steadily with time and because the ratio of the different compounds changes with time, any given year has a unique set of CFC-11, CFC-12, and CFC-113 concentrations. If water at the time of recharge to an aquifer is assumed to be in equilibrium with the atmospheric concentrations of CFC's, the CFC concentration of the water may be used to calculate the atmospheric concentration at the time of recharge; the calculated Henry's law atmospheric concentrations can then be matched to the year with the corresponding CFC concentrations. Thus, the CFC-model recharge date is the time ground water enters the aquifer and becomes isolated from the unsaturated zone. This method of using a CFC concentration in ground water to calculate the atmospheric concentration at the time of recharge, then correlating the atmospheric concentration to a given year, is referred to as the CFC model; the recharge years are referred to as CFC-model recharge dates. Because samples are easily contaminated with trace amounts of modern CFC's, CFC-model recharge ages need to be regarded as minimum estimates, assuming no dispersion or mixing of the ground-water sample during collection.

The main assumption used in the calculation of CFC-model recharge dates is that CFC-11, CFC-12, and CFC-113 concentrations in water are proportional to the atmospheric concentrations at the time of recharge; thus, as younger water with increasing amounts of CFC's recharges the aquifer, the CFC concentration of ground water increases. Implicit in this assumption is that CFC concentrations in the air and water of the unsaturated zone are in equilibrium with the atmosphere. This assumption of equilibrium applies only to thin unsaturated zones. In a study of several sites on the Southern High Plains of Texas, Weeks and others (1982) compared

theoretical effective-diffusion coefficients of CFC's in free air to analytical-model results and found that CFC transport is retarded through the unsaturated zone by tortuosity, solubility, and sorption, and that these effects tend to increase with depth. CFC's in ground water do not decay except in the presence of certain anaerobic bacteria.

CFC-12 was the first CFC produced, and its presence in ground water indicates post-1940 recharge. The presence of CFC-11 indicates post-1945 recharge, and of CFC-113 indicates post-1965 recharge. Because the processes of recharge and CFC sampling and analysis may affect the "true" concentration of the three CFC's differently, all three compounds are used to estimate a recharge date. Generally the CFC-12 age is considered to be the most reliable for several reasons: (1) CFC-12 is less likely than CFC-11 and CFC-113 to be introduced into the sample by contamination from sampling equipment (E. Busenberg and L.N. Plummer, U.S. Geological Survey, written commun., 1994); (2) CFC-12 is adsorbed onto soils less strongly than CFC-11 and CFC-113 (Weeks and others, 1982); and (3) CFC-12 has a lower solubility in water than CFC-11 and CFC-113 and thus is less affected by hydrodynamic dispersion (Plummer and others, 1993). As with most ground-water age-dating methods, however, waters of various ages may mix, thus producing an average or bulk water age.

Plummer and others (1993) listed six properties that render an aquifer most suitable for CFC dating: (1) a rural setting, which is less likely to be affected by local sources of CFC's that could cause anomalously high concentrations of CFC's; (2) a relatively thin unsaturated zone, probably less than 30 ft, where unsaturated-zone air has CFC concentrations similar to those in the atmosphere; (3) oxic ground water where there is no evidence of anaerobic microbial degradation of CFC's; (4) an unsaturated zone with minimal or no organic matter, thus preventing sorption of CFC's onto organic soil material during dry periods; (5) a temperate climate where the unsaturated zone is less likely to dry between recharge events; and (6) shallow ground water that contains detectable concentrations of CFC's. An additional consideration is that the aquifer should be free of volatile organic compounds (VOC's), which can mask the presence of CFC's.

Collection and Analysis of Ground Water for Chlorofluorocarbons

Of the 10 wells sampled for this study, five did not have pumps; four of these five wells were abandoned irrigation wells on Antelope Valley Ranch. When in use these irrigation wells had turbine pumps with oil drip lines to lubricate the downhole pump parts. When such pumps are in use this drip oil does not accumulate in the well. When irrigation stopped at the Antelope Valley Ranch, the drip oil valves were not closed. Consequently a foot or more of oil accumulated on top of the water column in the casing of the wells. In an attempt to remove this drip oil, a 4-in. electric submersible pump was set by a Texas Water Development Board crew, turned on, and raised in the well until an ammeter on the pump began to show that the pump was drawing small amounts of air. Wells that required removal of the irrigation drip oil are listed in table 1. This method did skim much of the floating oil off the water surface, though not all.

The submersible pump was set as close to the water table as possible (generally 2-5 ft) and pumped for several hours at approximately 12 gal/min until specific conductance, pH, and temperature of the ground water had stabilized. (Because the abandoned irrigation wells had casing diameters of 12 and 16 in. and hundreds of feet of water standing in the casing, less than one casing volume of water was evacuated before sampling all of these wells.) In several wells, drawdown of the water in the well made it necessary to stop the procedure, lower the pump, and resume pumping until the field water-quality properties stabilized. After the field properties stabilized, a Bennett submersible piston pump with a 1/4-in.-diameter discharge line made from refrigeration-grade copper tubing was lowered into the well to a depth of 10 to 20 ft below the water table and pumped for a minimum of 1 hour. The Bennett pump was not set higher because of the presence in some wells of drip oil. The CFC sampling apparatus was connected to the

discharge line either directly or through aluminum tubing. The single nonirrigation well without a pump was sampled in the same manner. The five wells with pumps were connected to the CFC sampling apparatus with aluminum tubing and pumped until field water-quality properties stabilized. More than one casing volume was pumped from these wells.

The water samples for CFC analysis were collected in 62-mL borosilicate glass ampules and flame sealed in the field with an oxygen-MAPP (methyl acetylene-propadiene mixture) gas torch to prevent contact with the atmosphere and thus sample contamination. Five samples for CFC analysis were collected at each well; labeled with location, date, and time of collection; and finally numbered in order of collection. The CFC sampling apparatus and procedures are described in Busenberg and Plummer (1992).

After collection, CFC samples were shipped to a USGS laboratory in Reston, Virginia, for analysis by purge-and-trap gas chromatography. The samples were analyzed by stripping the CFC's from the sample water with ultrapure N_2 gas and collecting them in a cold trap cooled to -30 °C. The trap was then heated to 100 °C to release the CFC's, which were then passed through a precolumn to separate CFC-11, CFC-12, and CFC-113 from other halocarbons. The sample was then passed into the analytical column. Once CFC-11, CFC-12, and CFC-113 entered the analytical column, the precolumn was backflushed to remove other halocarbons. By using the CFC concentrations in the water sample, the water-sample temperature, and the ampule water and headspace volumes, the CFC concentration in ground water can be calculated. Busenberg and Plummer (1992) presented a more detailed description of this analytical technique.

Multiple samples were collected at each site to provide for sample loss and to check for sample contamination. Two main types of contamination were of concern in the study area: contamination with modern air and the presence of VOC's. Because the introduction of minute amounts of modern air into a sample will produce a younger CFC-model recharge date but the sampling process cannot contaminate a sample to appear older, several samples from each site were analyzed. By assuming that all samples from a single site had the same CFC concentration, the sample with the oldest CFC-model recharge date is considered the most accurate. The second type of contamination, that by VOC's, also tends to produce younger than actual recharge dates by masking the CFC peaks on the chromatogram.

Five samples were collected from each of 10 wells and three were analyzed from each of 9 wells: usually vial numbers 2, 4, and 5. The other two vials were held in reserve for later analysis, if necessary. Six vials were collected and five were analyzed for the first well sampled, well 29407. For this well, vial number 5 was held in reserve.

Age Dating Ground Water with Tritium

Tritium (^{3}H) is the radioactive isotope of hydrogen and has a half-life of 12.43 years. Tritium is produced naturally in the Earth's atmosphere, though its main use in hydrology stems from its production in large quantities by atmospheric testing of thermonuclear bombs. Tritium activities in continental precipitation prior to the advent of atmospheric testing in 1952 were in the range of 1 to 20 TU's; however, as testing continued, activities increased by two to three orders of magnitude (Michel, 1989). In late 1963 a moratorium on atmospheric testing was declared, and tritium activities in precipitation have decreased since then to pre-1953 levels. Tritium is thus used as an indicator of pre-1953 or post-1953 recharge of ground water; however, it is actually a measure of the age of the precipitation and differs from the CFC-model age by the length of time a pulse of water takes to move through the unsaturated zone.

Precipitation derived from oceanic sources tends to be lower in tritium than that derived from continental sources. Oceanic sources of precipitation, combined with the location of the bomb-testing sites, causes worldwide variability in tritium activities in precipitation. Michel (1989) used data for 14 USGS tritium-monitoring stations and the International Atomic Energy

station at Ottawa, Ontario, Canada, to map tritium deposition and precipitation in the continental United States for 1953-83 by grid cells of 2° latitude by 5° longitude. By correcting these data for radioactive decay, "spikes" of post-bomb water in the subsurface can be identified. The largest annual average tritium activity in the grid cell covering the study area (Michel, 1989) was 1,000 TU's in 1963. This level would be reduced to 176 TU's by 1994 by simple radioactive decay, assuming no mixing or dilution with other water. Similarly, water recharged in 1953 would have decayed to 0.6 TU by 1994. Tritium activities less than 0.6 TU indicate water recharged prior to 1953.

Collection and Analysis of Ground Water for Tritium

Prior to CFC sample collection, a 1-L sample of unfiltered, unacidified water was collected in a high-density polyethylene bottle and sealed with a plastic cone-seal cap for tritium analysis. Samples were shipped to the USGS National Water Quality Laboratory in Arvada, Colorado, for analysis by the University of Miami Laboratory, Miami, Florida.

Samples were prepared by electrolytic enrichment and analyzed with a liquid scintillation counter. A liquid scintillation counter measures the number of disintegrations per minute as tritium decays by beta emission to stable helium. Because this decay rate is known, the tritium activity can be determined. Because the decays occur randomly, however, any count made over a necessarily short analytical time may not be a true measure of the number of decays. Thus, the counting uncertainty is indicated by the 2-sigma precision estimate, which may be read as "plus or minus" the counting error value.

GROUND-WATER QUALITY

General Water Quality

Results of the water analyses are listed in table 1. Water from all wells met U.S. Environmental Protection Agency (USEPA) national primary and secondary drinking water standards for all tested constituents except fluoride (U.S. Environmental Protection Agency, 1994). The primary maximum contaminant level (PMCL) for fluoride is 4 mg/L, and the secondary maximum contaminant level (SMCL) is 2 mg/L. Fluoride concentrations in ground water from wells 28803, 29712, and 29407 were 5.7, 3.5, and 2.4 mg/L, respectively.

Hem (1989) noted that concentrations of dissolved silica in natural waters typically range between 1 and 30 mg/L. Six of the wells sampled for this study exceed this range; however, neither the USEPA nor the State of Texas has drinking water guidelines for silica. The main problem with elevated silica concentrations is scaling associated with industrial processes.

The Ryan Flat subbasin is in the transition zone between the Basin and Range and the Great Plains Provinces, and a heat-flow measurement made at the Antelope Valley Ranch indicates a value intermediate between the two provinces (Taylor and Roy, 1980). Trans-Pecos Texas has many thermal waters, and the elevated water temperature in well 28803 (49 °C) probably indicates that the water is from a local geothermal source. Tom Cliett (written commun., 1991) noted that many wells at Antelope Valley Ranch have ground-water temperatures above 24 °C and that at least five wells have water temperatures between 43 and 49 °C.

Ground water in the study area is generally a sodium bicarbonate type water (fig. 4). The sample from well 30801 plots as an outlier near the boundary of the sodium bicarbonate type field. Water from this well has a larger percentage of calcium than samples from wells near the subbasin center. The relatively small percentage of calcium in water from wells near the subbasin center may indicate sodium/calcium ion exchange with clay minerals as ground water moves from the subbasin margins to the center of the subbasin.

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Na HCO₃ type
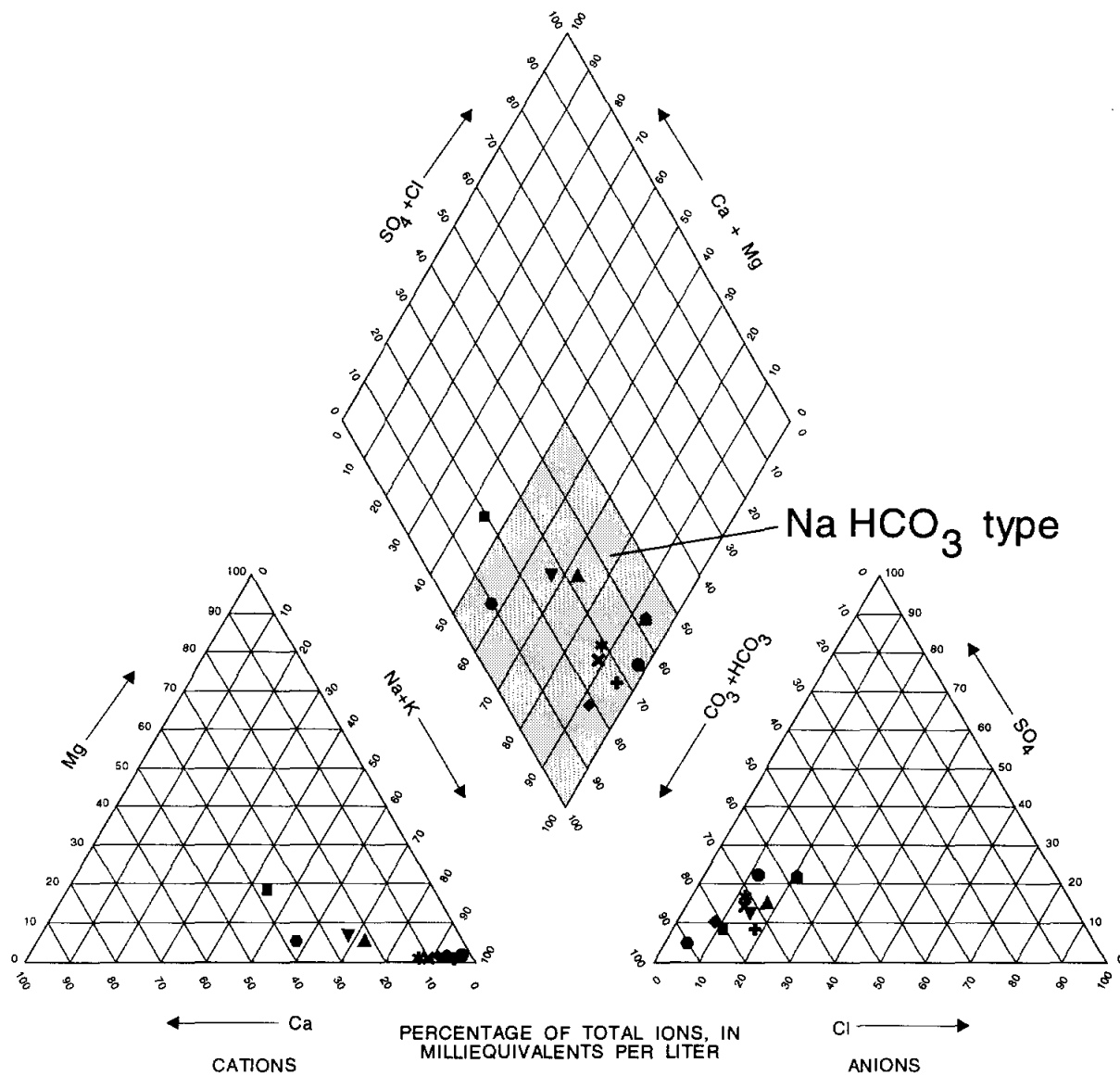
CHEMICAL CONSTITUENTS

SO₄ - Sulfate
Cl - Chloride
Ca - Calcium
Mg - Magnesium
Na+K - Sodium + potassium
CO₃+HCO₃ - Carbonate +
bicarbonate

PERCENTAGE OF TOTAL IONS, IN
MILLIEQUIVALENTS PER LITER

CATIONS

ANIONS

Figure 4.--Analyses of ground water collected in the Ryan Flat subbasin, Texas.

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Chlorofluorocarbon Content

Measured CFC concentrations in ground water from the 10 Ryan Flat subbasin wells sampled are shown in table 2 along with the data used to calculate recharge dates. (For identification of specific samples, a letter corresponding to the sample identification letter in table 2 is added to the well number in the text, for example 28303(A).) Concentrations of CFC-11 ranged from less than the detection limit of 0.3 pg/kg to 910.5 pg/kg, CFC-12 concentrations ranged from less than the detection limit of 0.3 pg/kg to 443.9 pg/kg, and CFC-113 concentrations ranged from less than the detection limit of 0.3 pg/kg to 300.6 pg/kg. The upper values reported here include several samples contaminated with modern air, resulting in concentrations much greater than actual concentrations in ground water. Such contamination was indicated by high concentrations of CFC compounds in a single sample from a well: samples 28803(C), 28901(C), and 30801(A).

Tritium Content

The measured tritium activities in ground water from nine of the Ryan Flat subbasin wells sampled are shown in table 1. (The tritium sample for well 29407 was damaged in transit to the laboratory.) Tritium activities ranged from less than the lower detection limit of 0.09 TU to 0.22 TU. The two-sigma precision estimate for all samples was 0.19 TU (table 1). Thus, tritium activities for all but one of the wells (29901) were less than the counting error.

AGE DATING GROUND WATER

Chlorofluorocarbon-Model Ages of Recharge

CFC-model recharge dates of ground water calculated for this study are shown in table 2 along with the data used in their calculation: recharge temperature, recharge elevation, barometric pressure when collected, CFC concentration in the sample, and calculated atmospheric partial pressure at the time of recharge. For all samples from six wells, the CFC-model recharge dates for CFC-12 are older than those for both CFC-11 and CFC-113. (VOC interferences in a seventh well prevented quantification of CFC-12.) This may be attributed to CFC contamination somewhere in the sampling process. Because CFC-12 is least affected by such contamination, the CFC-12 recharge date is regarded as the most reliable (Dunkle and others, 1993). Thus for samples from wells 28303, 28803, 28901, 29101, 29712, 29808, 29901, 30801, and 38101, a CFC-12 date was used to determine the CFC-model recharge date.

Samples from well 29712 had progressively younger dates with increased pumping time, probably indicating progressive contamination. In addition, although the CFC-12 date was older than the CFC-11 and CFC-113 dates in the first sample, the CFC-11 date was older than the CFC-12 and CFC-113 dates in the second and third samples. The date closest to the actual age is probably the CFC-12 date from the first sample.

Water from wells 29101 and 29901 had CFC-model recharge dates of early 1960's and early 1970's, respectively. (One sample, 29901(A), had a CFC-12 date of 1980, but an early 1970's date was chosen because of data for the other two samples from this well.) These CFC-12 dates are generally corroborated by the CFC-11 data.

The CFC-model recharge date for water from well 29407 is calculated as pre-1945, though the actual age is probably much older than 1945. Due to interferences from VOC's, low concentrations of CFC-12 could not be measured; the complete absence of CFC-11, however, indicates a recharge date prior to 1945. This masking of the chromatogram by VOC's is discussed in more detail later in this section. The most probable CFC-model recharge date for each well, based on these interpretations of the data, is listed in table 3.

Though CFC age dating has been used successfully at many sites, several potential limitations on the accuracy of these ages must be considered regarding the results. These include limitations applicable to all sites, such as uncertainties regarding the determination of recharge temperature and recharge elevation, and site-specific limitations.

Previous CFC studies have used the average annual temperature or average annual soil temperature as the equilibration temperature for recharge (Busenberg and Plummer, 1992; Busenberg and others, 1993). For the present study two such values were available: the average annual temperature of 16 °C at the Valentine meteorological observation site, and the average annual 4-in. soil temperature of 18.4 °C at Dell City, Texas (100 mi northwest of the study area). For this study the average annual temperature of 16 °C at Valentine was used in calculating the CFC-model recharge dates. Recalculation of the CFC-model recharge dates using the 18.4-°C soil temperature did not change any of the noncontaminated values by more than 1 year.

The elevation of recharge is another source of uncertainty in the calculation of CFC-model ages. In the current study recharge elevation could realistically be expected to range from approximately 3,800 ft, the lowest point of the water table in the Ryan Flat subbasin, to approximately 5,300 ft above sea level, the highest point of contact of alluvial deposits in the basin with the base of Tertiary volcanic outcrops in the Davis Mountains. By convention, the recharge elevation is calculated as the surface elevation of the well. The value shown for each well in table 2 is the surface elevation of the well. By varying the recharge elevation between the two extremes of 3,800 and 5,300 ft, the CFC-model ages for uncontaminated samples did not change by more than 0.5 year. Busenberg and others (1993) conducted sensitivity analyses on CFC-model recharge dates by calculating the effects of misestimating the recharge temperature (underestimation and overestimation by 3 °C) and recharge elevation (underestimation by 3,000 ft). They concluded that changes in these two values did not significantly affect CFC-model recharge dates that were greater than 20 years, which confirms the results of this study.

The "Age dating ground water with chlorofluorocarbons" section lists six desired properties of aquifers for CFC dating (Plummer and others, 1993). Some of these aquifer properties are not present in the study area and may thus affect the calculated CFC-model ages. The first of these, a rural setting, applies to the study area. Urban areas commonly have elevated concentrations of CFC's due to industrial activity and a large number of refrigeration units. In rural settings, CFC concentrations are more likely to be at background concentrations.

A second desirable aquifer property is a relatively thin unsaturated zone, preferably less than 30 ft, a condition that does not apply to the study area. This violates the primary model assumption that CFC concentrations in the air and water of the unsaturated zone are in equilibrium with the atmosphere. Weeks and others (1982) found that CFC concentrations decrease with depth in unsaturated zones greater than 160 ft; that CFC transport is retarded through the unsaturated zone by tortuosity, solubility, and sorption; and that these effects tend to increase with depth. Cook and Solomon (1995) found that this time lag can add as much as 8 to 15 years to a CFC-model recharge age for a water table at 98 ft. Because the water table in the study area is deeper than this, any recharging ground water would likely have lower concentrations of CFC's than current atmospheric concentrations and would result in recharge dates older than actual recharge dates.

A third condition, oxic ground water with no evidence of microbial degradation of CFC's, is met in the study area. Busenberg and Plummer (1992) and Cook and others (1995) summarized work by others that describes reduction of CFC concentrations by anaerobic microbial activity, thereby producing older calculated recharge dates. The rate of biodegradation decreases as the fluorine content of halocarbon increases; thus, for the three compounds discussed here, CFC-11 breaks down the most quickly, and CFC-113 breaks down the most slowly. This biodegradation is thought to be significant in highly reducing ground waters

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containing high dissolved organic carbon concentrations. Because eight samples contained dissolved oxygen at 1-percent saturation and because the rock types composing the Salt Basin aquifer are not typically associated with elevated concentrations of dissolved organic carbon, biodegradation is assumed not to be occurring in ground water in the Ryan Flat subbasin.

A fourth aquifer property, an unsaturated zone with minimal or no organic content, probably applies to the study area. In drier climates, CFC's may undergo sorption to organic soil material as the unsaturated zone dries (Busenberg and Plummer, 1992). The higher the solid-liquid partition coefficient, the more strongly a compound is sorbed. Solid-liquid partition coefficients are estimated to be 0.02, 0.0, and 0.1 for CFC-11, CFC-12, and CFC-113, respectively (Cook and Solomon, 1995). Therefore, if sorption onto organic soil material is occurring, concentrations of CFC-11 and CFC-113 in ground water would be reduced (and thus produce older recharge dates) relative to CFC-12. CFC-12 produced the youngest (most recent) recharge dates in ground water in only one well, 29712, though as discussed above, CFC-model results for this well are inconsistent.

The fifth condition, a temperate climate where the unsaturated zone is less likely to dry between recharge events, is not met. As stated above, the climate of the study area is subtropical arid (Larkin and Bomar, 1983). Plummer and others (1993) noted that water recharged through previously dried unsaturated zones may contain CFC concentrations larger than the atmospheric equilibrium. The mechanism responsible for this enrichment is CFC adsorption to soil material as the soil dries, then CFC desorption when the soil is rewetted. CFC-11 is more strongly adsorbed than CFC-12 and CFC-113, and upon rewetting is thus desorbed in larger concentrations than CFC-12 and CFC-113. In arid areas this sorption-desorption mechanism can lead to enrichment of CFC's and younger than actual ages, particularly for CFC-11.

The sixth condition, shallow ground water that contains detectable concentrations of CFC's, does not apply to the study area. Water levels in wells range from approximately 200 to 500 ft.

Another condition, hydrodynamic dispersion, can mix water of different ages, resulting in inaccurate CFC-model recharge age estimates (Plummer and others, 1993). Because CFC-12 is the least soluble in water and CFC-113 is the most soluble, CFC-12 is least affected by hydrodynamic dispersion (Plummer and others, 1993). Thus, if a sample has been affected by hydrodynamic dispersion, concentrations of the three compounds are reduced by different amounts (thereby producing older recharge dates), and the CFC-11 and CFC-113 dates are older than the CFC-12 date. One-dimensional advection-dispersion modeling described by Plummer and others (1993) showed that for CFC-11 and CFC-12, hydrodynamic dispersion can result in estimation of dates younger than actual recharge dates prior to 1973 and estimation of dates older than actual recharge dates after 1973. Only the second and third samples from well 29712 have CFC-11 and CFC-113 dates older than the CFC-12 date, but CFC-model results for this well are inconsistent, indicating probable contamination of some form.

In addition to these natural processes, anthropogenic effects may influence the results. Inconsistencies among the CFC-model dates may largely be due to the presence of organic compounds (such as drip oil) in ground water and CFC contamination of sampling equipment. Because CFC analysis is by gas chromatograph, VOC's mask small-concentration CFC peaks on the chromatogram; thus, concentrations of CFC-12 and CFC-113 were not reported for a few samples (table 2). Halocarbon contamination of sampling equipment has been described by several authors including Reynolds and others (1990). E. Busenberg and L.N. Plummer (written commun., 1994) described sample contamination by a variety of materials. They noted that polytetrafluoroethylene (PTFE or Teflon), tygon, polyethylene, polypropylene, natural and synthetic rubbers, silicone, and some other plastics will retain CFC-11 and CFC-113 and can contaminate a CFC sample. The younger CFC-model ages of these two compounds compared

with the CFC-12 ages for most samples are consistent with low-level CFC-11 and CFC-113 sample contamination.

Another process that could affect CFC-model recharge dates is the mixing of water of various ages in the well bore. This mixing of water could be due to lengthy screened intervals or casing breaches caused by corrosion or improper well completion. Such mixing is more likely to be a factor in wells with lengthy or multiple screened intervals. Wells 28303, 28803, and 29808 have multiple screened areas in zones of 2,890 ft, 1,558 ft, and 949 ft, respectively. Wells 29407 and 30801, the other two wells for which well-completion information is available, are screened over single intervals of 324 and 281 ft, respectively.

Tritium-Model Ages of Recharge

On the basis of tritium activities in ground water collected for this study, all samples were recharged prior to 1953. This determination was based on the largest tritium activity of 0.22 TU. By adding the 2-sigma precision estimate of 0.19 TU to the highest tritium activity of 0.22 TU, the activity is still less than 0.6 TU (the tritium activity to which recharge occurring in 1953 would have decayed).

Uncertainties are introduced into tritium recharge dates by several phenomena, one of which is the radioactive decay of tritium. As decay reduces tritium activities, formerly identifiable post-1953 activity spikes are reduced to a level at which only a pre- or post-1953 determination can be made. Because all tritium activities for this study indicated pre-1953 recharge, such dissipation did not influence the interpretations.

As with CFC recharge dates, uncertainty may be introduced by the mixing of ground water of various ages. This could decrease or increase tritium activities in the water of interest, thus affecting its apparent age. Such mixing could be caused by hydrodynamic dispersion or by the combining of waters of different ages in the well bore during pumping because of large screened intervals.

Age of Recharge

Table 3 lists CFC-model and tritium recharge dates as well as the most probable recharge date based on interpretation of the results. Figure 5 shows the location of wells and the most probable recharge dates for samples collected from the wells in the study area. For seven of the nine wells sampled for CFC's and tritium, the CFC-model ages are pre-1953; thus, the two methods corroborate each other. The CFC and tritium ages (early 1950's and pre-1953, respectively) for well 30801 were in approximate agreement.

CFC ages for samples from wells 29101 and 29901 were younger than the tritium ages for the same wells. As mentioned earlier, the CFC-model and tritium ages are actually the age of recharge and age of precipitation, respectively. As the thickness of the unsaturated zone increases (and the time required for infiltrating water to pass through it increases), the CFC-model age can be younger than the tritium age. However, the known presence of VOC's in other wells, possible errors associated with recharge through a thick vadose zone, and possible sample contamination are more probable reasons for the discrepancy between the CFC-model and tritium ages. Thus the pre-1953 tritium dates for these two wells may be considered the more reliable estimates of the age of ground-water recharge. This situation emphasizes the importance of using more than one age-dating method on a sample. Among the remaining available methods, carbon-14 dating may be the most useful due to the absence of carbonate rocks and its applicability to an older range of recharge dates.
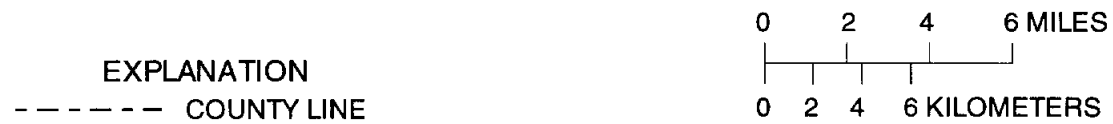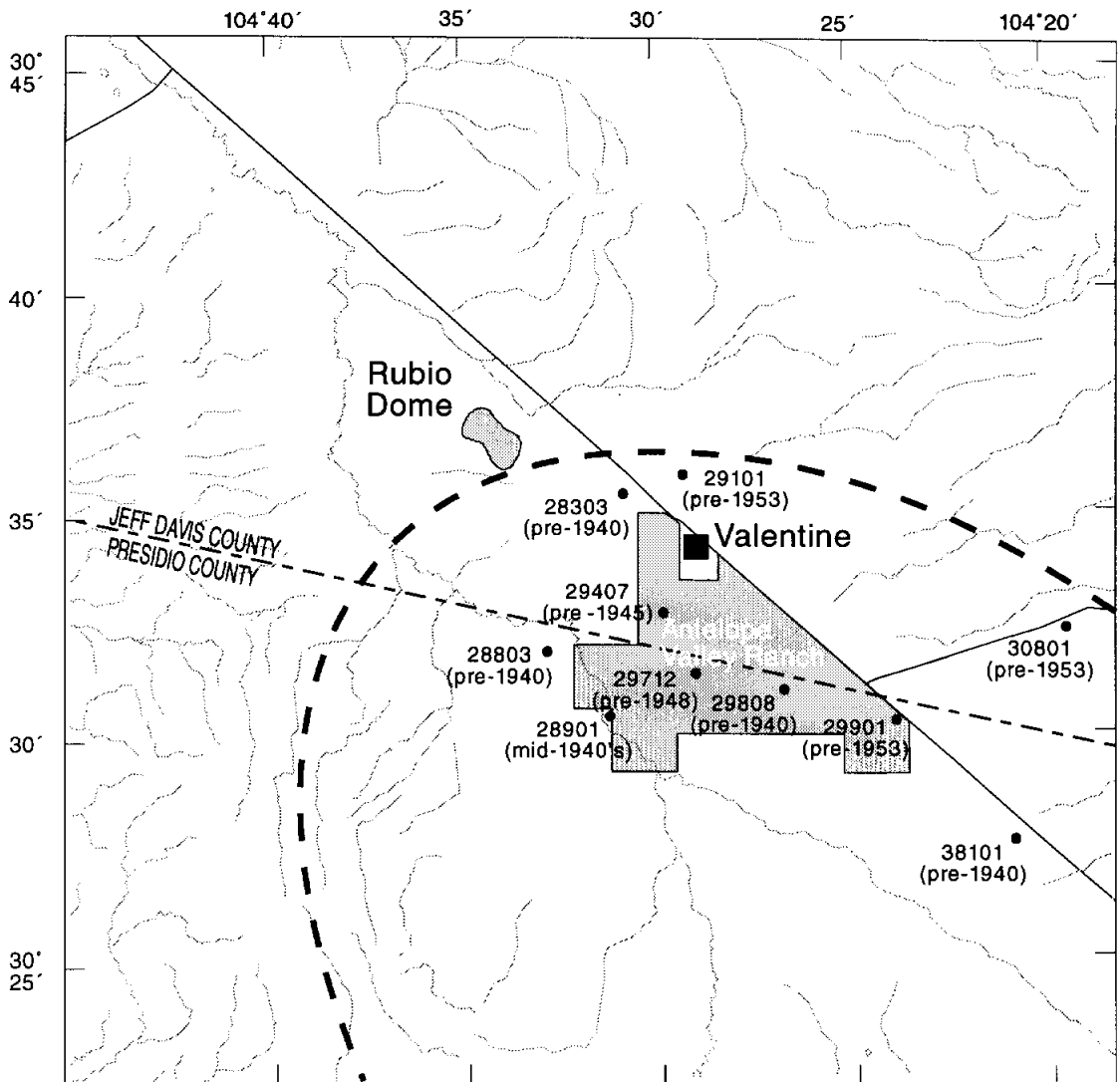
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Figure 5.--Wells sampled in the northern portion of the Ryan Flat subbasin and most probable recharge dates.

Because the tritium sample from well 29407 was damaged in transit, the CFC-model recharge date is used as the probable date. This conclusion is reasonable because the well is screened 420 ft below the water table and because the four other wells for which well-completion information is available are screened at shallower depths and CFC-model ages are pre-1940 and early 1950's.

Both tritium and CFC-model ages may be biased, either younger or older, at least for some wells. Several wells lack well logs. Others are known to be screened well below the water table (table 1), probably resulting in collection of a sample that is substantially older than water at the water table. In addition, though samples were not collected until water-quality properties stabilized, the sample may have been collected from standing water within the casing instead of from the aquifer near the water table because of the large volume of water standing in the abandoned irrigation wells. This would result in a sample taken some depth below the water table that again could be older than water at the water table.

As was mentioned earlier in the report, crops were irrigated during the 1980's on what is now Antelope Valley Ranch. This may have had the effect of increasing recharge; if any of this water had reached the aquifer prior to this study, however, it would be noticeable as post-1980 water in the CFC analyses. Because such water was not observed, either little or none of this water infiltrated or it has not reached the water table.

SUMMARY AND CONCLUSIONS

Concentrations of the chlorofluorocarbons CFC-11, CFC-12, and CFC-113, tritium, and selected water-quality properties and constituents were measured in water from 10 wells in the Ryan Flat subbasin of Trans-Pecos Texas. The age of ground-water recharge was calculated using both CFC-model and tritium results. The findings of the study are summarized below.

(1) Water from seven wells met USEPA national primary and secondary drinking water standards for all tested constituents. Three wells met the standards for all tested constituents except fluoride. Silica concentrations in water from six wells exceeded a range that is considered typical in natural waters. Analyses indicate that ground water in the area is generally a sodium bicarbonate type.

(2) CFC-model recharge dates ranged from pre-1940 to the early 1970's. Ground water in five wells had CFC-model dates of pre-1940 or pre-1945. Ground water in two wells had dates of the mid- to late 1940's. Ground water from one well had a recharge age of the early 1950's. Samples from the two remaining wells were most probably contaminated in some manner and are probably unreliable.

(3) Tritium activities in the nine wells for which tritium was analyzed all indicate pre-1953 recharge.

(4) Comparison and interpretation of the CFC and tritium results indicate that ground-water recharge in the wells sampled in the Ryan Flat subbasin is older than 1953.

(5) Despite violation of some of the CFC-model assumptions, CFC-model and tritium ages agree for seven of the nine wells sampled for both tritium and CFC's.

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Table 1.--Water-level, well-construction, and water-quality data for wells sampled in the Ryan Flat subbasin

[≅, approximately; --, parameter unknown or not measured; S, submersible; W, windmill; μS/cm, microsiemens per centimeter at 25 degrees Celsius (°C); NTU's, nephelometric turbidity units; dis, dissolved; <, less than; mg/L, milligrams per liter; IT, incremental titration; μg/L, micrograms per liter; pCi/L, picocuries per liter; TU's, tritium units]

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
Well location (fig. 2)	30352710 4305001	30315610 4325201	30303010 4311901	30355410 4291701	30324910 4294901	30312610 4290301	30310310 4264701	30302010 4235501	30322110 4193101	30273810 4205501
Well name	AVR 271	AVR 331	AVR 307	MEANS	AVR 233	AVR 194	AVR 120	AVR 18	DYER	RYAN R
Date (month/day/year)	11/11/94	11/12/94	11/15/94	11/15/94	11/08/94	11/13/94	11/09/94	11/11/94	11/10/94	11/13/94
Time	1500	1400	1530	1145	1530	1600	1430	0930	1530	1015
Water-level depth (feet)	343.5	192.6	211.6	211.6	214.4	256.8	316.0	≅ 306.4	318.4	≅ 478.6
Well depth (feet)	3,422	1,822	320	295	958	--	1,322	355	341	565
Depth to top of screen (feet)	532	264	--	--	634	--	373	--	60	--
Depth to top of gravel pack (feet)	0	0	--	--	0	--	0	--	≅ 0	--
Pump type	None	None	S/W	S	None	S	None	S/W	None	S
Specific conductance, field (μS/cm)	397	498	356	329	309	502	290	308	342	244
Specific conductance, lab (μS/cm)	393	492	367	353	344	532	320	305	337	257
pH, field (standard units)	8.4	8.9	7.8	8.4	8.8	8.5	8.5	8.2	7.5	8.3
pH, lab (standard units)	8.2	9.0	7.9	8.3	8.6	8.3	8.2	8.0	7.5	8.1

Table 1.--Water-level, well-construction, and water-quality data for wells sampled in the Ryan Flat subbasin--Continued

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
Temperature, air (°C)	23.5	23.5	14.5	16.0	29.5	21.5	22.0	17.5	22.5	17.0
Temperature, water (°C)	26.0	49.0	20.5	24.0	29.5	22.5	26.5	22.0	26.0	23.5
Turbidity (NTU's)	0.30	0.40	1.8	0.30	0.70	0.10	0.70	3.1	1.0	0.20
Oxygen, dis (mg/L)	0.1	--	0.1	0.1	<0.1	0	0.1	0.1	0.1	<0.1
Oxygen, dis (percent saturation)	1	--	1	1	1	0	1	1	1	1
Hardness, total (mg/L as $CaCO_3$)	19	--	80	22	9	14	17	48	92	33
Calcium, dis (mg/L as Ca)	6.2	1.6	28	7.3	3.3	4.9	5.9	15	25	11
Magnesium, dis (mg/L as Mg)	0.91	<0.01	2.3	0.88	0.12	0.52	0.63	2.4	7.1	1.4
Sodium, dis (mg/L as Na)	80	100	46	67	69	110	64	44	32	40
Sodium (percent)	89	--	54	86	90	94	87	66	42	71
Sodium adsorption ratio	8	--	2	6	10	13	7	3	1	3
Potassium, dis (mg/L as K)	2.0	0.80	5.1	1.8	6.1	0.70	2.3	0.80	2.2	1.8
Bicarbonate, whole water, IT, field (mg/L as HCO_3)	198	137	215	134	126	204	122	130	165	101

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Table 1.--Water-level, well-construction, and water-quality data for wells sampled in the Ryan Flat subbasin--Continued

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
Carbonate, whole water, IT, field (mg/L as CO_3)	0	18	0	13	12	4	20	0	0	2
Alkalinity, total, whole water, IT, field (mg/L as $CaCO_3$)	163	143	176	132	123	174	133	107	136	86
Alkalinity, total, whole water, fixed end-point titration, field (mg/L as $CaCO_3$)	163	143	178	131	123	175	132	106	137	87
Alkalinity, total, lab (mg/L as $CaCO_3$)	160	151	170	127	130	180	124	105	140	86
Sulfate, dis (mg/L as SO_4)	22	44	11	26	13	53	18	22	12	18
Chloride, dis (mg/L as Cl)	10	19	5.2	12	14	14	11	11	11	11
Fluoride, dis (mg/L as F)	1.4	5.7	0.60	1.0	2.4	3.5	1.3	1.8	1.6	1.5
Silica, dis (mg/L as SiO_2)	71	40	76	20	33	27	47	26	33	23
Dissolved solids, residue at 180 °C (mg/L)	294	322	270	224	229	337	228	202	216	169
Dissolved solids, sum of constituents (mg/L)	291	--	280	215	215	318	230	187	205	160

Table 1.--Water-level, well-construction, and water-quality data for wells sampled in the Ryan Flat subbasin--Continued

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
Dissolved solids (tons/acre-foot)	0.40	--	0.37	0.30	0.31	0.46	0.31	0.27	0.29	0.23
Aluminum, dis (µg/L as Al)	<10	30	<10	<10	10	20	<10	<10	<10	10
Barium, dis (µg/L as Ba)	5	<2	57	13	8	6	19	22	6	13
Cobalt, dis (µg/L as Co)	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
Iron, dis (µg/L as Fe)	8	14	130	6	32	4	12	34	100	10
Lithium, dis (µg/L as Li)	16	36	19	8	7	14	6	19	<4	7
Manganese, dis (µg/L as Mn)	<1	<1	3	<1	7	<1	12	2	44	<1
Molybdenum, dis (µg/L as Mo)	<10	<10	20	<10	10	<10	<10	20	<10	<10
Nickel, dis (µg/L as Ni)	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Selenium, dis (µg/L as Se)	1	1	<1	<1	<1	<1	<1	<1	<1	<1

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Table 1.--Water-level, well-construction, and water-quality data for wells sampled in the Ryan Flat subbasin--Continued

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
Silver, dis (μg/L as Ag)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Strontium, dis (μg/L as Sr)	160	1	160	260	33	91	75	310	260	140
Vanadium, dis (μg/L as V)	20	34	25	11	25	27	31	8	<6	17
Gross alpha, dis (μg/L as natural U)	7.6	1.8	8.1	3.7	1.3	2.8	1.1	2.3	10	2.4
Alpha radioactivity, water, dis (pCi/L as Th-230)	7.2	1.8	7.6	3.6	1.3	2.7	1.1	2.3	9.8	2.3
Alpha count, 2-sigma precision estimate, water, dis (μg/L as natural U)	1.8	0.85	1.9	1.2	0.73	1.0	0.72	0.91	2.2	0.96
Alpha count, 2-sigma precision estimate, water, dis (pCi/L as Th-230)	1.7	0.82	1.7	1.1	0.72	0.97	0.68	0.90	2.0	0.91
Gross beta, dis (pCi/L as Cs-137)	14	8.0	10	4.2	14	7.1	6.3	9.3	8.5	4.4
Gross beta, dis (pCi/L as Sr-90/Y-90)	7.0	4.1	8.0	3.3	7.7	4.2	4.3	4.9	4.4	2.8

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Table 1.--Water-level, well-construction, and water-quality data for wells sampled in the Ryan Flat subbasin--Concluded

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
Beta count, 2-sigma precision estimate, water, dis (pCi/L as Cs-137)	4.6	3.9	2.7	2.1	4.1	4.4	3.4	3.1	3.2	2.4
Beta count, 2-sigma precision estimate, water, dis (pCi/L as Sr-90/Y-90)	1.9	1.8	2.1	1.6	1.7	2.5	2.2	1.3	1.4	1.5
Tritium, total (TU's)	0.16	0.16	<0.09	<0.09	--	<0.09	0.16	0.22	<0.09	0.16
Tritium, 2-sigma precision estimate (TU's)	0.19	0.19	0.19	0.19	--	0.19	0.19	0.19	0.19	0.19
Did the well require oil removal?	Yes	Yes	No	No	Yes	No	Yes	No	No	No

Table 2.--Concentrations of dissolved chlorofluorocarbon-11, chlorofluorocarbon-12, and chlorofluorocarbon-113 in ground waters from wells sampled in the Ryan Flat subbasin

[Analytical detection limit of 0.3 picogram per kilogram (pg/kg) of solution. pptv, parts per trillion volume; °C, degrees Celsius; BP, barometric pressure; mm Hg, millimeters of mercury; <, less than; cntm, sample contaminated during collection; --, interferences on the chromatogram prevented quantification of the sample]

Well number (and sample identification)	Sampling		Recharge			Concentration in solution (pg/kg)[1]			Calculated atmospheric partial pressure (pptv)			CFC-model recharge dates		
	Date	Time	Temperature (°C)	Elevation (feet)	BP (mm Hg)	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113
28303 (A)	11/11/94	1535	16	4,395	646.7	57.6	0.7	<0.3	31.9	1.6	0.0	1966.0	Pre-1945	Pre-1966
28303 (B)	11/11/94	1550	16	4,395	646.7	49.0	<0.3	<0.3	27.1	0.0	0.0	1965.0	Pre-1940	Pre-1966
28303 (C)	11/11/94	1600	16	4,395	646.7	54.8	1.2	<0.3	30.4	2.9	0.0	1965.5	1946.5	Pre-1966
28803 (A)	11/12/94	1530	16	4,332	648.2	141.9	<0.3	1.8	78.5	0.0	2.5	1972.0	Pre-1940	1967.0
28803 (B)	11/12/94	1530	16	4,332	648.2	133.7	<0.3	<0.3	74.0	0.0	0.0	1971.5	Pre-1940	Pre-1966
28803 (C)	11/12/94	1600	16	4,332	648.2	616.5	140.1	37.8	341.0	327.9	52.1	cntm	1981.0	1986.0
28901 (A)	11/15/94	1610	16	4,355	647.7	1.4	0.8	<0.3	0.8	2.0	0.0	1950.5	1945.5	Pre-1966
28901 (B)	11/15/94	1630	16	4,355	647.7	2.1	0.8	2.0	1.2	1.9	2.7	1951.5	1945.5	1967.5
28901 (C)	11/15/94	1710	16	4,355	647.7	910.5	443.9	300.6	504.0	1,039.8	415.5	cntm	cntm	cntm
29101 (A)	11/15/94	1220	16	4,452	645.4	23.1	17.2	4.7	12.9	40.5	6.6	1961.0	1961.0	1969.5
29101 (B)	11/15/94	1245	16	4,452	645.4	22.0	19.2	6.4	12.2	45.1	8.8	1960.5	1962.0	1971.0
29101 (C)	11/15/94	1255	16	4,452	645.4	23.7	23.5	7.3	13.2	55.3	10.1	1961.0	1963.5	1971.5
29407 (A)	11/08/94	1600	16	4,400	646.6	<0.3	--	<0.3	0.0	--	0.0	Pre-1945	--	Pre-1966
29407 (B)	11/08/94	1610	16	4,400	646.6	<0.3	--	<0.3	0.0	--	0.0	Pre-1945	--	Pre-1966
29407 (C)	11/08/94	1620	16	4,400	646.6	<0.3	--	--	0.0	--	--	Pre-1945	--	--
29407 (D)	11/08/94	1635	16	4,400	646.6	<0.3	--	--	0.0	--	--	Pre-1945	--	--

Table 2.--Concentrations of dissolved chlorofluorocarbon-11, chlorofluorocarbon-12, and chlorofluorocarbon-113 in ground waters from wells sampled in the Ryan Flat subbasin--Concluded

Well number (and sample identification)	Sampling Date	Time	Recharge Temperature (°C)	Elevation (feet)	BP (mm Hg)	Concentration in solution (pg/kg) CFC-11	CFC-12	CFC-113	Calculated atmospheric partial pressure (pptv) CFC-11	CFC-12	CFC-113	CFC-model recharge dates CFC-11	CFC-12	CFC-113
29712 (A)	11/13/94	1640	16	4,423	646.1	0.5	1.7	<0.3	0.3	3.9	0.0	1948.5	1947.5	Pre-1966
29712 (B)	11/13/94	1700	16	4,423	646.1	8.6	127.2	--	4.7	298.8	--	1955.5	1979.5	--
29712 (C)	11/13/94	1730	16	4,423	646.1	431.6	231.1	47.1	239.5	542.5	65.2	1987.0	Modern	1988.0
29808 (A)	11/09/94	1550	16	4,515	643.9	145.9	<0.3	--	81.2	0.0	--	1972.0	Pre-1940	--
29808 (B)	11/09/94	1610	16	4,515	643.9	137.7	2.9	--	76.7	6.8	--	1971.5	1949.5	--
29808 (C)	11/09/94	1620	16	4,515	643.9	139.2	<0.3	--	77.5	0.0	--	1971.5	Pre-1940	--
29901 (A)	11/11/94	1030	16	4,614	641.5	79.0	129.8	35.7	44.2	307.0	49.8	1968.0	1980.0	1985.5
29901 (B)	11/11/94	1150	16	4,614	641.5	76.1	61.9	20.3	42.6	146.4	28.3	1967.5	1971.0	1981.0
29901 (C)	11/11/94	1200	16	4,614	641.5	77.5	68.8	21.6	43.3	162.8	30.2	1967.5	1972.0	1981.5
30801 (A)	11/10/94	1537	16	4,952	633.6	484.7	93.0	19.6	274.2	222.6	27.7	cntm	cntm	cntm
30801 (B)	11/10/94	1557	16	4,952	633.6	81.3	5.8	<0.3	46.0	14.0	0.0	1968.0	1953.5	Pre-1966
30801 (C)	11/10/94	1608	16	4,952	633.6	87.5	5.9	<0.3	49.5	14.1	0.0	1968.5	1953.5	Pre-1966
38101 (A)	11/13/94	1055	16	4,682	639.9	3.1	<0.3	4.4	1.8	0.0	6.1	1952.5	Pre-1940	1969.5
38101 (B)	11/13/94	1130	16	4,682	639.9	1.9	<0.3	2.6	1.1	0.0	3.7	1951.5	Pre-1940	1968.0
38101 (C)	11/13/94	1140	16	4,682	639.9	2.2	<0.3	2.9	1.2	0.0	4.1	1951.5	Pre-1940	1968.0

[1]For samples with CFC concentrations in solution below the analytical detection limit of 0.3 pg/kg, atmospheric partial pressures and hence recharge dates were calculated assuming a CFC concentration in solution of 0.0 pg/kg.

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Table 3.--Most probable ground-water recharge dates for wells sampled in the Ryan Flat subbasin

[--, sample not analyzed for tritium]

	Well number									
	28303	28803	28901	29101	29407	29712	29808	29901	30801	38101
CFC-model date	Pre-1940	Pre-1940	1945.5	Early 1960's	Pre-1945	Late 1940's	Pre-1940	Early 1970's	Early 1950's	Pre-1940
Tritium date	Pre-1953	Pre-1953	Pre-1953	Pre-1953	--	Pre-1953	Pre-1953	Pre-1953	Pre-1953	Pre-1953
Most probable recharge date	Pre-1940	Pre-1940	Mid-1940's	Pre-1953	Pre-1945	Pre-1948	Pre-1940	Pre-1953	Pre-1953	Pre-1940