Movement and Age of Ground Water in the Western Part of the Mojave Desert, Southern California, USA

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

CONVERSION FACTORS

Multiply	Ву	To obtain
kilogram (kg)	2.205	pound avoirdupois
kilometer (km)	0.6214	mile
square kilometer (km ²)	247.1	acre
liter (L)	0.2642	gallon
meter (m)	3.281	foot
meter per year (m/yr)	3.281	foot per year
nillimeter per year (mm/yr)	0.03937	inch per year

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

°F=1.8 °C+32.

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μ g/L).

VERTICAL DATUM

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

ABBREVIATIONS

Ca	calcium
Ca ²⁺	calcium ion having a charge of +2
δ13C	delta carbon-13
¹⁴ C	carbon-14
Cl	chloride
Cl ⁻¹	chloride ion having a charge of -1
>	greater than
HCO ⁻¹	bicarbonate ion having a charge of -1
Mg	magnesium
Mg ²⁺	magnesium ion having a charge of +2
Na	sodium
Na ⁺	sodium ion having a charge of +1

NETPATH	computer program for modeling net geochemical reactions along a flow path
NWIS	National Water Information System
PDB	Peedee Belemnite
pmc	percent modern carbon
per mil	parts per thousand
³ H	tritium
TU	tritium units
ybp	years before present

Organizations

MCAGCC	U.S. Marine Corps facility at 29 Palms, California
USGS	U.S. Geological Survey

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ABSTRACT

Tritium and carbon-14 data in water from wells in the Mojave River and the Morongo groundwater basins in the western part of the Mojave Desert show recent recharge focused in the floodplain aquifer along the Mojave River. Older ground water was present in parts of the regional aquifer that surround and underlie the floodplain aquifer. Movement of water between the floodplain and the regional aquifers occurs near on the upgradient side of faults as water from the regional aquifer discharges to the floodplain aquifer and on the downgradient side of the faults where water from the floodplain aquifer recharges the regional aquifer. On the basis of carbon-14 ages, corrected for mineralogic reactions with aquifer materials, water from some wells was recharged more than 20,000 years ago. Geochemical data show ground-water recharge has gradually decreased as the climate changed since that time.

INTRODUCTION

The Mojave River and the Morongo ground-water basins (referred to as the Mojave River and the Morongo basins, respectively) are in the western part of the Mojave Desert in southern California (fig. 1). The area is arid with cold winters and hot, dry summers. Population is growing rapidly and ground water is the only dependable source of water supply; however, ground-water recharge is small in comparison with the amount of water pumped. With increases in population and demand for water, water levels are declining (Mendez and Christensen, 1997), and there is increasing need to understand ground-water recharge and movement of water through the aquifers.

Purpose and Scope

The purpose of this study was to evaluate the movement and age of ground water in the Mojave River and the Morongo ground-water basins in the western part of the Mojave Desert. In this paper, the radioactive isotopes of hydrogen (tritium) and carbon (carbon-14) are used to determine the age of water from wells, the timing of ground-water recharge, and the movement of water between aquifers.

Background and Previous Studies

The combination of the radioactive isotopes of hydrogen (tritium) and carbon (carbon-14) is especially effective in arid environments for locating sources of recharge, determining the age (time since recharge) of ground water, and identifying geologic controls on the movement of ground water.

Tritium

Tritium (³H) is a naturally occurring radioactive isotope of hydrogen that has a half-life of 12.43 years. In this study, tritium was measured in tritium units (TU); one tritium unit is equivalent to one tritium atom in 10^{18} atoms of hydrogen (Taylor and Roether, 1982). Because tritium is part of the water molecule, tritium is not affected by reactions other than radioactive decay; therefore, tritium is an excellent tracer of the movement of ground water recharged less than 50 years before present.



Figure 1. Location of study area, the Mojave River and the Morongo ground-water basins, the floodplain aquifer, selected faults, and geologic section lines.

Tritium deposition at selected sites throughout the world has been measured by the International Atomic Energy Agency (1981) since the 1950s, and Michel (1989) estimated tritium deposition at unmeasured sites in the United States. The tritium concentration of precipitation in coastal California prior to 1952 was about 2 TU (International Atomic Energy Agency 1981; Michel, 1989) and, on the basis of Michel's (1989) data, tritium concentrations in precipitation in the southwestern United States increased with increasing distance from the coast. During 1952-62 about 800 kg of tritium was released to the atmosphere as a result of the atmospheric testing of nuclear weapons (Michel, 1976), and the tritium concentration of precipitation increased to about 700 TU at a coastal site near Santa Maria, California. Tritium concentrations in precipitation at sites farther inland in the continental United States were higher (Michel, 1989). After the cessation of atmospheric testing of nuclear weapons in 1962, the tritium concentration of precipitation decreased and presentday (2002) tritium levels in precipitation are near pre-1952 levels (Michel, 1989).

Begemann and Libby (1957) first demonstrated the use of tritium as a tracer of the movement of surface water, ground water, and oceanic circulation during the 1950s. In arid areas, tritium is especially useful for identifying areas where ground-water recharge occurs under present-day climatic conditions (Froehlich and Yurtsever, 1995). In the Mojave Desert of the southwestern United States, tritium has been used to estimate movement of water through thick unsaturated zones (Phillips, 1994; Striegl and others, 1996; Izbicki and others, 2000) and to define the areal extent of present-day recharge in the saturated zone underlying the upper part of the Mojave River (Izbicki and others, 1995). Most recently, tritium has been used in combination with its decay product helium-3 to produce more accurate estimates of ground-water ages and traveltimes in a wide range of hydrologic settings (Solomon and Cook, 1999).

Carbon-14 and Carbon-13

Carbon-14 (¹⁴C) is produced by interactions between cosmic rays and nitrogen gas in the earth's atmosphere and has a half-life of about 5,730 years (Mook, 1980). Carbon-14 data are expressed as percent modern carbon (pmc) by comparing ¹⁴C activities to the specific activity of National Bureau of Standards oxalic acid: 12.88 disintegrations per minute per gram of carbon in the year 1950 equals 100 pmc. Carbon-14 production varies with solar activity and has not been constant during the last 24,000 years (Stuiver and others, 1998). In addition to natural sources, ¹⁴C also was produced by the atmospheric testing of nuclear weapons (Mook, 1980), and ¹⁴C activities may exceed 100 pmc in areas where ground water contains tritium from nuclear weapons tests.

Libby and others (1949) and Libby (1952) first discovered the ubiquitous distribution of natural ¹⁴C in the biosphere. Since the early 1960s, ¹⁴C present in ground water as dissolved inorganic carbon has been used in hydrologic studies to determine the time since recharge of older ground water (Vogel and Ehhart, 1963). Carbon-14 activities are used to determine the age (time since recharge) of ground water on time scales ranging from recent to more than 20,000 years before present. Because ¹⁴C is not part of the water molecule, its activity and interpreted ¹⁴C ages may be affected by reactions between constituents dissolved in ground water and aquifer materials.

Carbon-13 (¹³C), a naturally occurring stable isotope of carbon, is used in conjunction with chemical and mineralogic data to evaluate chemical reactions that occur within aquifers. These reactions may add carbon that does not contain ¹⁴C to the dissolved phase or remove carbon the may contain ¹⁴C from the dissolved phase. Carbon-13 data are expressed in delta notation (δ) as per mil (parts per thousand) differences relative the ratio of ¹³C to ¹²C in standard Peedee Belemnite (PDB) (Gonfiantini, 1978, 1984).

Carbon-14 data have been used to evaluate ground-water ages in large aquifer systems throughout the arid southwestern United States. Winograd and Pearson (1976) used ¹⁴C data to estimate ground-water ages and identify interbasin flow in carbonate aquifers of southern Nevada. Phillips and others (1989a,b) used ¹⁴C dating for ground water in the San Juan Basin of New Mexico. Application of ¹⁴C dating techniques to hydrologic studies has increased with the development of computer programs to assess rock-water interactions (Plummer and others, 1991) and advances in analytical techniques that have simplified sample collection. Robertson (1992), Kalin (1994), and Zhu and Murphy (2000) used ¹⁴C data to estimate ground-water ages, direction of ground-water flow, and aquifer hydraulic properties in several different basins representing a range of hydrogeologic settings in Arizona. Izbicki and others (1995) used ¹⁴C data to demonstrate that water from wells at the downgradient ends of long flow paths through alluvial aquifers in the Mojave Desert of southern California had great age and was recharged many thousands of years ago.

Numerous researchers have recognized that older ground water in large aquifers reflects the environmental and climatic conditions at the time ground water was recharged rather than present-day conditions (Phillips and others, 1989a; Verhagen and others, 1991; Zhu and others, 1998). Ground water in large aquifers in arid areas has become increasingly important as an archive of paleoclimatic data because most of the water in these aquifers may have been recharged during pluvial periods when the climate was significantly different from present-day conditions. This concept is somewhat controversial in areas such as the regional carbonate aquifer underlying southern Nevada where Davisson and others (1999) suggested that low ¹⁴C activities could be explained by accretion of present-day recharge having low ¹⁴C activity as a result of reactions with carbonate aquifer material.

Sample Collection and Analyses

Tritium was measured by liquid scintillation (Thatcher and others, 1977) with electrolytic enrichment (Ostlund and Warner, 1962) on 1-L unfiltered samples collected in glass containers. Sample bottles were bottom-filled and allowed to overflow several times the bottle volume. The 2-sigma detection limit for tritium ranged from 0.2 to 1.2 TU and most samples had a detection limit of 0.4 TU. The detection limit was a function of the statistics associated with the liquid scintilation counter. In general, the longer the counting time the better the precision and the lower the detection limit.

Prior to 1994, ¹⁴C samples were collected in a 96-L nitrogen-filled stainless-steel vessel. The pH of unfiltered sample water was adjusted to pH>11 using carbon-dioxide-free sodium hydroxide, and bicarbonate was precipitated as strontium carbonate by supersaturating the sample with strontium chloride. The strontium carbonate precipitate was allowed to settle into a 1-L polyetheylene bottle at the bottom of the stainless-steel vessel. The 1-L bottle was shipped to a laboratory where ¹⁴C analyses were done by scintillation spectrophotmetry (Thatcher and others, 1977). After 1994, ¹⁴C samples were filtered and collected in 1-L glass bottles, in the same manner as tritium, and were analyzed for ¹⁴C by accelerator mass spectrometry (Beukens, 1992). Carbon-13 analyses were done on filtered water samples by mass spectrometry (Thatcher and others, 1977).

Isotopic and chemical data are available from the U.S. Geological Survey's National Water Information System (NWIS) data base. Lithologic data, geophysical data, well construction, water-level measurements, and results of samples collected from observation wells installed as part of this study were published by Huff and others (2003).

Acknowledgments

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HYDROGEOLOGY

The study area and surrounding uplands includes about 13,000 km² of the Mojave Desert east of the San Gabriel and the San Bernardino Mountains east of Los Angeles, California. With the exception of the higher altitudes in the San Gabriel and the San Bernardino Mountains, the climate of the study area is characterized by low precipitation and low humidity. The temperature commonly excees 40°C during the summer and frequently falls below 0°C during the winter. In the northern and western parts of the study area most precipitation falls during the winter rainy season (November-March); in the southeastern part of the Morongo basin more precipitation falls during the summer months (July-September) than during the winter rainy season (Freidman and others, 1992). Although average annual precipitation in the higher altitudes of the mountains may exceed 1 m/yr; average annual precipitation in most of the study area is less than 150 mm/vr.

With the exception of small streams in the San Gabriel and the San Bernardino Mountains and short reaches of the Mojave River where faults and other barriers to ground-water flow cause ground water to discharge at land surface, there are no perennial streams in the study area. During occasional winter stormflows, the Mojave River flows east past Barstow into the Mojave Valley (fig. 1), and if flows are large enough through Afton Canyon out of the study area (Lines, 1996). Other large streams, such as Pipes Wash in the Morongo basin, flow for considerable distances during brief stormflows. A brief discussion of groundwater occurrence and movement is provided in this paper. Additional information on ground water occurrence and movement is given by Thompson (1929), Hardt (1971), and Stamos and others (2001).

Mojave River Ground-Water Basin

The Mojave River ground-water basin contains an unconsolidated alluvial aquifer along the Mojave River known as the floodplain aquifer. The floodplain aquifer is highly permeable and composed of sand and gravel weathered from granitic rocks in the San Gabriel and the San Bernardino Mountains. The floodplain aquifer is surrounded and underlain by unconsolidated alluvial deposits that constitute an aquifer known locally as the regional aquifer. The regional aquifer includes interconnected alluvial basins that drain toward the Mojave River. The regional aquifer also includes topographically closed basins that drain toward El Mirage, Harper, and Coyote Lakes (dry). In the geologic past, flow in the Mojave River may have reached Harper Lake, maintaining surface water in the lake (Meek, 1999). The regional aquifer is less permeable than the floodplain aquifer, except where highly-permeable deposits from the ancestral Mojave River are present. Lacustrine deposits are present throughout the area near present-day playas and in areas, such as near Victorville or in the Mojave Valley, where large lakes were present during the Pleistocene (Cox and Hillhouse, 2001). In some areas, especially near the front of the San Bernardino and the San Gabriel Mountains, ground-water pumping is limited by the depth to water which commonly approaches 100 m and may exceed 300 m.

Under present-day climatic conditions, recharge to the regional aquifer is small compared to recharge from infiltration of surface flow from the Mojave River (Lines, 1996; Stamos and others, 2001). The recharge that does occur results primarily as infiltration from small streams near the flanks of the San Bernardino and the San Gabriel Mountains that flow as a result of winter stormflows and snowmelt runoff (Hardt, 1971; Lines, 1996; Izbicki and others, 1998, 2000; Stamos and others, 2001). Smaller amounts of recharge also may occur as infiltration of runoff from streams that drain the mountains in the Mojave Desert. As in most of the desert southwest, recharge from the direct infiltration of precipitation typically does not occur in the study area and large accumulations of chloride and other soluble salts are present near the top of the unsaturated zone (Izbicki and others, 1998, 2000).

Under predevelopment conditions, ground-water movement in much of the Mojave River ground-water basin was from sources of recharge to the regional aquifer near the front of the San Gabriel and the San Bernardino Mountains to the floodplain aquifer where it discharged as streamflow to the Mojave River or as evapotranspiration by phreatophytes (Hardt, 1971; Stamos and others, 2001). Smaller amounts of discharge occurred as ground-water movement toward dry lakes where water discharged by evaporation (Stamos and others, 2001). The area is highly faulted and faults can act as barriers to ground-water flow in both the floodplain and the regional aquifers, often causing ground water to discharge at land surface (Thompson, 1929; Hardt, 1971; Mendez and Christensen, 1997; Stamos and others, 2001). As a result of ground-water development, pumping is the largest source of ground-water discharge in the study area under present-day conditions (Stamos and others, 2001) and in some areas water levels are declining at rates exceeding 0.3 m/yr (Mendez and Christensen, 1997).

Morongo Ground-Water Basin

The Morongo ground-water basin includes a number of small alluvial subbasins that maintain separate ground-water flow systems typically terminating in dry lakes scattered throughout the area (Lewis, 1972; Mendez and Christensen, 1997). These alluvial subbasins are separated by faults and bedrock outcrops. Under predevelopment conditions perennial springs, such as Surprise Spring, existed where ground water discharged at land surface as a result of faults acting as barriers to flow (Londquist and Martin, 1991). Perennial springs also were present near the margins of some dry lakes where water discharged by evaporation. Ground water near the dry lakes in the Morongo (and the Mojave) basins is typically highly saline.

Unconsolidated deposits in the Morongo basin are similar to those found in the regional aquifer underlying the Mojave River basin and are weathered from the surrounding mountains composed of similar crystalline bedrock, with the exception of deposits weathered from limestone present along the eastern edge of the San Bernardino Mountains near Lucerne Valley (and adjacent parts of the Mojave River groundwater basin). In some areas, alluvial aquifers in the Morongo basin have been divided into upper and lower aquifer systems having different water levels and distinct hydrologic properties (Londquist and Martin, 1991).

TRITIUM

In this paper, water containing tritium is interpreted as water recharged after 1952, and water not containing measurable tritium is interpreted as water recharged before 1952. In areas where the tritium concentrations along a flow path are known, it is possible to identify the peak tritium concentrations that correspond to ground water recharged during 1962 when the atmospheric deposition of tritium from nuclear weapons testing was greatest (Izbicki and others, 1995). In some settings, low concentrations of tritium may be difficult to interpret without understanding the local geologic setting or the history of well installation and development. For example, mixing of younger water containing measurable tritium and older water not containing tritium may occur within long-screened production wells. Incomplete well development and removal of drilling fluids may complicate interpretation of low concentrations of tritium collected from short-screened observation wells.

Tritium was detected in 46 percent of water samples from 234 wells in the Mojave River and the Morongo ground-water basins at values as high as 14.9 TU. Concentrations of tritium near the 2-sigma detection limit may accurately reflect the presence of post-1952 ground-water recharge or may result from effects related to well construction or development. Water from 25 observation wells installed as part of this study was resampled to confirm the presence or absence of low concentrations of tritium.

Most wells having measurable tritium were in the floodplain aquifer along the Mojave River upstream from Mojave Valley. In the Mojave Valley, tritium is present only in water from wells adjacent to the river, and much of the floodplain aquifer in this area contains water that was recharged prior to 1952. Tritium also is present in water from wells in alluvial fans and canyons along the front of the San Gabriel and the San Bernardino Mountains in the Mojave River and the Morongo basins (fig. 2) where recharge occurs as infiltration of flow in streams that drain the mountains and along alluvial fans at the base of the mountains.



Figure 2. Tritium in water from wells in the Mojave River and the Morongo ground-water basins, western Mojave Desert, southern California, 1992–2000.

Tritium was detected in water from some production wells in the regional aquifer. In the upper part of the basin near Victorville, extensive pumping from the regional aquifer has caused water levels to decline; allowing the movement of water from the floodplain aquifer into the regional aquifer. Farther downstream near Hinkley Valley, tritium data suggest rapid movement of ground water from the floodplain aquifer into the regional aquifer and toward discharge areas near Harper Lake. In addition, tritium also was detected in observation wells in the regional aquifer and underlying deposits downgradient from the Helendale and the Waterman Faults.

CARBON-14 AND CARBON-13

Inorganic carbon-14 activities for water from 167 wells in the Mojave River and Morongo basins ranged from 117 to 0.5 percent modern carbon (pmc). The δ^{13} C compositions of water these wells ranged from 0.1 to -19.2 per mil. In general, δ^{13} C values increased (became less negative) with decreasing ^{14}C activity. Carbon-14 and $\delta^{13}C$ data were used to estimate the areal distribution of ground-water ages (time since recharge) in areas where water from wells did not contain tritium. These data also were used to evaluate the movement of water through aguifers, the hydraulic connection between aquifers, and the effect of faults on ground-water movement along selected geologic sections. Corrections to ¹⁴C activity and ground-water ages for reactions that may add or remove carbon from the ground water were made for water from wells along three flow paths that represent different geochemical settings in the study area. These corrections were made on the basis of changes in $\delta^{13}C$ compositions and changes in the chemical composition of water from wells along selected flow paths through the aquifers using the computer program NETPATH (Plummer and others, 1991).

Areal Distribution of Carbon-14 Activities

The highest ¹⁴C activities, exceeding 90 pmc, were in water from wells in the floodplain aquifer along the Mojave River and in other areas where tritium and recent recharge are present (fig. 3). Water from wells exceeded 100 pmc where recently

recharged water containing tritium is present and the ¹⁴C activity of ground water has been increased by the atmospheric testing of nuclear weapons. Carbon-14 activities decrease downgradient from areas of recent ground-water recharge and are between 50 and 90 pmc in parts of the regional aquifer within the Mojave River basin (1) near the front of the San Gabriel and San Bernardino Mountains where recharge occurs as infiltration of flow in streams that drain the mountains and along the alluvial fans at the base of the mountains, (2) near Cajon Pass where recharge occurs as infiltration from intermittent streams and as groundwater movement from Summit Valley, and (3) in Hinkley and Mojave Valleys where ground water is recharged by infiltration of surface flows from the Mojave River. Carbon-14 activities also are between 50 and 90 pmc in area near Yucca Valley, along Pipes Wash, and downgradient from streams that drain the San Bernardino Mountains near Lucerne Valley (fig. 3). Carbon-14 activities less than 30 pmc are present throughout much of the Mojave River basin away from the front of the San Gabriel and the San Bernardino Mountains and in large areas of the Morongo basin.

Assuming only radioactive decay, 100 pmc in the recharging ground water, and neglecting geochemical reactions that occur between ground water and aquifer materials, ground water having 90 pmc would have recharged 370 years before present, and ground water having 50 pmc would have been recharged 5,730 years before present. (These ages are referred to as "uncorrected ages"; ground-water ages corrected for the initial ¹⁴C activity of recharging ground water and geochemical reactions that occur between ground water and aquifer materials will be presented for selected wells later in this paper.) Much of the ground water in the regional aquifer in the Mojave River and the Morongo basins has ¹⁴C activities less than 30 pmc and an uncorrected ground-water age greater than about 10,000 years before present.

The lowest ${}^{14}C$ activities, less than 2 pmc, having uncorrected ground-water ages greater than 30,000 years before present, are in water from deep wells at the downgradient ends of long flow paths through the regional aquifer in the Mojave River basin. This water often underlies younger ground water that has higher ${}^{14}C$ activity and is not apparent in <u>figure 3</u>.



Figure 3. Carbon-14 activity in water from wells in the Mojave River and the Morongo ground-water basins, western Mojave Desert, southern California, 1992–2000.

Carbon-14 Activities Along Selected Geologic Sections in the Mojave River Basin

Changes in ¹⁴C activity with depth in water from selected observation wells were evaluated along five geologic sections in the Mojave River basin to determine the movement of water between the regional and the floodplain aquifers. Sections A-A', B-B' and C-C' (figs. 4 and 5) are perpendicular to the Mojave River and through different reaches of the floodplain and the regional aquifers. Each section represents hydrologic conditions in the basin (1) upstream from Victorville (Section A-A'), (2) downstream from Victorville in an area known locally as the "transition zone" (Section B-B'); and (3) farther downstream in the Mojave Valley (Section C-C'). Sections D-D' and E-E' (fig. 6) are parallel to the Mojave River and cross the Helendale and the Waterman Faults, respectively. These sections represent hydrologic conditions upgradient and downgradient from the faults, which are barriers to ground-water flow.

Carbon-14 activity was not measured on all wells sampled for tritium, but where measured, ¹⁴C activity in the floodplain aquifer commonly exceeded 100 pmc as a result of the atmospheric testing of nuclear weapons.

Sections A–A', B–B', and C–C'

Section A-A' is located in the upper part of the Mojave River basin near Victorville. The ¹⁴C activities of water from sampled observation wells in the regional aquifer along section A-A' ranged from 95 to 0.5 pmc (fig. 4). Although the ¹⁴C activity of water from sampled observation wells decreased with depth to low values across the entire section, there was not a sharp contrast in ground-water age between the floodplain and the regional aquifers. Water from wells in the floodplain aquifer contains tritium and was recently recharged. Although ground water discharged to the floodplain aquifer along this reach under predevelopment conditions (Hardt, 1971; Stamos and

others 2001), some water may have moved from the floodplain aquifer into the regional aquifer as a result of ground-water pumping.

Section B-B' is downstream from Victorville in an area known locally as the "Transition Zone." The ¹⁴C activities of water from sampled observation wells in the regional aquifer along section B-B' ranges from 87 to 2.7 pmc (fig. 5). The lowest ${}^{14}C$ activities were in deep wells beneath the floodplain aquifer where ground water from the regional aquifer discharged to the overlying floodplain aquifer under predevelopment conditions. Similar to section A-A' water from wells in the floodplain aquifer contains tritium and was recently recharged. The contrast in ground-water age is much greater along the western part of section B-B' than along section A-A', reflecting predevelopment ground water discharge from the regional aquifer to the floodplain aquifer along this section. Carbon-14 activities to the east of section B-B' are relatively high and ground water in this area does not have great age suggesting movement of water between the aquifers in this area.

Section C-C' is located farthest downstream in the Mojave Valley. The floodplain aquifer in this area is larger and ground-water flow paths through this area are longer than along either sections A-A' or B-B'. The quantity of recharge to the regional aquifer from the surrounding mountains is small. Large amounts of ground-water discharge from the regional aquifer to the floodplain aquifer did not occur in this area under predevelopment conditions (Hardt, 1971; Stamos and others, 2002) and water infiltrated from the Mojave River is present in both the floodplain and the regional aquifers along this section. The ¹⁴C activity of water from sampled wells along section C-C' ranged from 1 to 34 pmc (fig.5). Along this section and throughout most of the Mojave Valley, recent water is present only in the part of the floodplain aquifer adjacent to the Mojave River and carbon-14 activities are low throughout the remainder of the floodplain and the regional aquifers. The lowest ¹⁴C activities were in wells completed in the underlying consolidated rocks.



Figure 4. Delta-deuterium composition and carbon-14 activity of water from selected observation wells along Section *A*–*A*', Mojave River ground-water basin, southern California. See figure 1 for location of section. (Modified from Stamos and others, 2001; delta deuterium data from lzbicki, 2004)



Figure 5. Delta-deuterium composition and carbon-14 activity of water from selected observation wells along Sections *B–B*' and *C–C*', Mojave River ground-water basin, southern California. See figure 4 for explanation and figure 1 for location of sections. (Modified from Stamos and others, 2001; delta deuterium data from Izbicki, 2004.)



Figure 6. Delta-deuterium composition and carbon-14 activity of water from selected observation wells along Sections *D*–*D*' and *E*–*E*', Mojave River ground-water basin, southern California. See figure 4 for explanation and figure 1 for location of sections; per mil, parts per thousand. (Section *D*–*D*' modified from Stamos and others, 2001. Section *E*–*E*' modified from Densmore and others, 1997; delta deuterium data from Izbicki, 2004.)

Sections D-D' and E-E'

Ground-water discharge supported phreatophyte growth under predevelopment conditions at the Helendale Fault near section D-D' (Thompson, 1929). The ¹⁴C activity of water sampled from wells along section D-D' ranged from 27 to 116 pmc (fig. 6). Carbon-14 activity in water from wells on the downgradient side of the fault is higher than ¹⁴C activity from deep wells on the upgradient side. ¹⁴C activity data are consistent with the downward movement of more recently recharged water from the floodplain aquifer into the regional aquifer and underlying consolidated rocks on the downgradient side of the Helendale Fault. The lowest ¹⁴C activities are in water from deep wells in consolidated rocks on the upgradient side of the Helendale Fault. This deep ground water is slightly saline, having dissolved-solids concentrations as high as 3,190 mg/L (Huff and others, 2003).

Section E-E' crosses the Waterman Fault downstream from Barstow. The Waterman Fault is a barrier to flow in both the floodplain and the regional aquifers, and large changes in the water-table surface occur near the fault. The subsurface geology near the Waterman Fault is complex and the fault in this area is actually composed of five separate faults mapped as faults A through E (Densmore and others, 1997). The ¹⁴C activity of sampled wells in the regional aquifer and underlying deposits along section E-E' ranged from 4 to 108 pmc (fig. 6). The higher ${}^{14}C$ activities are in water from sampled wells in the regional aquifer on the downgradient side of the fault. The floodplain aquifer downgradient from the Waterman Fault is the recharge area of the Mojave Valley. Lower ¹⁴C activities in deep wells on the upgradient side of the Waterman Fault reflect discharge of deeper, older ground water to the floodplain aquifer in this area. Ground water from deeper wells upgradient from the

Waterman Fault is similar to water from deep wells upgradient from the Helendale Fault in that it is slightly saline, having dissolved-solids concentrations as high as 2,300 mg/L.

Interpretation of Ground-Water Age Along Selected Flow Paths

Carbon-14 activities were used to estimate ground-water ages along selected flow paths in the Mojave River and the Morongo ground-water basins. Interpretation of ¹⁴C activities and calculation of ground-water ages requires estimates of the initial ¹⁴C activity of ground water after recharge and an evaluation of the geochemical reactions that have occurred within an aquifer. These reactions may remove inorganic carbon from the dissolved phase or add inorganic carbon from aquifer materials that may or may not contain ¹⁴C.

The effect of different geologic settings and geochemical reactions on ¹⁴C activities and interpreted ages was evaluated along three flow paths (fig. 3) developed on the basis of water-level-contour data. Flow path 1, located in the Surprise Springs area of the Morongo basin, represents ground-water evolution in a simple geochemical setting dominated by silicate weathering and influenced by recent climatic change. Flow path 2, located in the regional aquifer in the upper part of the Mojave River basin east of the Mojave River, represents a more complex geochemical setting where ground water has reacted with soluble carbonate minerals prior to and after recharge. Flow path 3, located in the regional aquifer in the upper part of the Mojave River basin west of the Mojave River, represents ground-water reactions with aquifer minerals in deep aquifers over long periods of time (<u>fig. 3</u>).

Initial Carbon-14 Activity

Neglecting geochemical reactions that occur within an aquifer, the age (time since recharge) of ground water can be estimated from the equation for radioactive decay according to the following:

$$t = \frac{\lambda_{1/2}}{\ln 2} \ln \frac{A_0}{A_{meas}} \tag{1}$$

where

- *t* is the age (time since recharge) of the ground water,
- 1/2 is the isotope half-life; for ¹⁴C the half-life is 5,730 years,
- A_0 is the ¹⁴C activity of the water sample at the time of recharge, and
- A_{meas} is the measured ¹⁴C activity of the water sample.

The ¹⁴C activity of ground water at the time of recharge (A₀) is rarely equal to 100 pmc because of reactions that occur between infiltrating water, soil gases (primarily carbon dioxide), and carbonate minerals in the unsaturated zone. It is not possible to measure this value directly by sampling at the water-table surface in ground-water recharge areas because atmospheric testing of nuclear weapons increased the ¹⁴C activity of ground water recharged since 1952 to greater than natural, pre-bomb, values.

A number of analytical approaches have been developed to calculate ground-water age that rely on estimates of the ¹⁴C activity of ground water at the time of recharge. Approaches developed by Vogel and Ehhart (1963), Tamers (1967), and Ingerson and Pearson (1964) assume equilibrium of recharging water with the atmosphere or soil gases, and account for the resulting dissolution of carbonate minerals within the unsaturated zone. These models are suitable for use in areas receiving large amounts of recharge where the unsaturated zone has been well leached and contains only small amounts of soluble carbonate minerals. Approaches developed by Fontes and Garnier (1979) and Mook (1980) extend these models to account for isotopic fractionation and isotopic exchange between ground water and carbonate minerals. These models are suitable for use in areas where the unsaturated zone has not been leached of soluble carbonate minerals, either because of their local abundance or because recharge amounts are small. Kalin (2000) and Zhu and Murphy (2000) summarized the use and limitations of these approaches to determine the initial ¹⁴C activity of ground water.

Although widely used, these analytical approaches are applicable for the specific, often simplified, geochemical settings for which they were developed and may not reflect geochemical conditions in an other study areas (Zhu and Murphy, 2000). To address this problem, the initial ¹⁴C activity of ground water in the study area was estimated through the collection of a many of ground-water samples in, and downgradient from, recharge areas. When using this approach, the greatest ¹⁴C activity of water from wells that no longer contains tritium is selected as the initial 14 C activity, A₀, of ground-water recharge. If sufficient data are available, this approach provides a better estimate of the initial carbon-14 activity of ground water prior to nuclear weapons testing than do analytical estimates because it reflects conditions within the study area. The approach does not account for radioactive decay that occurred since 1952; however, given the half-life of ${}^{14}C$, the decrease in ${}^{14}C$ activity resulting from radioactive decay since 1952 is small and can be neglected.

Carbon-14 data collected in the Mojave River and the Morongo basins are shown in rank order, expressed as percent greater than or equal to, from largest to smallest in figure 7. Carbon-14 activities exceeded 84 pmc in water samples from all but one well containing tritium, suggesting that this value may be an appropriate estimate of the initial carbon activity, A_0 , in parts of the study area where data are not available. This value agrees with results of analytical models developed by Vogel and Ehhart (1963), which predict the ¹⁴C activity of recharge water in wellleached, carbonate-poor settings should be about 85 ± 3 pmc.



Figure 7. Carbon-14 activities and tritium data in water from wells in the Mojave River and the Morongo ground-water basins, southern California, 1992–2000.

Water from wells in ground-water recharge areas along the flanks of the San Bernardino Mountains in the Mojave River and the Morongo basins near Lucerne Valley that contains tritium has ¹⁴C activities between 71 and 63 pmc. No large streams drain the mountains in this area, and much of the recharge occurs through alluvial fan deposits composed of detritus weathered from carbonate rocks in the surrounding mountains. Carbonate minerals are not likely to have been completely leached from these deposits. Lower ¹⁴C activities probably occur in ground water in this area as a result of dissolution and isotopic exchange with carbonate minerals. An initial ${}^{14}C$ activity of 63 pmc is consistent with ¹⁴C activities predicted for recharge water in poorly-leached unsaturated zones using analytical models developed by Fontes and Garnier (1979) or Mook (1980).

Ground water containing measurable tritium but low ¹⁴C activity occurs in several other settings in the study area as a result of other processes. For example, water from well 9N/1W-12N5, located on the downgradient side of the Waterman Fault (fault C) (fig. 6), contains low levels of tritium and has a comparatively low carbon-14 activity of 53 pmc. Water from this well is a mixture of water from the floodplain and the regional aquifers, each containing different tritium concentrations and carbon-14 activities. In another setting, water from a short-screened watertable observation well beneath an artificial-recharge pond in Lucerne Valley in the Morongo basin also contains measurable tritium but has low ¹⁴C activity. Carbon-14 activity is interpreted to have decreased as a result of dissolution of carbon containing minerals that do not contain ¹⁴C and isotopic exchange with carbon in these minerals as recharge water infiltrated through the thick, carbonate-rich unsaturated zone beneath the pond. Similar processes also occur as a result of natural recharge through thick unsaturated zones beneath intermittent streams. Unsaturated zones beneath some stream reaches are often poorly leached and contain water near saturation with highly soluble calcium and sodium-carbonate minerals (Izbicki and others, 2000). Carbon-14 activity in a short-screened water-table well beneath a wash near Cajon Pass was 32 pmc (Izbicki and others, 2000). Small amounts of recharge occur at this site under present-day climatic conditions and the water is younger than ¹⁴C-activity data suggest. However, the water did not contain tritium because at

least 250 years are required for water to infiltrate to the water table and recharge the aquifer 197 m below land surface (Izbicki and others, 2002).

Geochemical Reactions

Geochemical reactions that affect the age (time since recharge) of ground water can be incorporated into the equation for radioactive decay according to the following:

$$t = \frac{\lambda_{1/2}}{\ln 2} \ln \frac{A_0}{A_{meas} - \Sigma A_{react}}$$
(2)

where ΣA_{react} is change in ¹⁴C activity that has occurred as a result of geochemical reactions between ground water and aquifer material since ground water was recharged. All other parameters have the same meaning as in equation 1.

Geochemical reactions that occur between ground water and aquifer material are evaluated using carbon-13 (¹³C), a naturally occurring stable isotope of carbon, in conjunction with chemical and mineralogic data. These reactions may add carbon that does not contain ¹⁴C to the dissolved phase or remove carbon that may contain ¹⁴C from the dissolved phase. For example, dissolution, isotopic fractionation, or isotopic exchange with carbonate tends to increase δ^{13} C values. Although their composition is variable, marine carbonates have average values near 0 per mil (Coplen and others, 2002) and nonmarine carbonate minerals that cement alluvial deposits have average values near -4 per mil (Robertson, 1992; Izbicki and others, 1995). In contrast, reactions with organic carbon in aquifer materials, having values near -21 per mil for marine deposits and near -28 per mil for continental deposits, tend to decrease δ^{13} C values.

In complex ground-water systems more than one reaction may occur simultaneously and carbon from different sources, having different isotopic compositions, may contribute to the isotopic composition of ground water. Computer programs have been developed that use chemical, mineralogic, and isotopic data to account for the net effect of different reactions on δ^{13} C composition and 14 C activity of water from wells along a flow path.

Interpretation of Carbon-14 Ages Along Selected Flow Paths

The computer program NETPATH (Plummer and others, 1991) was used to calculate the mass transfer of constituents between the aquifer and ground water, estimate changes in isotopic composition, and interpret ¹⁴C ages by evaluating the complex reactions that control ¹⁴C activity. The general approach to interpreting the data is summarized in figure 8. Inputs to NETPATH include the chemical and isotopic composition of water from wells, and chemical equations that describe equilibrium reactions and mass transfer that occur within the aquifer. Regardless of the geochemical setting, the interpretation of ¹⁴C ages using NETPATH begins with an evaluation of changes in major-ion chemistry along the flow path. Constituents that have large changes in concentration or are especially important to carbonate chemistry, such as calcium, need to be included in the interpretation. It is desirable to include as many constituents as possible to ensure a complete representation of ground-water chemistry along the flow path.

Chemical and thermodynamic data are used to calculate saturation indexes for minerals within the alluvial deposits. Ground water is supersaturated with respect to minerals having a saturation index greater than zero; these minerals may precipitate but will not dissolve. Ground water is undersaturated with respect to minerals having a saturation index less than zero; these minerals may dissolve but will not precipitate. Dissolved-aluminum concentrations were not measured as part of this study, and saturation indexes for alumino-silicate minerals were estimated by assuming equilibrium with the mineral gibbsite [Al(OH)₃]. Saturation indexes and the potential for precipitation or dissolution constrain model results. The amount of minerals, gases, or organic material that must dissolve, precipitate, or otherwise react with ground water at one well to produce the observed chemistry at another well farther downgradient is calculated. The effect of these reactions on the $\delta^{13}C$ composition, ¹⁴C activity, and age of ground water also is calculated.

A small number of dissolved constituents and minerals were included in initial models. Additional constituents and minerals were added incrementally and incorporated into the interpretation. All mass-transfer calculations must conform to thermodynamic constraints indicated by saturation indexes. The observed $\delta^{13}C$ composition was compared with the calculated $\delta^{13}C$ composition. The reaction set and calculated mass-transfers between ground water and aquifer materials that minimized the difference between observed and calculated $\delta^{13}C$ compositions along the entire flow path, without violating thermodynamic constraints, were used to calculate ^{14}C ages.

Flow Path 1: Surprise Spring Basin

Ground water in the Surprise Spring subbasin within the Morongo basin flows from recharge areas near the end of Pipes Wash towards discharge areas at Surprise Spring near the Surprise Spring Fault (Londquist and Martin, 1991). The Surprise Spring Fault is a barrier to ground-water flow, and under predevelopment conditions water discharged at land surface in this area. Ground-water levels have declined more than 30 m as a result of pumping since the 1950s and ground water no longer discharges at land surface. The flow path is bounded by faults to the north and south that also are barriers to flow, and the alluvial deposits can be divided into upper and lower aquifers. The upper aquifer is composed of material weathered from granitic rocks in the San Bernardino Mountains. On the basis of x-ray diffraction analysis, quartz, plagioclase, and potassium feldspar account for about 80 percent of the aquifer material. Mica, chlorite, calcite, amphibole, amorphous material, and montmorillonite and other minerals also are present. The lower aquifer is composed of locally derived material weathered from surrounding volcanic and metamorphic rocks. The upper aquifer is the primary water-bearing unit and the wells selected for this flow path are completed in the upper aquifer.



Figure 8. Interpretation of changes in chemistry, thermodynamics, mass transfer, and isotopic composition of water from wells along a flow path.

Ground water in the Surprise Spring area has dissolved solids concentrations ranging from 177 to 310 mg/L (table 1). Dissolved-oxygen concentrations range from 10.8 mg/L near the recharge area and decrease to 1.0 mg/L downgradient. Ground water having high concentrations of dissolved oxygen are not unusual in alluvial aquifers in arid areas. The pH values range from 7.9 to 8.8 and increase with distance downgradient. Dissolved-solids, calcium, magnesium, bicarbonate (alkalinity), and chloride concentrations decrease with distance downgradient. Sodium and silica concentrations do not change greatly with distance downgradient.

Mass-transfer calculations were done assuming that water from well 3N/6E-16A1 approximated the initial chemical and isotopic composition of water sampled from wells farther downgradient. The masstransfer calculations account for oxidation of organic carbon, precipitation of carbonate minerals, cation exchange, and dissolution of primary silicate minerals (simulated as dissolution of anorthite) within the aquifer (fig. 9). The small decreases in dissolvedoxygen concentrations along the flow path suggest that only a small amount of organic matter (simulated as having a δ^{13} C composition of -28 per mil) is present within aquifer deposits and it oxidizes as water flows downgradient. Chemical and thermodynamic data suggest that carbonate minerals precipitate primarily as calcite (simulated as having a δ^{13} C composition of -4 per mil) as water flows downgradient. Calculations show that smaller amounts of magnesium carbonate also precipitate. Calcium and magnesium concentrations, and therefore the thermodynamic equilibria for carbonate minerals, are affected by the exchange of calcium and magnesium for sodium on clay-mineral surfaces and to a lesser extent by the addition of calcium through the dissolution of anorthite. The dissolution of primary silicate minerals, such as anorthite, is responsible for the increase in pH measured along the flow path. The δ^{13} C composition of ground water decreases (becomes more negative) as water flows downgradient from -8.8 to -10.2 per mil as a result of the oxidation of organic material and precipitation of carbonate minerals.

Decreases in the concentration of non-reactive constituents, such as chloride or bromide, cannot be explained by chemical precipitation of minerals along the flow path: chloride and bromide salts are highly soluble and thermodynamic data show that they will not precipitate. Instead, these data were interpreted as reflecting increased aridity of the present-day climate, decreased ground-water recharge, and increased concentrations of these non-reactive constituents in more recently recharged water. This effect was simulated in NETPATH through the normalization of chloride concentrations to present-day values prior to the mass-transfer calculations using the evaporation/dilution option within the computer program. It was not possible to obtain reasonable masstransfer results, calculated δ^{13} C values, and interpreted ¹⁴C ages without accounting for increased aridity of the present-day climate using chloride data. The magnitude of the effect suggests that as little as 1,400 to 5,000 years before present, recharge may have been from 1.3 to 1.6 times greater than under present-day climatic conditions. Rather than a uniform desiccation of the climate and subsequent decrease in ground-water recharge during this period, it is more likely that infrequent, extended wet periods occurred in the past.

Measured carbon-14 activities along the flow path ranged from 86 to 41 pmc and decreased with distance downgradient (table 1). The initial carbon-14 activity was very near the initial carbon-14 activity estimated for well-leached unsaturated zones throughout the Mojave River and the Morongo basins (fig. 7). Assuming only radioactive decay and no correction for mineralogic reactions, ground-water ages along this flow path range from 1,280 to 7,320 years before present. Interpreted carbon-14 ages for water from wells along the flow path through the Surprise Spring subbasin range from recent to 5,090 years before present (table 2). Measured delta carbon-13 values and calculated carbon-13 values for water from wells along the flow path agree within 1.5 per mil, with most values agreeing within 0.7 per mil (<u>table 2</u>). Interpreted ages increased in a simple monotonic fashion with increasing distance downgradient and are almost 30 percent less than uncorrected carbon-14 ages.

Simpler interpretations that incorporate only oxidation of organic material and precipitation of carbonate minerals match measured δ^{13} C values poorly, and calculated values are only within ±3.5 per mil of the measured values. However, interpreted ¹⁴C ages differ by no more than 300 years from the interpretation shown in figure 9. Inclusion of cation exchange improves the match between measured and calculated δ^{13} C values only slightly.

Physical properties, chemical composition, isotopic composition, and saturation indexes, with respect to selected mineral phases, of water from selected wells along flow path 1 through the Surprise Springs subbasin, Morongo ground-water basin, southern California Table 1.

[Saturation indexes greater than 0 indicate supersaturation and the mineral phases would tend to precipitate; saturation indexes less than 0 indicate undersaturation and the mineral would tend to dissolve; mg/L, milligrams per liter; °C, degrees Celsius; dissolved solids is residue on evaporation at 105°C; per mil, parts per thousand; pmc, percent modern carbon]

State well No.	Date	Dis- solved oxygen (mg/L)	표	Tempera- ture (°C)	Calcium (mg/L)	Magne- sium (mg/L)	Pota- sium (mg/L)	Sodium (mg/L)	Bi- carbonate (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Silica (mg/L)	Dissolved solids (mg/L)
3N/6E-16A1	08/11/1994	10.8	7.9	25.0	42	6.5	2.9	47	114	26	38	21	310
3N/7E-19N1	08/10/1994	8.6	8.1	25.5	23	2.4	2.4	41	64	20	32	20	215
3N/7E-29F1	08/18/1994	6.4	8.1	26.0	17	نہ	2.0	41	64	17	29	20	200
3N/7E-29R1	07/12/2000	1.0	8.3	25.5	17	9.	6.	44	88	18	29	19	226
2N/7E-3A1	08/17/1994	4.0	8.7	31.8	9.9	5	2.2	48	57	19	31	18	192
3N/7E-35P2	08/17/1994	3.9	8.8	28.0	5.4	.1	1.6	49	56	16	25	18	177
	Delta	Delta	Carbon-14	Delta				Satur	ation indexes o	f selected mine	ral phases		
State well No.	oxygen-18 (per mil)	deuterium (per mil)	activity (pmc)	carbon-13 (per mil)		Calcite	Gypsum	Albite	Anorthite	Orthoclase	Biotite	Kaolinite	Montmoril- Ionite
3N/6E-16A1	-11.0	-78	86	-8.8		0.13	-2.16	-2.34	-4.73	-1.21	3.37	0.79	-0.78
3N/7E-19N1	-11.5	-81	72	-8.1		14	-2.42	-2.58	-5.19	-1.48	2.49	.12	-1.57
3N/7E-29F1	-11.3	-81	53	-8.2		25	-2.57	-2.53	-5.26	-1.52	2.44	.13	-1.55
3N/7E-29R1	-11.2	-82	53	-7.8		.07	-2.58	-2.60	-5.10	-1.60	2.00	00.	-2.00
2N/7E-3A1	-11.3	-85	43	-10.4		.12	-2.78	-2.63	-4.97	-1.71	1.39	-1.06	-2.89
3N/7E-35P2	-11.4	-84	41	-10.2		-00	-3.11	-2.48	-5.30	-1.66	1.40	-0.99	-2.82



Figure 9. Chemistry, mass transfer, and isotopic composition of water from selected wells along flow path 1 through the Surprise Spring basin, Morongo ground-water basin, southern California. Chemical and saturdation index data given in table 1.

Table 2. Measured and calculated delta carbon-13 composition, carbon-14 activity, and uncorrected and interpreted carbon-14 ages for water from wells along selected flow paths through the Mojave River and the Morongo ground-water basins, southern California

State well No.	Measured delta carbon-13 (per mil)	Calculated delta carbon-13 (per mil)	Measured carbon-14 activity (pmc)	Uncorrected carbon-14 age (ybp)	Interpreted carbon-14 age (ybp)
Flow Path 1					
3N/6E-16A1	-8.8		86	1,280	<50
3N/7E-19N1	-8.1	-7.6	72	2,590	1,430
3N/7E-29F1	-8.2	-8.9	53	5,200	3,800
3N/7E-29R1	-7.8	-9.2	53	5,310	3,900
2N/7E-3A1	-10.4	-9.1	43	7,000	5,000
3N/7E-35P2	-10.2	-8.8	41	7,320	5,090
Flow Path 2					
3N/1W-1R1	-10.6	_	69	3,120	0
4N/1W-26J1	-10.3	-6.8	52	5,410	1,750
4N/1W-19G1	-9.8	-9.8	43	7,030	3,840
4N/2W-9Q1	-11.9	-12.7	38	8,040	4,820
5N/3W-27E1	-10	13.9	36	8,280	4,760
Flow Path 3					
4N/7W-33J1	-13.3	_	90	834	0
5N/7W-4D4	-10.6	-7.0	8.6	20,300	18,800
5N/6W-22E2	-10	-9.3	10.7	18,500	16,900
4N/4W-3A2	-9.6	-9.8	4	25,600	25,300
4N/4W-1C2	-9.3	-10.8	.5	43,800	43,000

I	Per mil	narts	ner thousand	nmc nercei	t modern	carbon: y	hn	vears before	nresent. <	less than:	no datal
l	r er min,	parts	per mousanu,	pine, percei	it mouern	caroon, j	yop,	years before	present, <,	, iess man, –	, no uataj

More complex interpretations that incorporate clay precipitation and include adjustments for changes in natural recharge match measured δ^{13} C values to within ± 1 per mil—with most values agreeing to within ± 0.4 per mil. The agreement between measured and calculated δ^{13} C values is better than the interpretation shown in figure 9; however, saturation indexes suggest that the water from several downgradient wells along the flow path is undersaturated with respect to montmorillonite, and precipitation of this mineral is not thermodynamically possible. This interpretation may not be correct, because montmorillitic clays have a wide range of compositions and associated thermodynamic data. However, the error is small because interpreted ¹⁴C ages for calculations that include clay precipitation differed by at most 80 years from interpreted ages presented in figure 9, with most ages differing by less than 20 years.

Flow Path 2: Upper Part of the Mojave River Basin to the East of the Mojave River

Ground water in the upper part of the Mojave River basin to the east of the Mojave River flows from recharge areas in alluvial fans along the flanks of the San Bernardino Mountains near the Lucerne Valley in the Morongo ground-water basin to discharge areas near the floodplain aquifer along the Mojave River. Alluvial deposits in the area are composed of material weathered from the slopes of the San Bernardino Mountains; although the rocks are primarily granitic, some limestone crops out in this area. Farther downgradient along this flow path, fine-grained basin fill and lacustrine deposits are present in the subsurface. On the basis of x-ray diffraction data, the mineral composition of the aquifer in this area is similar to the Surprise Spring flow path except that calcite abundance is greatly increased, accounting for as much as 20 percent of the material in some samples. Material for mineralogic analysis of fine-grained lacustrine deposits was not available for this study.

Ground water along this flow path (fig. 10) has dissolved solids that range from 356 to 668 mg/L (table 3), dissolved-oxygen concentrations that range from 8.0 to <0.2 mg/L and decrease downgradient; and pH values that range from 7.5 to 8.0 (table 3). Unlike the flow path through the Surprise Spring area, pH values initially increase then decrease and are lowest in the farthest downgradient well. Dissolved-solids, calcium, magnesium, chloride, and sulfate concentrations initially decreased and then increased with distance downgradient. Because of the increase in chloride concentrations along the flow path, it was not possible to include climatic effects in the interpretation of ¹⁴C ages, although these changes almost certainly occur and were important in the interpretation of ¹⁴C data in the Surprise Spring area. Bicarbonate concentrations (alkalinity) decreased downgradient. Silica concentrations did not change greatly with distance downgradient (<u>table 3</u>).

Mass-transfer calculations were done assuming that water from well 3N/1W-1R1 approximated the initial chemical and isotopic composition of water from wells farther downgradient. The calculations account for oxidation of organic material, precipitation of carbonate minerals, and cation exchange in the same manner as in the calculations done along the Surprise Spring flow path. The calculations do not account for the dissolution of primary silicate minerals, although they account for the contribution of solutes from finegrained lacustrine deposits along the downgradient end of the flow path.

The measured increase in solutes with distance downgradient was assumed to result from the finegrained lacustrine deposits along the downgradient part of the flow path and was simulated in the model as dissolution of gypsum and halite. Unlike the problem considered by Izbicki and others (1995) it was not necessary to include dissolution of sodium carbonate minerals to explain changes in ground-water chemistry measured along this flow path. It is highly unlikely that halite, or other chloride containing evaporite minerals, are present in lacustrine deposits along this flow path; it is more likely that high-chloride water within these deposits mixes with fresh ground water. Use of halite is an approximation that probably does not reflect the complex chemical composition of ground water in the lacustrine deposits. As a result of this approximation, measured and calculated δ^{13} C values for water from wells along the flow path agree only within ± 3.5 per mil-although measured and calculated values from the two wells in the middle of the flow path are in much closer agreement (fig.10).



Figure 10. Mass transfer and isotopic composition of water from selected wells along flow path 2 through the upper part of the Mojave River groundwater basin east of the Mojave River, southern California. Chemical and saturation index data given in table 3.

Physical properties, chemical composition, isotopic composition, and saturation indexes, with respect to selected mineral phases, of water from selected wells along flow path 2 through the regional aquifer east of the Mojave River, southern California Table 3.

[Saturation indexes greater than 0 indicate supersaturation and the mineral phases would tend to precipitate. Saturation indexes less than 0 indicate undersaturation and the mineral would tend to dissolve. mg/L, milligrams per liter; °C, degrees Celsius; dissolved solids is residue on evaporation at 105°C; per mil, parts per thousand; pmc, percent modern carbon; <, less than]

Dissolved Tempera- Magn Date oxygen pH ture Calcium Magn () pH ture (mg/L) (Dissolved Tempera- Magn oxygen pH ture Calcium Magn oxygen pH ture (mg/L) sium	Tempera- Calcium Magn pH ture Calcium sium (nov) (mg/L) (Tempera- Calcium Magn ture Calcium sium (ac) (mg/L) (Calcium Magn sium (mg/L) ,	Magn sium	۔ م	Pota- sium	Sodium (mg/L)	Bi- carbonate	Chloride (mg/L)	Sulfate (mg/L)	Silica (mg/L)	Dissolved solids
		(mg/L)		(72)		(mg/L)	(mg/L)		(mg/L)				(mg/L)
3N/1W-1R1	05/18/1995	8.0	7.6	19.0	59	32	2.7	11	307	6.6	47	33	508
4N/1W-26J1	03/30/1994	3.6	7.9	24.5	44	19	2.3	16	202	5.0	28	24	356
4N/1W-19G1	04/27/1995	1.6	7.9	21.5	33	14	5.2	78	171	10	160	61	536
4N/2W-9Q1	04/27/1995	i.	8	25.0	54	10	2.7	45	115	20	140	34	427
5N/3W-27E3	03/10/1994	<.2	7.5	23.8	75	19	3.1	100	107	160	170	29	668
	delta	dalta	Carhon-14	dalta				Saturation	n indexes of s	elected miner	al phases		
Ctate well No.	Overan 10	Doutorium	ontinity.	Carbon 12	1								
State well NO.	(per mil)	(per mil)	activity (pmc)	carbon-13 (per mil)		Calcite	Gypsum	Albite	Anorthite	Ortho- clase	Biotite	Kaolinite	Montmoril- Ionite
3N/1W-1R1	-11.8	-85	69	-10.6		0.28	-2.02	-2.30	-4.76	-0.50	4.48	1.82	0.65
4N/1W-26J1	-12	-87	52	-10.3		.38	-2.30	-3.21	-6.22	-1.71	1.07	67	-2.26
4N/1W-19G1	-12.2	-88	43	-9.8		.24	-2.11	-1.92	-4.54	76	3.77	1.11	18
4N/2W-9Q1	-11.6	-84	38	-11.9		.28	-1.57	-1.73	-4.32	61	3.67	.95	24
5N/3W-27E3	-11.3	-89	36	-10		16	-1.43	-1.81	-4.90	96	3.82	1.37	.01

Measured ¹⁴C activities along the flow path ranged from 69 to 36 pmc (table 3). Assuming only radioactive decay, an initial ¹⁴C activity of 100 pmc, and no correction for mineralogic reactions, uncorrected ¹⁴C ages ranged from 3,115 to 8,277 years before present (fig. 10). On the basis of the masstransfer calculations presented in this paper, interpreted ¹⁴C ages along this flow path ranged from recent to 4,820 years before present. The ¹⁴C activity of water from well 3N/1W-1R1, 63 pmc, was used as the initial ¹⁴C activity for mass-transfer calculations. This value is consistent with the initial ¹⁴C activity previously estimated for poorly-leached or carbonate-rich unsaturated zones in the Morongo and the Mojave River ground-water basins (fig. 7). Use of the lower initial ¹⁴C activity resulted in a greater difference between the uncorrected ¹⁴C age and the interpreted age of the ground water than along the Surprise Spring flow path.

Simpler interpretations that do not account for measured increases in chloride concentrations and simulate the contribution of solutes from the finegrained lacustrine deposits solely as the dissolution of gypsum match measured and calculated δ^{13} C values within ±1.9 per mil. Interpreted ¹⁴C ages range from recent to 4,820 years before present and are only slightly younger than ¹⁴C ages that account for measured increases in chloride.

It was not possible to obtain a solution to masstransfer calculations and interpretations of groundwater ages along the study flow path if more complicated calculations that include dissolution of silicate minerals and (or) precipitation of clay minerals were included. Although these reactions probably occur, their effect on pH and other constituents is masked by the contributions of solutes from the lacustrine deposits. Results of calculations done along this flow path are poorly understood and that the measured changes are not accurately simulated by the dissolution of mineral phases.

Flow Path 3: Upper Part of the Mojave River Basin to the West of the Mojave River

Ground water in the upper part of the Mojave River basin to the west of the Mojave River flows from recharge areas in the alluvial fans along the flanks of the San Bernardino Mountains to discharge areas near the Mojave River. As a result of tectonic activity near Cajon Pass and subsequent erosion, the alluvial fans are connected to the San Bernardino Mountains only in the western part of the study area near Sheep Creek, and ground water in the regional aquifer flows radially outward from this area. Alluvial deposits in this part of the basin are composed of material weathered from the granitic and metamorphic rocks in the San Bernardino Mountains. Fine-grained basin-fill and lacustrine deposits also are present in this area farther from the mountain front; however, these deposits were not encountered along the flow path presented. On the basis of x-ray diffraction data, the mineral composition of the aquifer in this area is similar to that of the Surprise Spring flow path except that mica, chlorite, amorphous material and calcite were more abundant. However, calcite was not as abundant as in deposits along the flow path east of the Mojave River.

Many of the wells sampled along this flow path are observation wells having short screen lengths (typically about 6 m) completed in deeper parts of the aquifer. Changes in the chemical and isotopic composition of water from wells along this flow path were studied previously by Izbicki and others (1995) and Kulongoski and others (in press).

Dissolved-solids concentrations ranged from 239 to 736 mg/L and decreased downgradient. Dissolved oxygen was not measured in sampled wells near the mountain front but was present in water from wells farther downgradient. The pH values ranged from 7.3 to 9.6 and increased with distance downgradient. In general, calcium, magnesium, potassium, chloride, and sulfate concentrations decrease downgradient. Bicarbonate (alkalinity) concentrations decrease and then increase with distance downgradient. In contrast to previous flow paths, the δ^{13} C composition of water along this flow path became less negative with distance downgradient.

Mass-transfer calculations were done assuming that water from well 4N/7W-33J1 approximated the initial chemical and isotopic composition of water from wells farther downgradient. The calculations account for oxidation of organic carbon, precipitation of carbonate minerals, cation exchange, and dissolution of primary silicates in the same manner as calculations along the other flow paths. In addition, it was possible to incorporate precipitation of secondary silicate minerals, simulated as montmorillonite.

Carbon-14 activities range from 90 to 0.5 pmc (table 4). Assuming only radioactive decay and no correction for mineralogic reactions, uncorrected ¹⁴C ages range from 834 to 43,800 years before present (fig. 11). Interpreted ${}^{14}C$ ages range from recent to 43,000 years before present but are subject to great uncertainty and exceed the practical range of the dating technique of 20,000 years before present. The great age of water from wells along this flow path is a function of three factors: small recharge rates, aquifer geometry (ground-water movement is radially away from a single recharge location), and the deep short-screened wells sampled along this section. This last factor results in data that contrasts with data collected from longscreened production wells that integrate larger volumes of water than the short screened observation wells.

Simpler interpretations that included only oxidation of organic matter and precipitation of carbonate minerals yielded δ^{13} C values that differed by 2 to 3 per mil from measured values. Four of the five interpreted ¹⁴C ages calculated on the basis of these simpler interpretations were within 100 years of the more complex interpreted age was about 800 years. Given the great age of ground water along this flow path, a difference in estimated ground-water age of 800 years may not be important.

Limitations on Carbon-14 Interpretations

Carbon-14 ages calculated for ground water are interpretive and subject to considerable uncertainty. Davis and Bentley (1982) estimated that, for aquifers where chemistry is well understood, interpreted ¹⁴C ages are within ±20 percent of the actual age. For areas where chemistry is less well understood, Davis and Bentley (1982) estimated that the error may be as great as ±100 percent of the actual age. Results of this study show that although the calculated δ^{13} C composition of ground water along the flow path is sensitive to chemical reactions simulated by the mass-transfer calculations done using NETPATH, the interpreted ¹⁴C ages are not as sensitive. As a result, interpreted carbon-14 ages estimated on the basis of a reasonable, but simple, representation of ground-water geochemistry may be sufficiently accurate for most purposes.

In many studies the greatest source of uncertainty in interpreting ¹⁴C data is in estimating the initial chemistry and isotopic composition of the recharge water. This is a common problem in areas where present-day recharge is absent or very small. In this study, the initial chemistry and isotopic composition of recharge water was estimated through sample collection. In some areas, such as in the Surprise Spring area, the results compared well with theoretical values and measured values in other aquifers. In areas where large amounts of carbonate minerals were present, initial ¹⁴C activities of recharging ground-water were significantly lower-but the actual composition of water that recharged the aquifer thousands of years ago can not be precisely known. This type of error is most significant in the estimate of the absolute age of water from a well and is less important in estimates of the time-of-travel from one well to another farther downgradient (Izbicki and Martin, 1998; Zhu and Murphy, 2000).

Another source of uncertainty in estimating ground water age is that ¹⁴C production varies with solar activity and has not been constant during the last 24,000 years (Stuiver and others, 1998). Changes in ¹⁴C production as a result of changes in solar activity during recent geologic time were not factored into ground-water ages estimated as part of this study.

DISCUSSION

Tritium and ¹⁴C have been used to estimate ground-water recharge, ages, and travel times in aquifers throughout the southwestern United States and in other parts of the world. In most of these studies, the application of the environmental tracers has been restricted to ground water along simplified flow paths from recharge areas to discharge areas. The areal distribution of ground-water ages and the complex interaction of ground water between riparian aquifers and surrounding basin-fill aquifers, such as those found in the Mojave River ground-water basin, have not been routinely considered. Physical properties, chemical composition, isotopic composition, and saturation indexes, with respect to selected mineral phases, of water from selected wells along flow path 3 through the regional aquifer west of the Mojave River, southern California Table 4.

[Saturation indexes greater than 0 indicate supersaturation and the mineral phases would tend to precipitate; saturation indexes less than 0 indicate undersaturation and the mineral would tend to dissolve; mg/L, milligrams per liter; ^oC, degrees Celsius; dissolved solids is residue on evaporation at 105^oC; per mil, parts per thousand; pmc, percent modern carbon; —, no data]

Dissolved solids (mg/L)	736	355	266	270	239		Montmoril- Ionite	0.16	11	11	.11	02
Silica (mg/L)	15	15	15	19	16		Kaolinite	1.84	1.40	1.53	1.55	1.50
Sulfate (mg/L)	160	160	86	2.3	11	l phases	Biotite	4.45	5.12	4.78	5.40	5.33
Chloride (mg/L)	6.2	3.4	3	1.9	5.1	elected minera	Orthoclase	-1.12	51	84	25	24
Bi- carbonate (mg/L)	376	71	83	171	171	indexes of se	Anorthite	-5.44	-2.72	-3.94	-2.66	-3.09
Sodium (mg/L)	15	80	62	68	31	Saturation	Albite	-3.14	-1.42	-1.82	50	96
Potasium (mg/L)	5.5	3.4	2.8	.S	9.		Gypsum	-1.28	-1.92	-2.42	-5.05	-4.35
Magnesium (mg/L)	35	2.4	1.6	60.	.06		Calcite	0.26	.25	37	.03	.01
Calcium (mg/L)	120	19	9.2	6.	.89							
Tempera- ture (°C)	15.5	29.5	26.4	21.5	17.5	delta	Carbon-13 (per mil)	-13.3	-10.6	-10	-9.6	-9.3
H	7.3	8.6	8.2	9.6	9.6	Carbon-14	activity (pmc)	06	8.6	10.7	4	5.
Dissolved oxygen (mg/L)			3.4	1.1	i.	delta	Deuterium (per mil)	-80	-84	-85	-86	-80
Date	06/08/93	05/27/93	06/01/94	03/09/94	01/13/93	delta	Oxygen-18 (per mil)	-11.6	-11.8	-11.8	-11.9	-11.1
State well No.	4N/7W-33J1	5N/7W-4D4	5N/6W-22E2	4N/4W-3A2	4N/4W-1C2		State well No.	4N/7W-33J1	5N/7W-4D4	5N/6W-22E2	4N/4W-3A2	4N/4W-1C2



Figure 11. Mass transfer and isotopic composition of water from selected wells along flow path 3 through the upper part of the Mojave River ground-water basin west of the Mojave River, southern California. Chemical and saturation index data given in table 4.

Altitudes of the San Gabriel and the San Bernardino Mountain ranges control the distribution of ground-water recharge to aquifers in the Mojave River and the Morongo ground-water basins (Izbicki and others, 1995). Low-altitude gaps in these mountain ranges allow cool, moist air masses to enter the Mojave Desert and produce precipitation. For example, winter precipitation near Cajon Pass gives rise to stormflows in the Mojave River that recharge the floodplain aquifer along the entire length of the river as far east as Afton Canyon, 160 km from the mountain front. In most areas, ground water in the floodplain aquifer contains tritium and was recharged after 1952. However, the ¹⁴C activity ground water in the floodplain aquifer in the Mojave Valley suggests that this water has great age. The surrounding and underlying regional aquifer is recharged by infiltration of streamflow from the higher altitudes of the San Gabriel and the San Bernardino Mountain ranges. Most water in the regional aquifer recharged many thousands of years ago, and recently recharged water containing tritium is found only in canyons and along alluvial fans near the mountain front. Under predevelopment conditions, ground water in the regional aquifer discharged to the floodplain aquifer and ultimately to the Mojave River.

Although the aquifers are hydraulically connected, in most areas the isotopic composition of ground water in the two aquifers is distinct. Izbicki and others (1995) observed sharp contrasts in the δ^{18} O and δD composition and large differences in the ¹⁴C activity of water in the two aquifers were observed. The oldest ground water sampled was from deep observation wells at the downgradient ends of long flow paths through the regional aquifer near where under predevelopment conditions ground water discharged to the floodplain aquifer. Movement of water between aquifers occurred near faults that acted as barriers to ground-water flow. On the upgradient side of these faults, ground water from the regional aquifer discharged to the floodplain aquifer. On the downgradient side of the faults, ground water from the floodplain aquifer recharged the regional aquifer and

underlying deposits. Detailed sample collection from depth-dependent observation wells is required to observe the complex exchange of water between the floodplain aquifer and the surrounding and underlying regional aquifer systems.

An inverse mass-balance modeling approach using the computer program NETPATH (Plummer and others, 1991) was used to interpret ¹⁴C activity data and estimate ground water ages in the Mojave River and the Morongo ground-water basins. The flow path through the Surprise Spring area of the Morongo ground-water basin is representative of reactions that occur in relatively non-reactive desert aquifer systems, characterized by an absence of organic material and increases in pH as a result of primary silicate weathering. The effects of gradual desiccation resulting from decreasing recharge were required to interpret changes in ground-water chemistry measured in this simple geochemical system. These effects were masked along the other study flow paths by uncertainty in the estimates of the initial ¹⁴C activity of recharging ground water, and by the dissolution of soluble minerals along the study flow paths, but the effects almost certainly were present. Changes in rechargewater chemistry with time have probably occurred for aquifers throughout the southwestern United States and in other arid areas; however, these changes are not usually incorporated into the interpretation of ¹⁴C data.

Corrections to measured ¹⁴C activity data were most important in estimates of ground water ages less than 10,000 years before present. In this range, interpreted ¹⁴C ages were about 30 percent lower than uncorrected ages estimated assuming an initial ¹⁴C activity of 100 pmc and neglecting rock-water reactions (fig. 12). Corrections to measured ¹⁴C activity data for mineralogic reactions are greater in areas having higher dissolved-solids concentrations. In general, interpreted ages in areas having high-dissolved solids concentrations are probably less accurate than interpreted ages in areas having low dissolved-solids concentrations.



Figure 12. Comparison of uncorrected carbon-14 ages and interpreted carbon-14 ages for ground water in the Mojave River and the Morongo groundwater basins, southern California.

In relatively non-reactive alluvial aquifers, such as those studied within the western Mojave Desert ground water having low ¹⁴C activity tended to have great age regardless of the corrections applied during the interpretation of the data (fig. 12). However, results of this study show that recently recharged water that has passed through thick unsaturated zones beneath intermittent streams may have low ¹⁴C activity. Similarly, recently recharged water in strongly reducing coastal aquifers in southern California can have ¹⁴C activities as low as 14 pmc (Izbicki and others, 1992). In both cases the water can be readily identified on the basis of unique chemical composition. Care must be taken to ensure that the hydrologic setting and ground-water chemistry are sufficiently well characterized that appropriate, reasonable reactions are used to interpret ¹⁴C activity data and estimate groundwater age.

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