Geochemical Analyses of Ground-Water Ages, Recharge Rates, and Hydraulic Conductivity of the N Aquifer, Black Mesa Area, Arizona

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CONVERSION FACTORS

Multiply	**By**	**To obtain**
inch (in.)	25.40	millimeter
inch (in.)	2.540	centimeter
foot (ft)	0.3048	meter
acre-foot (acre-ft)	0.001233	cubic hectometer
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
pound (lb)	0.907	megagram

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

$$°F = 1.8(°C) + 32$$

ABBREVIATED WATER-QUALITY UNITS

Chemical concentration and water temperature are given only in metric units. Chemical concentration in water is given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. For concentrations less than 7,000 milligrams per liter, the numerical value is about the same as for concentrations in parts per million. Specific conductance is given in microsiemens per centimeter (µS/cm) at 25 degrees Celsius. Radioactivity is expressed in picocuries per liter (pCi/L), which is the amount of radioactive decay producing 2.2 disintegrations per minute in a unit (liter) of water.

VERTICAL DATUM

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."

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Abstract

The Navajo Nation and Hopi Tribe of the Black Mesa area, Arizona, depend on ground water from the N aquifer to meet most tribal and industrial needs. Increasing use of this aquifer is creating concerns about possible adverse effects of increased ground-water withdrawals on the water resources of the region. A thorough understanding of the N aquifer is necessary to assess the aquifer's response to ground-water withdrawals. This study used geochemical techniques as an independent means of improving the conceptual model of ground-water flow in the N aquifer and to estimate recharge rates and hydraulic conductivity.

Ground water flows in a south-southeastward direction from the recharge area around Shonto into the confined part of the N aquifer underneath Black Mesa. Ground-water flow paths diverge in the confined part of the aquifer to the northeast and south. The N aquifer thins to extinction south of Black Mesa. This discontinuity could force ground water to diverge along paths of least resistance. Ground water discharges from the confined part of the aquifer into Laguna Creek and Moenkopi Wash and from springs southwest of Kykotsmovi and southeast of Rough Rock after a residence time of about 35,000 years or more. Recent recharge along the periphery of Black Mesa mixes with older ground water that discharges from the confined part of the aquifer and flows away from Black Mesa.

Dissolved-ion concentrations, ratios of dissolved ions, dissolved-gas concentrations, tritium, carbon-13, and chlorine-36 data indicate that water in the overlying D aquifer could be leaking into the confined part of the N aquifer in the southeastern part of Black Mesa. The boundary between the leaky and nonleaky zones is defined roughly by a line from Rough Rock to Second Mesa and separates ground waters that have significantly different chemistries. The Dakota Sandstone and Entrada Formation of the D aquifer could be the sources of leakage.

Adjusted radiocarbon ground-water ages and data on isotopes of oxygen and hydrogen indicate that more than 90 percent of the water in the confined part of the N aquifer is older than 10,000 years and was recharged during glacial periods. Estimates of recharge rates made on the basis of ground-water ages, aquifer thicknesses, and assumed porosities indicate that the annual average recharge rate in the northwestern part of the study area during the glacial periods was about four times the average annual rate of the past 10,000 years, and that recharge rates for the past 10,000 years are less than modern recharge rates assumed in a previous study. Estimates of horizontal hydraulic conductivity were 0.95 and 1.16 feet per day for the northeast and southwest flow paths, respectively. These values are within the range of hydraulic conductivities calculated from aquifer tests, which ranged from 0.05 to 2.1 feet per day and averaged 0.65 foot per day.

INTRODUCTION

The growing population and industrial development of the Black Mesa area, Arizona (fig. 1), have increased the demand for water in an area with sparse water resources. The Navajo Nation and Hopi Tribe depend on ground water to sustain municipal, domestic, livestock, and industrial needs. Peabody Coal Company also uses ground water to transport coal mined from Black Mesa through a 273-mile pipeline to the Mohave Generating Station near Laughlin, Nevada. Most of the water demands in the Black Mesa area are met by pumpage from the N aquifer, and withdrawals from this aquifer have increased about sixfold during the last 25 years (Littin, 1992). Increased ground-water withdrawals have raised concerns about the adequacy of the N aquifer to sustain tribal growth and industry, potential degradation of ground-water quality by leakage from saline aquifers, and reduced flow from sacred springs. Since 1971, these concerns have led to a continual effort by The Navajo Nation, the Navajo Tribal Utility Authority (NTUA), the Hopi Tribe, the Bureau of Indian Affairs (BIA), the Peabody Coal Company, and the U.S. Geological Survey (USGS) to monitor the water resources of the Black Mesa area. This study was done by the USGS in cooperation with the BIA and the Navajo Department of Water Resources Management.

Purpose and Scope

This report describes how geochemical techniques were used to improve the conceptual model of the N-aquifer flow system of the Black Mesa area. The conceptual model of ground-water flow is the basis for a numerical model that represents the N-aquifer flow system and the response of the aquifer to pumping. Data from analyses of major ion, radioactive carbon-14, tritium, oxygen-18, hydrogen-2, carbon-13, and chlorine-36 were used to estimate ground-water ages, delineate flow directions, and estimate recharge rates and aquifer properties. Estimated ground-water flow directions, recharge rates, average linear velocities, and hydraulic conductivities were compared with values estimated in previous studies. Emphasis of sampling and interpretation was on the approximately 3,500-square-mile area of the confined N aquifer and selected nearby areas where the aquifer is unconfined (fig. 1).

Acknowledgments

The Navajo Tribal Utility Authority, Hopi Department of Water, and Peabody Coal Company assisted in sampling logistics and provided information on well construction.

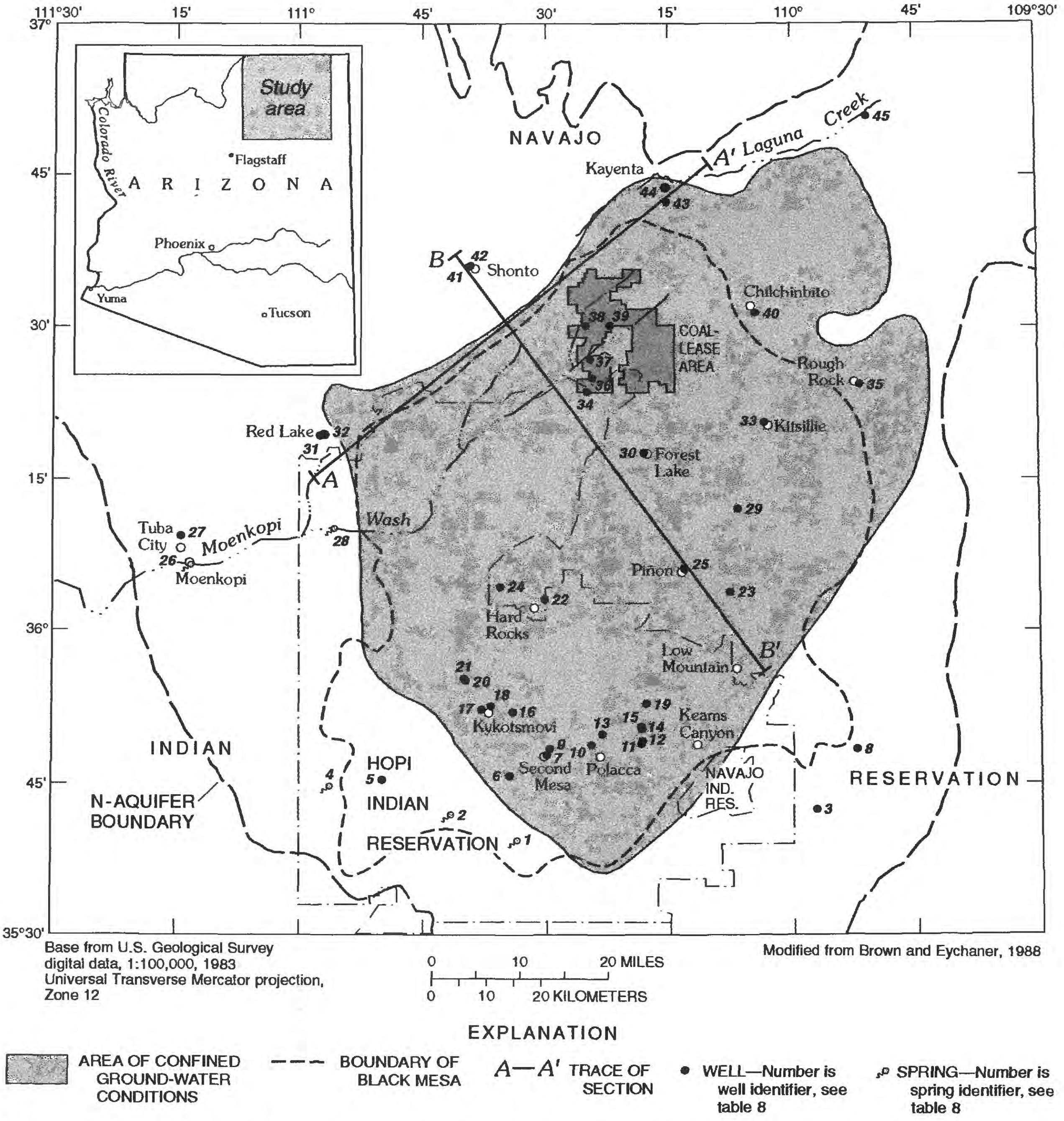
DESCRIPTION OF THE BLACK MESA AREA

The study area is about 11,000 mi^2 of the Navajo and Hopi Indian Reservations in arid to semiarid northeastern Arizona (fig. 1). Black Mesa is a plateau near the center of the study area and has an area of about 2,000 mi^2. Black Mesa abruptly rises about 3,000 ft above the surrounding lowlands on the northeast and slopes gently from the northeast to the southwest where it becomes indistinct from the surrounding lowlands. Elevations in the study area range from about 4,000 to 8,000 ft. The total population of the study area is about 28,500; Tuba City is the largest city, with about 7,300 inhabitants (U.S. Department of Commerce, 1991). Grazing of sheep and cattle, tourism, and the coal mines are important to the life and economy of the area.

Geology and Aquifer Systems

The study area is underlain by a complex intertonguing of layered mudstone, siltstone, sandstone, silty sandstone, limestone, conglomerate, coal, and gypsum that range in age from Permian to late Tertiary (Cooley and others, 1969). These sedimentary rocks have a total thickness that ranges from about 1,000 ft to more than 10,000 ft and overlie granitic and metamorphic basement rock of Precambrian to Cambrian age. A thin, discontinuous veneer of unconsolidated to weakly consolidated Quaternary sediments overlies the series of sedimentary rocks.

Black Mesa is the remnant of rocks of Jurassic to Cretaceous age that were eroded from most of

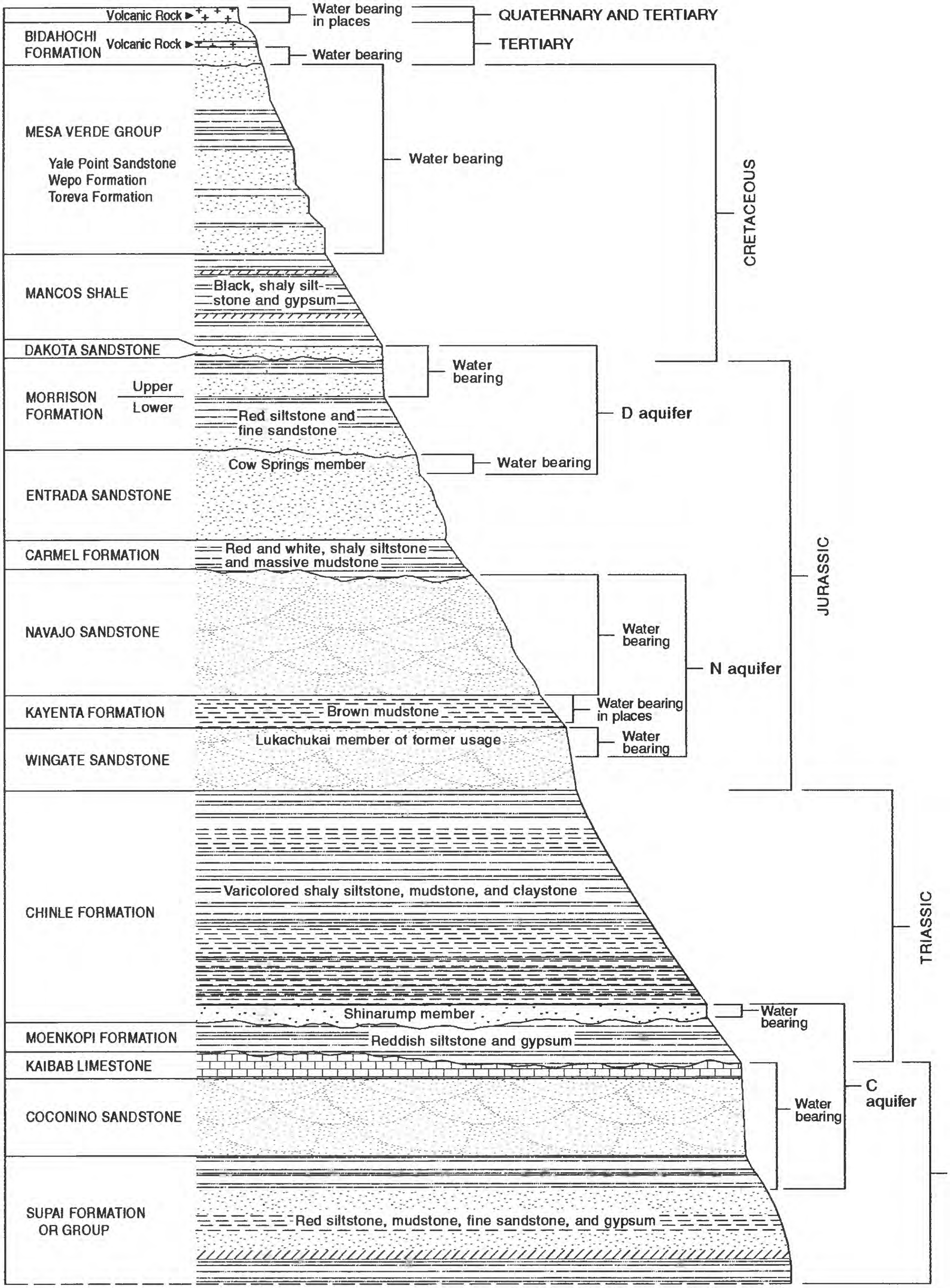


Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection, Zone 12

Modified from Brown and Eychaner, 1988

Figure 1. Location of study area and trace of hydrogeologic sections, Black Mesa area, Arizona.

the study area. The N aquifer underlies the plateau and is the primary aquifer in the Black Mesa area. The N aquifer is actually a multiple-aquifer system that encompasses several lithologic formations and heterogeneities within the formations (Cooley and others, 1969). The Navajo Sandstone is the principal lithologic unit of the N aquifer. The Navajo Sandstone is a medium- to fine-grained cross-bedded sandstone that locally contains lenticular beds of cherty limestone and is one of the most conspicuous formations in the area. In the northern and eastern parts of the study area, the Kayenta Formation and the Wingate Sandstone also are included in the N aquifer (fig. 2). The Kayenta Formation intertongues with the overlying Navajo Sandstone and primarily is a grayish-red mudstone



Modified from Harshbarger and others (1966)

Figure 2. Rock formations of the Black Mesa area, Arizona. The N aquifer is approximately 1,000 feet thick.

with fine- to very fine-grained sandstone with interbedded siltstone. The Wingate Sandstone is the lowest unit in the N aquifer and is a fine- to very fine-grained sandstone. Grains of these three units are composed primarily of quartz with trace amounts of volcanic rock fragments and calcite that are weakly cemented with calcium carbonate and silica (Harshbarger and others, 1957, p. 10–22; Geotrans, Inc., 1993). The primary water-bearing units of the N aquifer are the Navajo Sandstone and the fine-grained sandstones of the Wingate Sandstone and Kayenta Formation. Rocks of the N aquifer are more than 1,200 ft thick in the northwestern part of the study area and thin to extinction in the southeastern part of the study area (fig. 3, *B–B′*). Recharge to the N aquifer is mostly in the north and northwest where rocks of the N aquifer crop out (fig. 3, *B–B′*).

The D aquifer overlies the N aquifer throughout the Black Mesa area; erosion has removed the rocks of the D aquifer from the rest of the study area. The D aquifer has been described by Cooley and others (1969, p. A42) as "consisting of several thin isolated semiconnected sandstone water-bearing units that are separated by thick sequences of mudstone and siltstone." The D aquifer is a multiple-aquifer system composed of the Dakota Sandstone, Westwater Canyon Member of the Morrison Formation, and the Cow Springs Member of the Entrada Sandstone (fig. 2). The texture and composition of the Dakota Sandstone vary widely; the unit generally is coarse grained to fine grained and includes minor amounts of conglomerate, shale, and coal. Grains of the Dakota Sandstone are composed primarily of quartz and are firmly cemented with iron oxide. The Westwater Canyon Member is one of eight members of the Morrison Formation found on the Colorado Plateau (Peterson, 1988). Most members of the Morrison Formation are mudstone and shale. The Westwater Canyon Member is a medium-grained sandstone; minor amounts of shaley mudstone and stringers of conglomerate are present locally. The Cow Springs Member of the Entrada Sandstone is a cross-bedded, fine-grained sandstone (Peterson, 1988). Grains of the Cow Springs Member are mostly quartz and occasional feldspar that are firmly cemented with calcium carbonate. The underlying Entrada strata are flat-bedded silty sandstones. The Dakota Sandstone is the primary water-bearing unit in the multiple-aquifer system. Rocks of the D aquifer are about 700 ft thick in the southeastern part of the study area and thicken to about 1,300 ft near the center of the study area before thinning to less than 100 ft to the northwest (fig. 3, *B–B′*).

The D aquifer is separated from the N aquifer by the Carmel Formation (figs. 2 and 3). The Carmel Formation is less than 300 ft thick and consists of weakly cemented mudstone, siltstone, and sandstone layers. The sandstone layer primarily is found in the southwestern part of the study area (Harshbarger and others, 1957, fig. 16). Although the Carmel Formation forms the upper confining bed of the N aquifer, it is known to yield water to small springs west of the study area (Cooley and others, 1969). The water-bearing units of the Carmel Formation generally are sandstones and lesser amounts of siltstone. Rocks of the D aquifer are overlain by the Mancos Shale throughout the Black Mesa area. The Mancos Shale is a 500-foot-thick-confining unit of marine mudstone and gypsum. Recharge to the D aquifer occurs on the east slopes of the mesa (fig. 3, *A–A′*), where the aquifer is at high elevations and has the largest exposure.

Hydrology

The climate of the Black Mesa area is arid to semiarid. The mean annual precipitation ranges from about 7 in. near Tuba City to about 18 in. near Shonto and at the higher elevations of Black Mesa. Mean annual precipitation and the proportion of precipitation that falls as snow increases with elevation in the Black Mesa area (Cooley and others, 1969). Several large washes on Black Mesa drain runoff to the southwest and into the Little Colorado River.

Previous studies have provided valuable information on the hydrology of the N-aquifer system. Water levels (Eychaner, 1983) indicate that the potentiometric surface is highest near Shonto and lowest along Moenkopi Wash and near Laguna Creek. Ground water would thus flow from the Shonto area generally in a southward direction under Black Mesa. The flow divides under the mesa and part of the flow moves westward to Moenkopi Wash and part moves eastward and

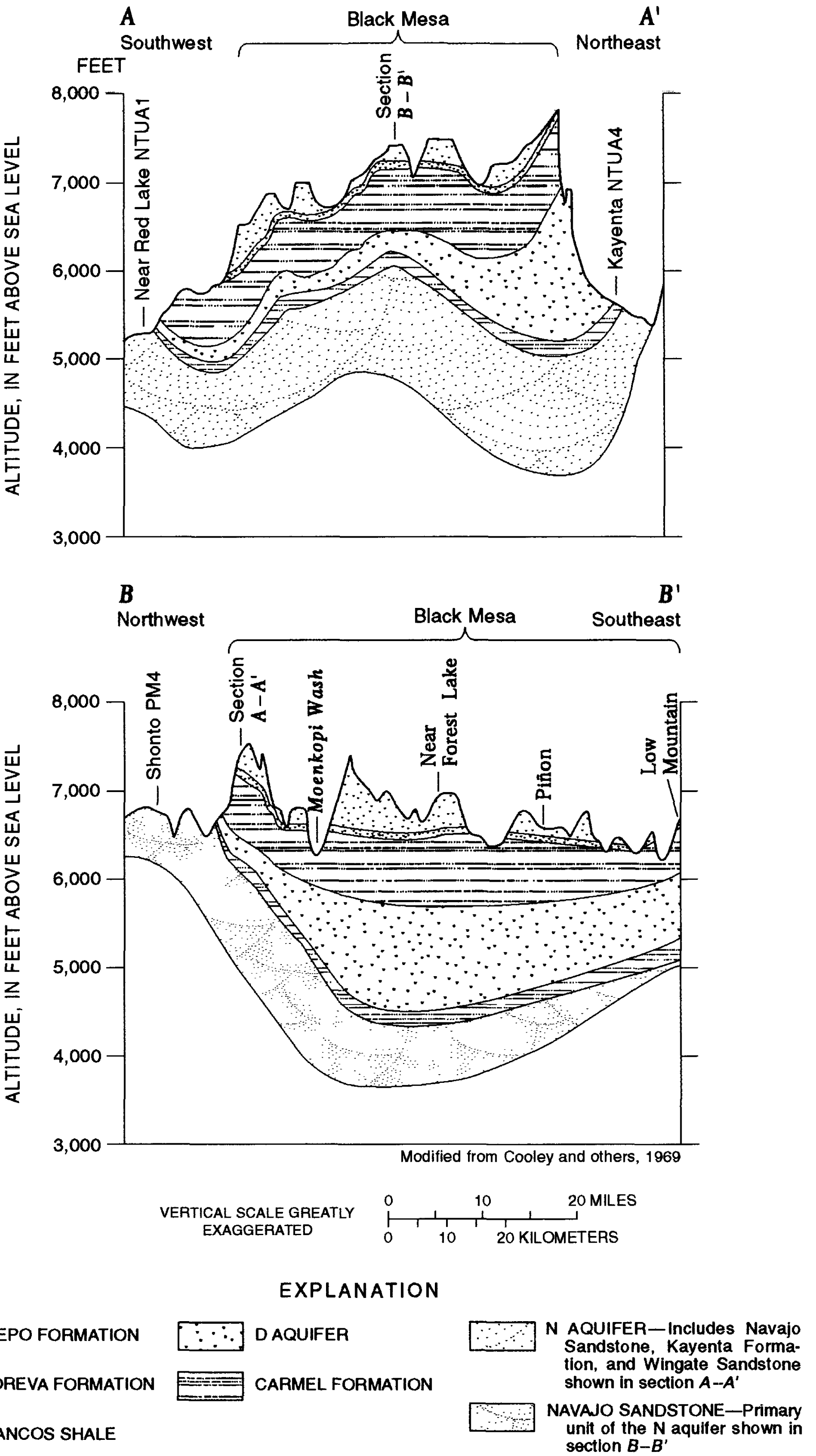


Figure 3. Generalized hydrogeologic sections showing aquifer thickness and continuity, Black Mesa area, Arizona. Traces of sections are shown on figure 1. (Source: Data from Cooley and others, 1969; and selected well logs from U.S. Geological Survey files.)

northeastward toward Laguna Creek. Water levels indicate that precipitation recharges the N aquifer primarily in the Shonto area where the Navajo Sandstone is exposed. Recharge has been assumed to be about 3 percent of the precipitation in the outcrop area near Shonto and about 1 percent in other outcrop areas (Eychaner, 1983).

A numerical model of the Black Mesa ground-water system was developed by Eychaner (1983) to improve the understanding of the N aquifer and to compare possible effects of alternative pumping scenarios. Improved methods in simulating ground-water systems and additional data on the N aquifer were used by Brown and Eychaner (1988) to update the numerical model. These models assumed annual recharge to the system in the Shonto area to be about 4,800 acre-ft and that leakage from the D aquifer into the N aquifer was estimated to be 200 acre-ft annually. The potentiometric surface of the D aquifer in 1964, however, was as much as 600 ft higher than the surface of the N aquifer (Eychaner, 1983); therefore, it is possible that leakage from the D aquifer accounts for a larger percentage of water in the N aquifer. The Carmel Formation is known to yield water to springs and generally is between 150 and 250 ft thick in the study area. Although the leakage rate through the Carmel Formation may be small, the areal extent of contact between the two aquifers provides a major pathway for ground-water flow. An investigation of the D- and N-aquifer geochemistry by Geotrans, Inc. (1993) identified data that indicate leakage occurs between the D and N aquifers.

Since 1972, effects of pumping have been monitored using several monitor wells (Littin, 1992). Total pumpage from the N aquifer for 1994 was about 7,020 acre-ft (Littin and Monroe, 1995); about 75 percent of the total pumpage was from the confined part of the N aquifer. Municipal water use has increased steadily, and in 1994, municipal use was 42 percent of the total pumpage. Peabody Coal Company has pumped water from the confined part of the N aquifer since 1969. Since 1986, Peabody Coal Company has pumped about 4,000 acre-ft/yr from the confined part only. Total pumpage from the D aquifer is unknown but could be two orders of magnitude less than pumpage from the N aquifer because the D aquifer is not used by municipalities or industry.

Monitoring efforts have shown that changes in water levels are deviating from predictions of the numerical model, especially in the Kayenta area (Littin, 1992) where measured water levels are declining more than was indicated by the numerical models. These differences could be caused by pumping rates that are different from those used in simulations or the inability of the model to simulate the complexities of the actual aquifer system and its response to pumping, or both.

SAMPLE COLLECTION AND ANALYTICAL METHODS

Ground-water samples were collected from 5 springs and 40 municipal, industrial, and livestock wells screened in the N and D aquifers of the Black Mesa area between March 1993 and August 1995 (see Basic Data section at the end of the report, tables 8, 9, and 10). Geologic and (or) drillers' logs, electric logs, and well-construction information were reviewed to ensure that wells were being pumped from a particular aquifer and that the wells had been sealed from other aquifers. Production wells are constructed to obtain the greatest yield of water that is of suitable quality for the intended uses. Not all production wells, however, are useful for chemical or water-level monitoring because these wells commonly draw water from more than one aquifer and characteristics of individual aquifers cannot be easily distinguished.

Ground-Water Sample Collection and Analyses

All wells were purged before sampling; temperature, specific conductance, dissolved-oxygen concentration, and pH were monitored during purging. Samples were collected after three well volumes had been purged from the wells or after field measurements had stabilized, or both (Radtke and Wilde, in press). Purging commonly took more than 8 hours because most wells exceeded 1,000 ft in depth and pumping rates generally were less than 60 gal/min. Ground-water samples were collected for analysis of dissolved-constituent concentrations; the radioactive isotopes—tritium (^3H), carbon-14 (^{14}C), and chlorine-36 (^{36}Cl); and ratios of the stable isotopes of carbon ($^{13}C/^{12}C$), oxygen ($^{18}O/^{16}O$), and hydrogen ($^2H/^1H$) (tables 8, 9, and 10). Samples for dissolved-constituent analysis were filtered in the field using a 0.45-micrometer effective pore-size filter. Concentrated nitric acid was added to filtered samples for dissolved-metal analysis. Dissolved alkalinity was measured in the field by incremental titration using sulfuric acid and by the fixed end-point method.

The USGS National Water-Quality Laboratory, Arvada, Colorado, analyzed samples for dissolved-constituent concentrations. All ion-balance calculations were within 5 percent; this level of accuracy indicated that most major ions were accurately quantified in the samples. $^2H/^1H$ and $^{18}O/^{16}O$ were analyzed at the USGS Isotope Fractionation Project Laboratory, Reston, Virginia, and ^3H was analyzed at the USGS Water-Quality Laboratory, Menlo Park, California, and by Dr. H. Gotte Ostlund at the University of Miami. Samples for ^{14}C and ^{13}C were analyzed at the Radiocarbon Dating Laboratory, University of Arizona, Tucson. Samples for ^{36}Cl were measured by accelerator-mass spectrometer at Purdue University's PRIME laboratory.

Geochemical Approach and Methods

Geochemical techniques provide an independent means of understanding an aquifer system and can be used to test a conceptual-flow model developed using hydrologic methods. These techniques include collection of additional information on the chemical composition of ground water in aquifers and use of geochemical-modeling programs to evaluate conceptual models of geochemical processes occurring in the aquifers.

Major-ion chemistry data were used to characterize water from the N aquifer and evaluate the hydraulic connection of the N aquifer with other water-bearing formations. An earlier study of the aquifer by Eychaner (1983) noted a small amount of leakage from the D aquifer into the N aquifer and that an increase in leakage should appear as an increase in dissolved-solids concentrations in wells in the N aquifer. Major-ion chemistry data obtained in this study made possible an examination of the extent of leakage between the D and N aquifers.

Isotope data also are useful in determining if an aquifer is hydraulically connected to other water-bearing units. Isotopes used here to determine if isotopic differences exist between the D and N aquifers and provide additional information about leakage between the aquifers include the radioactive isotopes of ^3H, ^{14}C, and ^{36}Cl and the stable isotopes of ^{18}O, ^2H, and ^{12}C and ^{13}C. Concentrations of radioactive isotopes (radionuclides) are referred to as activities because analyses measure the energy emissions in a given volume of sample rather than the mass of radionuclides. Concentrations of stable isotopes typically are measured relative to a standard in which the ratios of two isotopes (for example, $^{13}C/^{12}C$) are known. Differences from the standard are expressed by delta notation (δ) in parts per thousand ($^o/_{oo}$), which is called per mil. The delta notation is computed from the equation:

$$\delta = \left(\frac{R_x - R_{std}}{R_{std}}\right)1,000, \qquad (1)$$

where

δ = delta notation,

R_x = ratio of isotopes measured in sample, and

R_{std} = ratio of same isotopes in the standard.

Water that is enriched in lighter isotopes relative to the standard has negative delta values.

The stable isotopes, ^{18}O and ^2H, are useful in hydrologic studies because these isotopes are part of the water molecule. Ratios of $^{18}O/^{16}O$ and $^2H/^1H$ are measured relative to an arbitrary standard known as standard mean ocean water (SMOW), and evaporation and condensation are the most significant processes that change the proportions of these isotopes (Fritz and Fontes, 1980). Variations in $^{18}O/^{16}O$ and $^2H/^1H$ in ground water reflect differences in latitude, elevation, and seasonal or paleoclimatic variations, which are factors that affect recharge temperature. The ratios of these isotopes are virtually unaffected by relatively low-temperature geochemical processes in ground-water systems (Muir and Coplen, 1981), such as occur in the N aquifer.

The ratio $^{13}C/^{12}C$ is affected by photosynthesis and other biological and environmental factors (Drever, 1988). Ground water acquires a $^{13}C/^{12}C$ value that depends on the isotopic composition of carbon dioxide in soil from the recharge area and on reactions between carbonate minerals and ground water. The ratio $^{13}C/^{12}C$ is measured in relation to a belemnite of the Pedee Formation (PDB) in South Carolina. The ratios measured in ground water from the aquifer can be used to identify biological and depositional environments and are used to adjust ground-water ages determined from ^{14}C data.

Radioactive isotopes can be used to calculate the time since recharged water was isolated from the atmosphere. Under steady-state flow conditions, lines of equal water age (isochrons) can be used to estimate flow directions, assuming that water flows perpendicular to the isochrons. Ground-water ages can be estimated if the following are known: (1) the initial radionuclide activity in the recharge water, (2) the radionuclide activity in ground water at some time after recharge has occurred, (3) geochemical processes occurring within the aquifer that affect the activity of the radionuclide, and (4) the radionuclide-decay rate. Estimates of ground-water age are made by assuming that radionuclide production in the atmosphere is constant and that ground waters from different aquifers and (or) of different ages do not mix.

Ground water can have a wide range of age; therefore, different radionuclides are needed to estimate ground-water ages. ^{3}H has a half life of 12.3 years (Fritz and Fontes, 1980). Measurable concentrations of ^{3}H indicate that ground water was recharged since 1953, when large amounts of ^{3}H, ^{14}C, and ^{36}Cl were released into the atmosphere during the testing of nuclear weapons (Michel, 1976; Koide and others, 1982; and Michel, 1989). The half-life of ^{36}Cl is about 300,000 years, which makes it suitable for dating in the range of 1 million to 60,000 years before present (Coplen, 1993). ^{36}Cl also is useful for recognizing waters recharged since about 1953. ^{36}Cl, used as a method of age dating, is measured as a ratio of ^{36}Cl atoms to the total number of chlorine atoms in the sample (table 10, at the back of the report). In order to accurately date the ^{36}Cl in the water, however, in-situ production of ^{36}Cl and the elemental concentrations of the rock units must be known. $^{36}Cl/Cl$ ratios, therefore, were used to qualitatively evaluate ^{14}C dates and possible mixing of waters from the D and N aquifers. Analyses from duplicated and triplicated samples collected from nine wells were comparable, indicating that $^{36}Cl/Cl$ ratios were reproducible.

^{14}C has a half life of 5,730 years (Fritz and Fontes, 1980) and can be used to date dissolved-inorganic carbon in ground water to about 35,000 years before present. Inorganic carbon enters ground water from precipitation, by dissolution of carbon dioxide into recharge in the unsaturated zone, and by dissolution of carbonate minerals. Bomb-related ^{14}C also can enter ground water, which will result in underestimated ground-water ages if activities are not corrected for this source. The initial activity of ^{14}C in recharge and the activity at a point in the flow system must be known to date the carbon and estimate ground-water ages. Estimating ages is a two-part process: (1) definition of this initial ^{14}C activity, and (2) adjustment of the initial activity for water-rock reactions that affect the ^{14}C activity of dissolved-inorganic carbon along the flow path (Wigley and others, 1978). Many techniques for correcting ^{14}C activities for water-rock reactions have been developed (Ingerson and Pearson, 1964; Tamers, 1975; Fontes and Garnier, 1979; and Eichinger, 1983), however, it is beyond the scope of this report to describe these techniques in detail. Ground-water ages and traveltimes can be calculated using the corrected ^{14}C activities and the radioactive-decay equation:

$$\Delta t = \frac{5,730}{ln2} ln\left(\frac{A_{nd}}{A_{meas}}\right), \qquad (2)$$

where

Δt = age or traveltime, in year,

ln = natural logarithm,

A_{nd} = initial ^{14}C activity, corrected for reactions assuming no radioactive decay, and

A_{meas} = measured ^{14}C activity at a point downgradient from the initial well.

CHEMICAL EVIDENCE OF LEAKAGE IN THE N AQUIFER

Ratios of dissolved ions, dissolved-ion and dissolved-gas concentrations, $\delta^{13}C$ data, ^{36}Cl data, and ^{3}H data indicate that water in the D aquifer could be leaking into the confined part of the N aquifer in the southeastern part of Black Mesa. On the basis of the available data, the boundary between the leaking and nonleaking zones was drawn as a line that extends in a roughly northeastward to southwestward direction from Rough Rock to Second Mesa (fig. 4). Additional data are needed to determine whether the leakage boundary is a gradual transition, an abrupt change in ground-water chemistry, or if isolated areas of leakage occur in the confined part of the aquifer. Leakage could be occurring northwest of this boundary, but the amount of leakage is too small to significantly change the chemistry of water in the N aquifer. For a constant leakage rate, the proportion of water from the D aquifer into the N aquifer is larger to the south than to the north of the boundary because the N aquifer is thinner to the south. Constituent concentrations and ion ratios in the D aquifer are varied, few data exist to characterize the spatial distribution of concentrations and ratios, and recharge areas and flow directions are not well defined. Additional data are needed to have meaningful estimates of the amount of leakage from the D aquifer into the N aquifer.

Ratios of anions in ground water north of the leakage boundary are different from ratios of anions in ground water south of the leakage boundary (fig. 5*A* and 5*B*). Thirty-eight ground-water samples collected north of the leakage boundary have calcium sodium bicarbonate compositions. The proportions of sodium and bicarbonate increase along flow paths from the recharge area into the confined aquifer (fig. 5A). Nineteen ground-water samples collected south of the leakage boundary have sodium compositions with varying proportions of bicarbonate, sulfate, and chloride. Nine samples from the D aquifer also have sodium compositions and proportions of anions similar to ground water from the N aquifer south of the leakage boundary, which suggests that water from the D aquifer is affecting the major ion chemistry of water in this part of the N aquifer (fig. 5*C*).

A one-way analysis of variance using Tukey's multiple-comparison test and a 5-percent level of significance was used to compare ground-water samples collected north and south of the leakage boundary and from the D aquifer. Concentrations of dissolved boron, chloride, and fluoride are significantly larger south of the leakage boundary than concentrations to the north (fig. 6), and $\delta^{13}C$ values for ground water south of the boundary generally are heavier than those for ground water north of the boundary. $\delta^{13}C$ values, however, were not significantly different at a level of 5 percent. Concentrations of boron and chloride were not significantly different between samples south of the leakage boundary and the D aquifer.

Boron-to-alkalinity ratios south of the leakage boundary were significantly larger than ratios to the north, and ratios were nearly constant for most ground-water samples north of the leakage boundary (fig. 7). South of the leakage boundary, these ratios lacked a linear trend in comparison with those north of the boundary. The constant ratio indicates that dissolution of aquifer material controls the concentrations of boron and alkalinity north of the leakage boundary. The large ratios and lack of linearity indicate that one or more sources of boron are leaking into the southern part of the confined part of the N aquifer. Samples collected from the Dakota Sandstone and Entrada Formation of the D aquifer had similar concentrations of boron and boron-to-alkalinity ratios as samples south of the leakage boundary. These similarities indicate that these formations could be the source of leakage.

For most of the confined part of the N aquifer, dissolved-oxygen concentration and the partial pressure of carbon dioxide are significantly correlated (rank correlation of 0.76), and each gas significantly correlates with water temperature (-0.65 and -0.67, respectively) and well depth (-0.76 and -0.74, respectively; fig. 8). The rank correlation refers to the Spearman rank correlation, which correlates two variables using their relative ranking rather than using absolute values and gives outliers less weight in the correlation. Water temperature was positively correlated with well depth (rank correlation of 0.90; fig. 8) and increases about 5°C/1,000 ft. This slope indicates

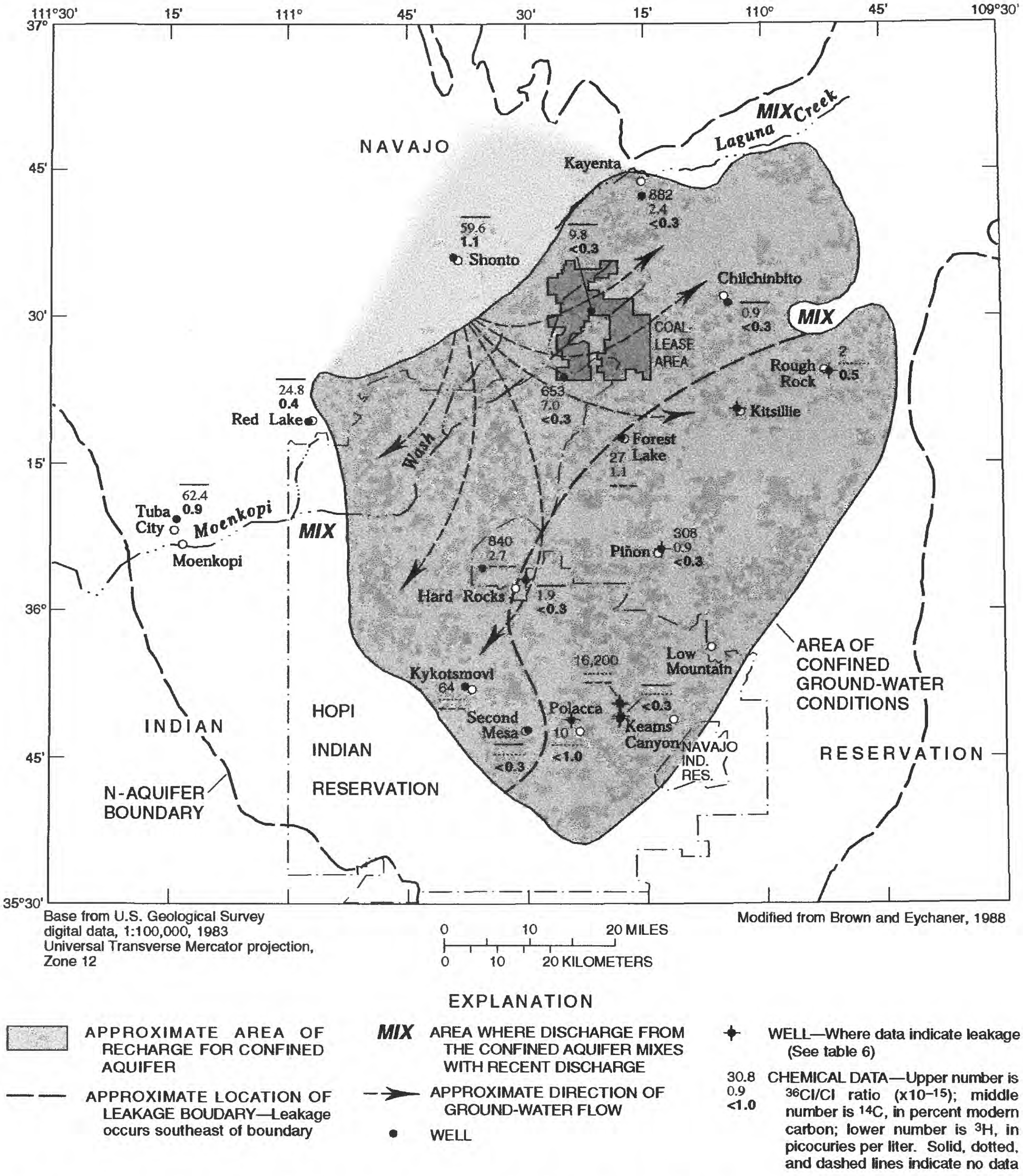


Figure 4. Flow directions and area of possible leakage in the N aquifer, Black Mesa area, Arizona.

that the geothermal gradient controls water temperatures (Domenico and Palciauskas, 1973). Wells south of the leakage boundary have significantly less dissolved oxygen than wells north of the leakage boundary, indicating that water with small dissolved-oxygen concentrations is leaking into the N aquifer or that oxidation-reduction reactions could be occurring, or both. Wells at the coal mines

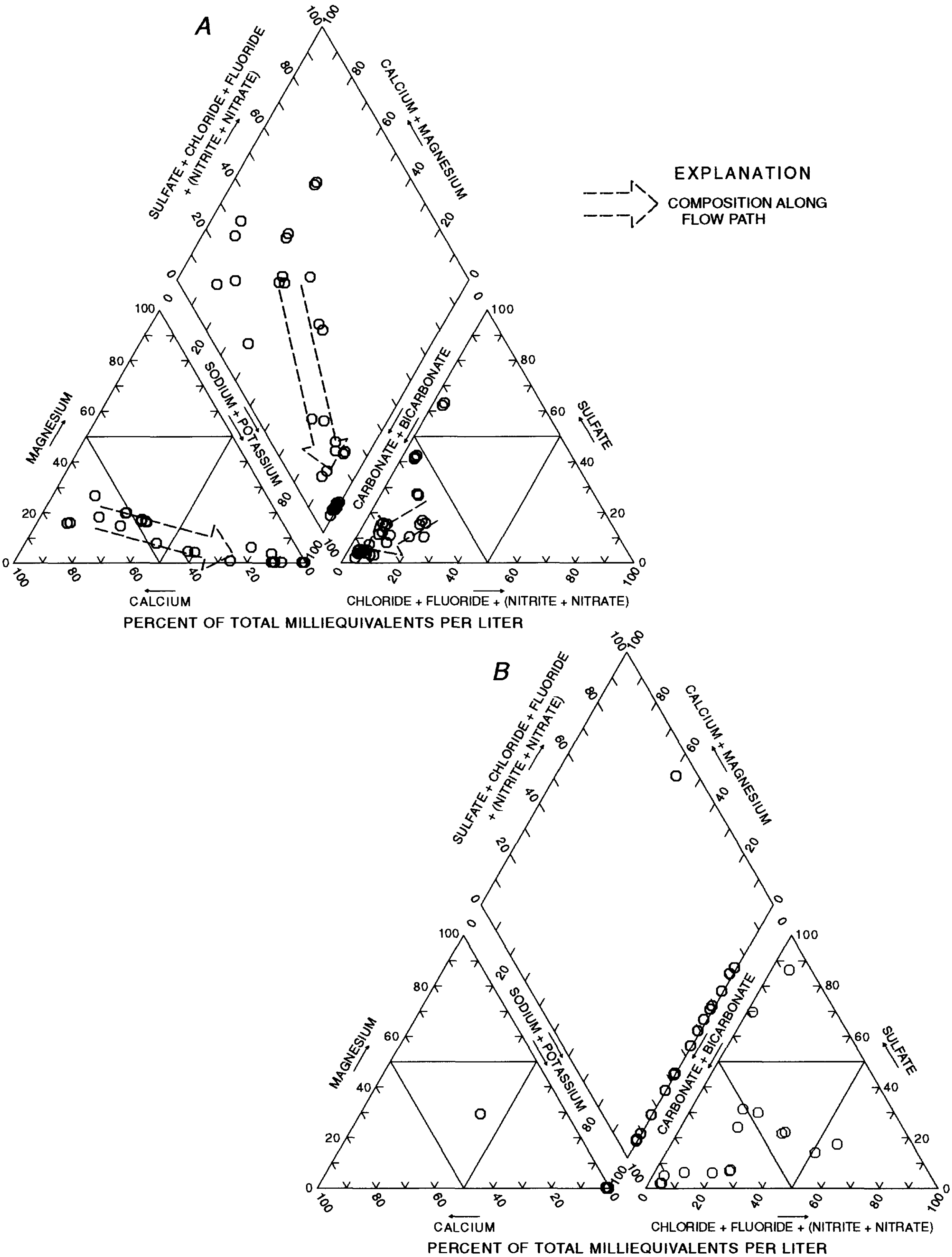


Figure 5. Relative compositions of ground-water samples collected from the N and D aquifers, Black Mesa area, Arizona, 1993–95. *A*, N aquifer north of leakage boundary. *B*, N aquifer south of leakage boundary. *C*, D aquifer.

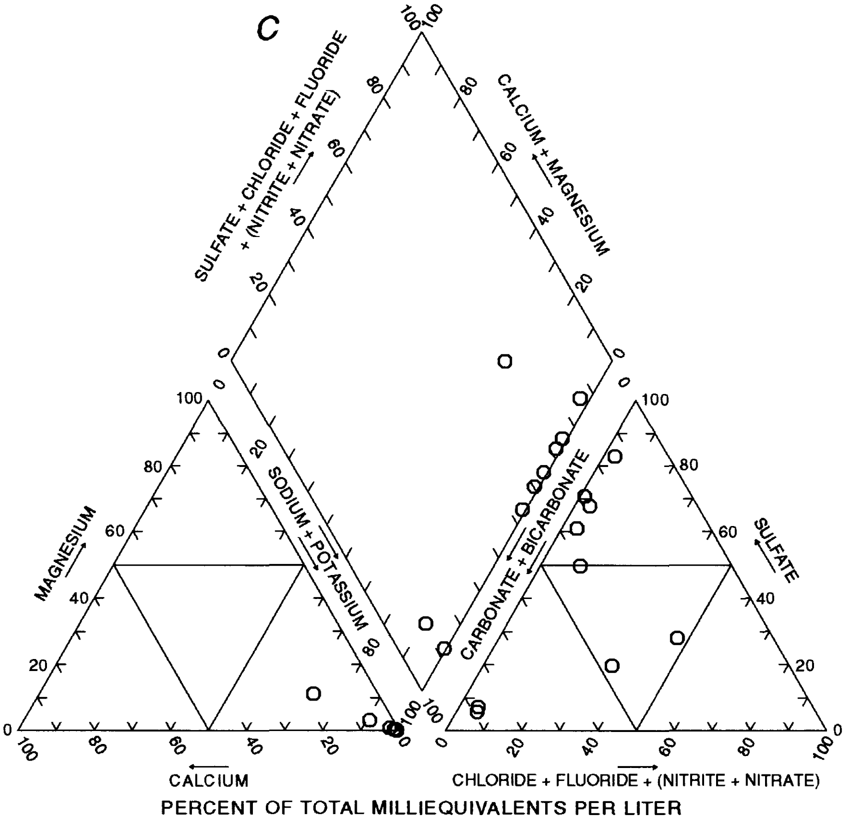


Figure 5. Continued.

have unusually large dissolved-oxygen concentrations, which could be caused by aeration in the wells.

^{36}Cl/Cl was measured at 10 wells—8 samples were from the N aquifer and 2 were from the D aquifer. ^{36}Cl/Cl values in the D aquifer are small ($127\text{x}10^{-15}$ and $10\text{x}10^{-15}$; table 10 at the end of the report) compared with calculated ^{36}Cl/Cl values of about $650\text{x}10^{-15}$ in precipitation and dry fallout near the study area (Bentley and Davis, 1982). The small values may indicate that ^{36}Cl decay has occurred and that chloride in the D aquifer is older than 100,000 years or are related to input of old chloride from overlying evaporite deposits of the Mancos Shale (Stanley N. Davis, professor, University of Arizona, oral commun., 1996).

^{36}Cl/Cl values from Rocky Ridge, Kayenta NTUA4, and Peabody #9 were $840\text{x}10^{-15}$, $882\text{x}10^{-15}$, and $653\text{x}10^{-15}$, respectively, which indicates that leakage from the overlying D aquifer has not affected ^{36}Cl values and that decay of ^{36}Cl has not occurred; therefore, the chloride in water from these sites is less than 100,000 years old. ^{36}Cl/Cl values from Kykotsmovi PM2, Forest Lake, Rough Rock, and Piñon wells of $64\text{x}10^{-15}$, $27\text{x}10^{-15}$, $2\text{x}10^{-15}$, and $308\text{x}10^{-15}$, respectively, indicate that the ^{36}Cl in the water has decayed or been diluted with old chloride from water in the overlying D aquifer. The small value is indicative of chloride with an age of more than 100,000 years (Stanley N. Davis, professor, University of Arizona, oral commun., 1996). A ^{36}Cl/Cl value of $16{,}200\text{x}10^{-15}$ for Keams Canyon PM2 indicates contamination from nuclear detonation or ^{36}Cl accumulation from an uranium-rich formation. The large value at Keams Canyon PM2 is somewhat problematic because the well is screened in a 200-foot interval of the Navajo Sandstone.

CARBONATE CHEMISTRY

Understanding the carbonate chemistry of the N aquifer is necessary to accurately estimate ground-water ages. This section only focuses on the carbonate chemistry of the N aquifer north of

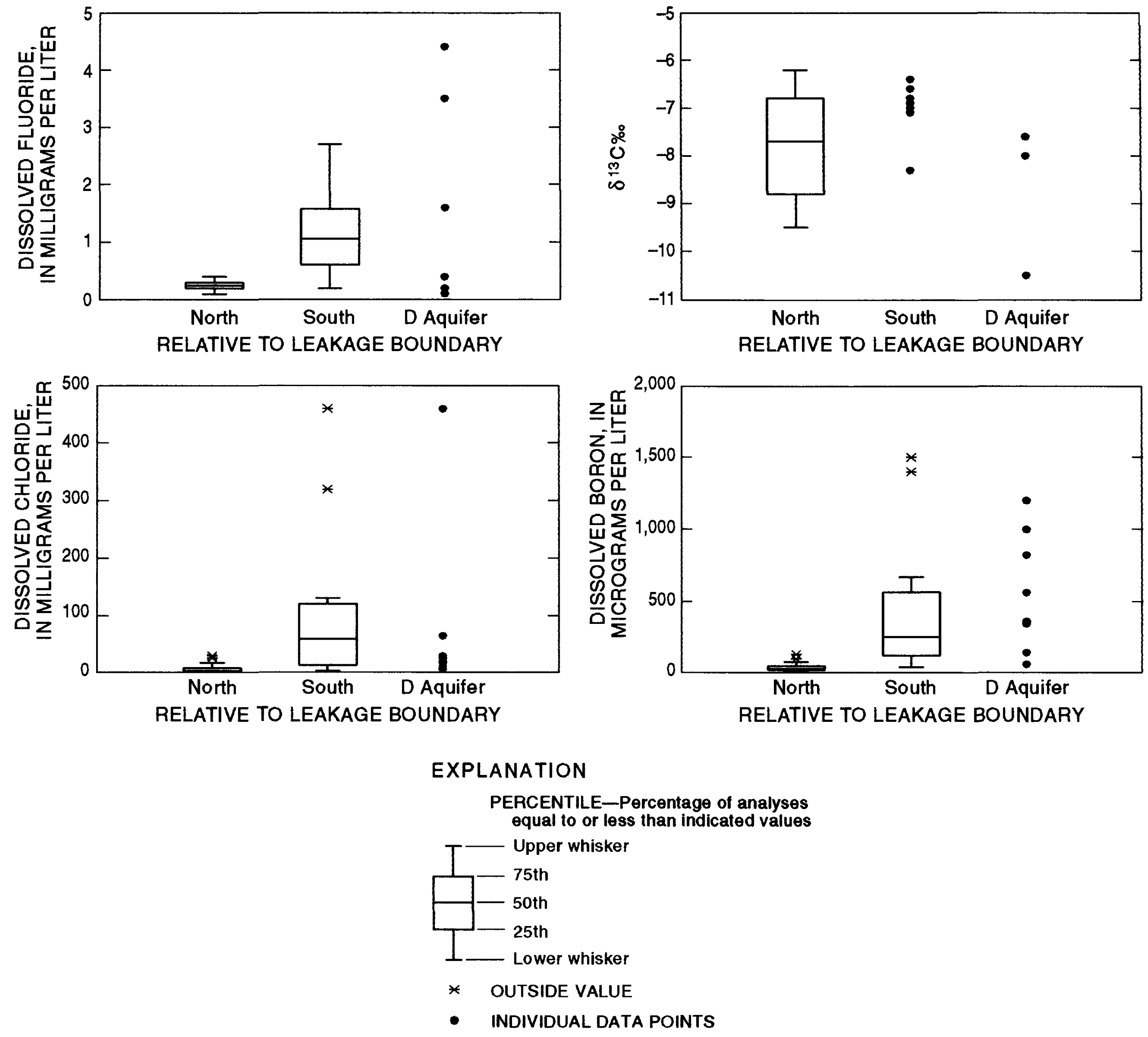


Figure 6. Ranges in selected constituent concentrations and $\delta^{13}C$ values relative to the N-aquifer leakage boundary, Black Mesa area, Arizona (see figs. 1 and 4; tables 8, 9, and 10).

the leakage boundary. ^{14}C activities south of the leakage boundary cannot be corrected without additional data on the D aquifer. The N aquifer is an unconfined, open system around Shonto where precipitation recharges the aquifer directly through the exposed Navajo Sandstone. The open system is indicated by the high partial pressure of carbon dioxide (P_{CO_2}) in ground water ($\mathrm{Log}_{10}(P_{CO_2}) = -2.85$) and the ^{14}C activity of carbonates in two soil samples collected during the study in the unconfined part of the aquifer near Tuba City and Red Lake, which had 45 and 97 percent modern carbon (pmc), respectively.

Reactions change the chemistry of ground water as it flows from the recharge area around Shonto into the confined parts of the N aquifer (fig. 9). Calcium and magnesium concentrations are about 45 and 6 mg/L, respectively, around Shonto and decrease to less than 10 and 1 mg/L, respectively, in the confined part of the aquifer. Alkalinity and sodium concentrations increase by several factors with distance from Shonto. These trends reflect water-rock interactions that change the ionic composition of water from mostly calcium and bicarbonate in the recharge area to mostly sodium and bicarbonate in the confined part

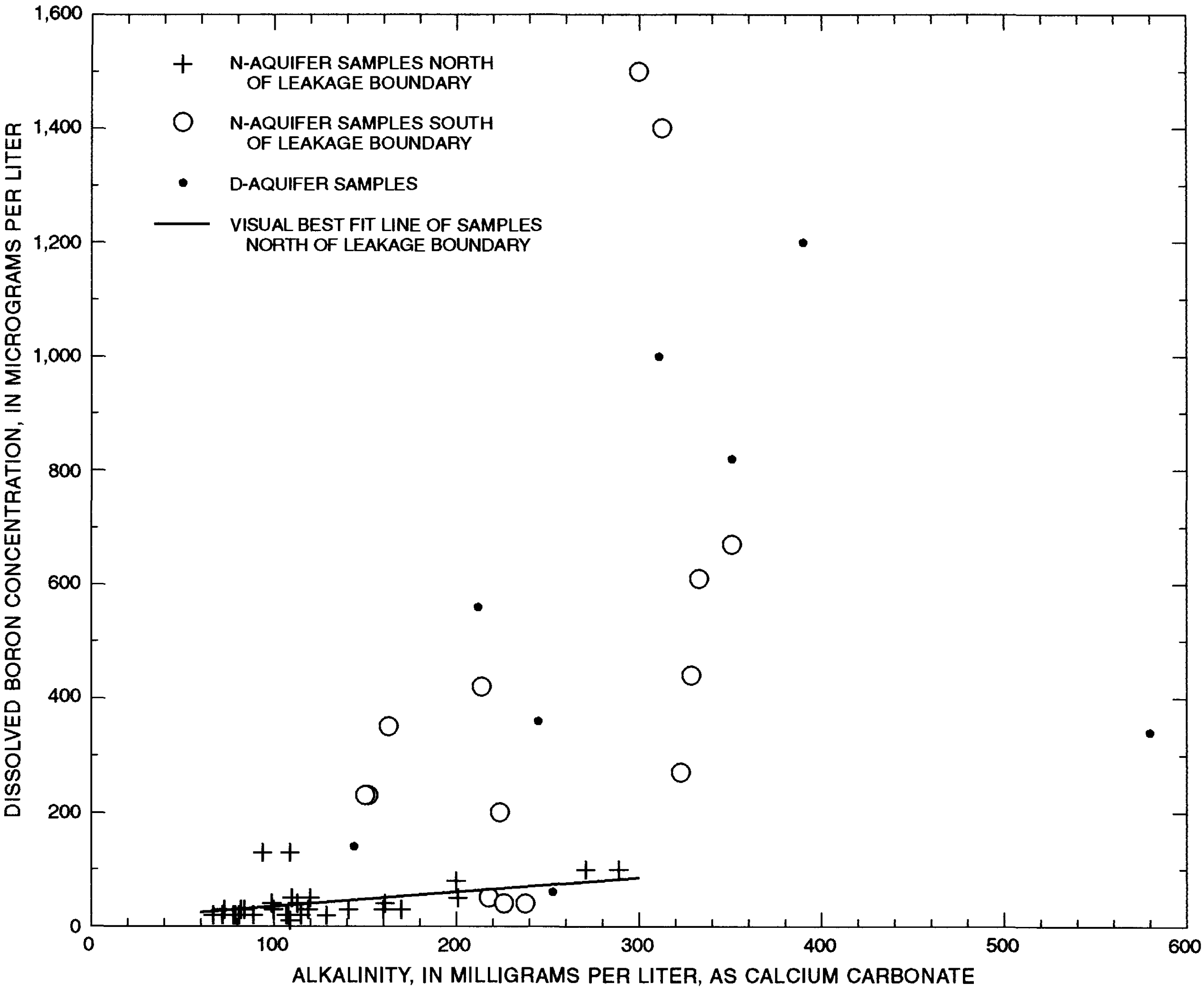


Figure 7. Boron concentration as a function of alkalinity relative to the N-aquifer leakage boundary, Black Mesa area, Arizona.

of the aquifer. These reactions also could change the ^{14}C activity of dissolved inorganic carbon.

Precipitation becomes acidic by dissolving carbon dioxide and forming carbonic acid as it flows through the unsaturated zone. The dissolution of carbon dioxide in water and the dissociation of carbonic acid (H_2CO_3) into hydrogen and bicarbonate can be represented by the equation:

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^- . \quad (3)$$

The acidic recharge can dissolve carbonate minerals from aquifer material. Previous investigations of the mineralogy of the N aquifer (Harshbarger and others, 1957; Geotrans, Inc., 1993) indicate that calcite is the only carbonate mineral present; calcite ($CaCO_3$) also can have small amounts of magnesium. Calcite reacts with hydrogen ions from carbonic acid and releases calcium and bicarbonate ions, which would explain the high concentration of calcium at Shonto:

$$H^+ + CaCO_3 = Ca^{2+} + HCO_3^- . \quad (4)$$

The initial ^{14}C activity and ^{13}C value of ground water that flows into the confined part of the aquifer, therefore, is mostly due to the carbon from carbon dioxide and calcite in the unsaturated zone. Ground water is near saturation with calcite at

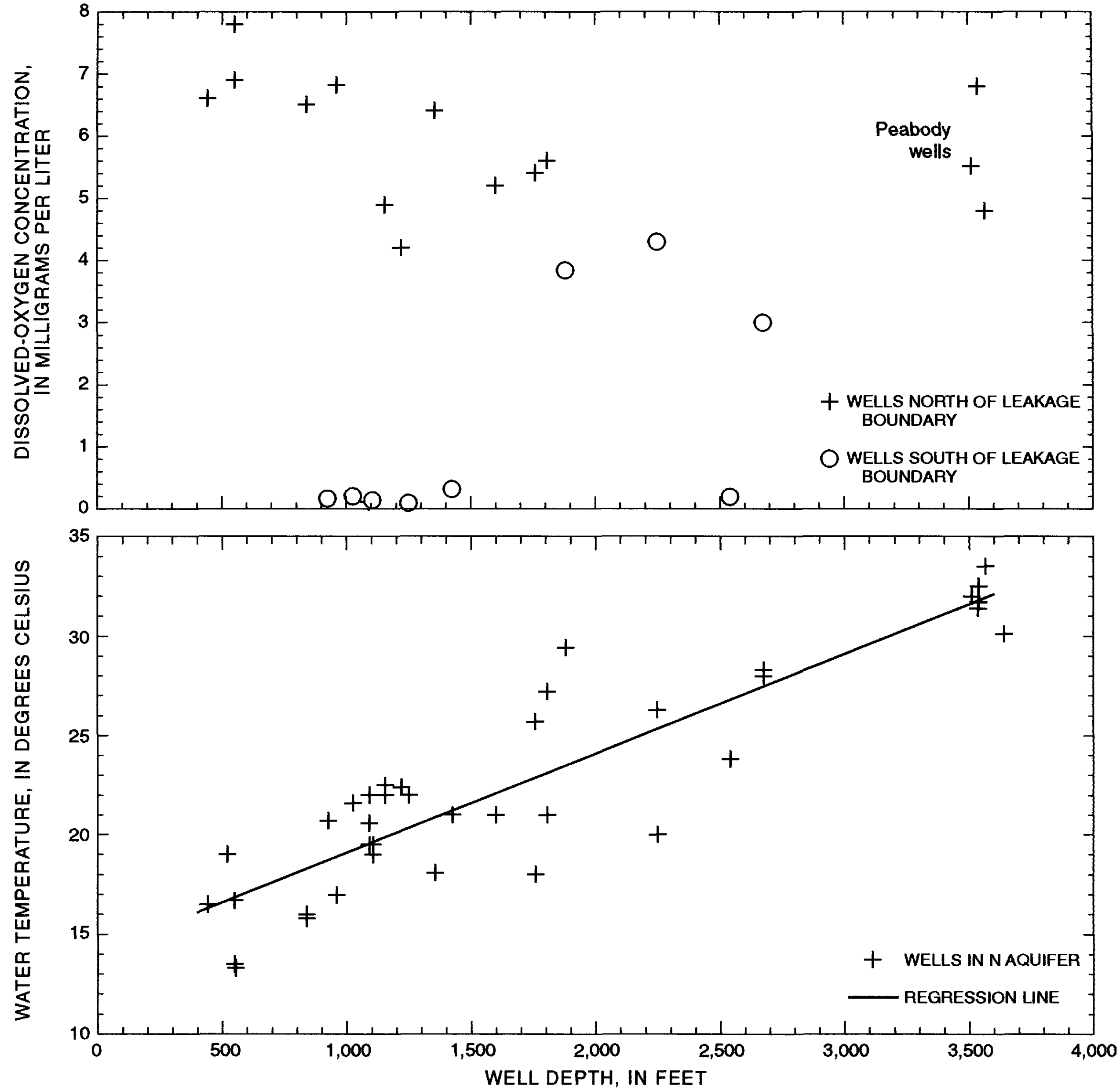
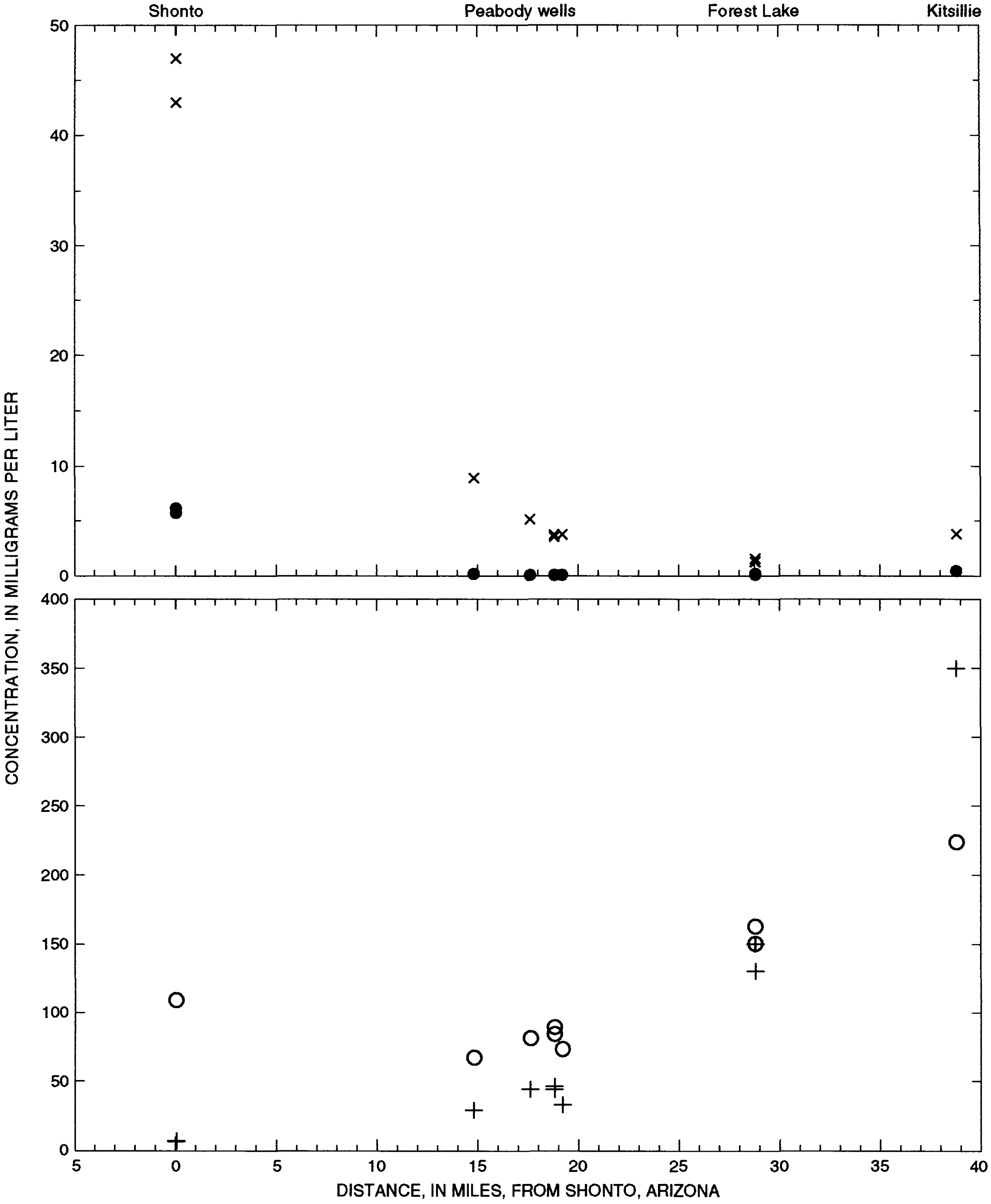


Figure 8. Dissolved-oxygen concentration and water temperature as functions of well depth, Black Mesa area, Arizona.

Shonto and in most of the confined part of the aquifer (table 1). As ground water flows south into the confined part of the aquifer, reactions with other minerals cause calcite to precipitate, which results in a decrease in calcium concentrations.

Units of the N aquifer are composed mostly of quartz with minor amounts of primary silicates and secondary minerals, which are coated on the quartz and primary silicates (Harshbarger and others, 1957; Geotrans, Inc., 1993). Silicate hydrolysis and exchange of calcium for sodium on clays are reactions that could affect calcite equilibrium. Plagioclase is a solid solution of sodium (albite) and calcium (anorthite) feldspars and is a reactive primary silicate. An example reaction of silicate hydrolysis for an intermediate member in the solid solution series is:



EXPLANATION

× CALCIUM ● MAGNESIUM ○ SODIUM + ALKALINITY AS BICARBONATE

Figure 9. Constituent concentrations as a function of the distance south from Shonto, Arizona.

Table 1. Saturation indices of ground water from the N aquifer, Black Mesa area, Arizona

Well	Saturation index				$\mathrm{Log}(P_{CO_2})$
	Calcite	Dolomite	Gypsum	Chalcedony	
Shonto PM4	0.072	-0.55	-2.50	0.085	-2.85
Red Lake NTUA1	.082	-.27	-3.59	-.030	-3.48
Red Lake PM1	-.077	-.48	-3.62	-.092	-3.31
Tuba City #3	-.26	-1.03	-3.01	-.088	-2.97
Peabody #6	-.27	-2.22	-3.79	-.031	-4.41
Peabody #9	-.013	-1.46	-4.18	-.056	-3.84
Kayenta NTUA4	.35	.31	-3.25	-.092	-4.06
Chilchinbito NTUA1	-.026	-.94	-5.00	-.11	-4.28
Dennehotso PM2	.60	.82	-3.12	-.063	-4.05
Forest Lake	-.001	-.59	3.43	-.10	-4.15
Rough Rock	-.11	-.80	-3.14	-.10	-3.44
Kitsillie	.046	-.40	-2.38	-.18	-3.44
Piñon	.12	-1.03	-5.25	-.36	-5.27
Hard Rocks	-.19	-1.04	-3.71	-.029	-3.94
Rocky Ridge	-.37	-1.64	-4.98	-.11	-4.50
2nd Mesa PM2	-.12	-1.08	-4.67	-.051	-4.13
Kykotsmovi PM2	-.16	-1.30	-4.85	-.054	-4.62
Hopi HS-1	.26	.24	-2.87	-.19	-3.57
Hopi HS-2	-.19	-.74	-3.18	-.21	-3.09
Polacca	.022	-.52	-4.41	-.18	-4.08
Keams Canyon PM2	-.045	-.50	-4.07	-.17	-3.70
Keams Canyon PM3	-.048	-.48	-4.30	-.22	-3.83
Oraibi	-.24	-1.33	-4.98	-.15	-4.94
Hotevilla	-.020	-1.16	-4.83	-.13	-4.70
Burro Spring	.92	.96	-1.85	-.094	-3.18
Whisky Spring	.46	.45	-1.31	.129	-3.14
Moenkopi School Spring	-.46	-1.37	-2.41	.026	-2.43
Sand Spring	-.43	-1.57	-1.99	-.035	-2.47
Burro Corn Spring Well	.22	-.96	-2.61	-.26	-3.31
Rock Ledge Spring	.44	.27	-.42	.14	-2.77
Peabody #7	-1.48	-5.17	-3.44	.06	-2.12
Peabody #2	.38	-1.16	-3.33	.02	-4.01
Shonto	.01	-1.28	-2.44	.11	-2.75
Kayenta PM2	.26	-.647	-1.80	.10	-3.05

$$
\begin{aligned}
&1.25CO_2 + Na_{0.6}Ca_{0.4}Al_{1.4}Si_{2.6}O_8 + 2.69H_2O = \\
&\quad 0.18Al_2Si_2O_5(OH)_4 + \\
&&(5)\\
&0.22Ca^{0.33}Al_{4.67}Si_{7.33}O_{20}(OH)_4 + 0.6Na^+ + \\
&\quad 0.32Ca^{2+} + 0.63H_4SiO_4 + 1.25HCO_3^- .
\end{aligned}
$$

The calcium and bicarbonate produced from this reaction would cause waters that are saturated, such as ground water near Shonto, to be supersaturated with calcite. Calcite should precipitate as ground water flows into the confined part of the aquifer, as indicated by the saturation indices and decrease in calcium concentrations. Precipitation of calcite, however, would not affect ^{14}C activities unless isotopic fractionation occurs between calcite and ground water.

Hydrolysis of plagioclase feldspars produces an excess amount of bicarbonate compared to calcium. As calcite precipitates, the ground water will increase in alkalinity and sodium concentrations and decrease in calcium concentrations, as observed in the N aquifer (fig. 9). The ratio of sodium to alkalinity (Na/Alk) in ground water where silicate hydrolysis is the primary reaction is determined by the stoichiometry of equation 5 and, for this example, is about 0.5. The ratio Na/Alk in the northern part of the N aquifer is about 1 (fig. 10), which indicates other reactions could be occurring. Wickham (1992) concluded that cation exchange is another important reaction in the N aquifer:

$$\text{Clay} - 2Na^+ + Ca^{2+} = \text{Clay} - Ca^{2+} + 2Na^+ . \quad (6)$$

Exchange of calcium for sodium on clays will increase sodium concentrations and the Na/Alk ratio, decrease calcium concentrations, and decrease the saturation of calcite. Cation exchange could explain why some ground water in the confined part of the N aquifer is slightly undersaturated with calcite. Calcite could be dissolving along certain flow paths where cation exchange is occurring, which would affect the ^{14}C activity of dissolved inorganic carbon.

NETPATH (Plummer and others, 1994) was used to determine which combinations of mineral reactions are possible along flow paths in the N aquifer north of the leakage boundary. NETPATH determines the net mass transfer between specified phases and the initial water to obtain the chemistry

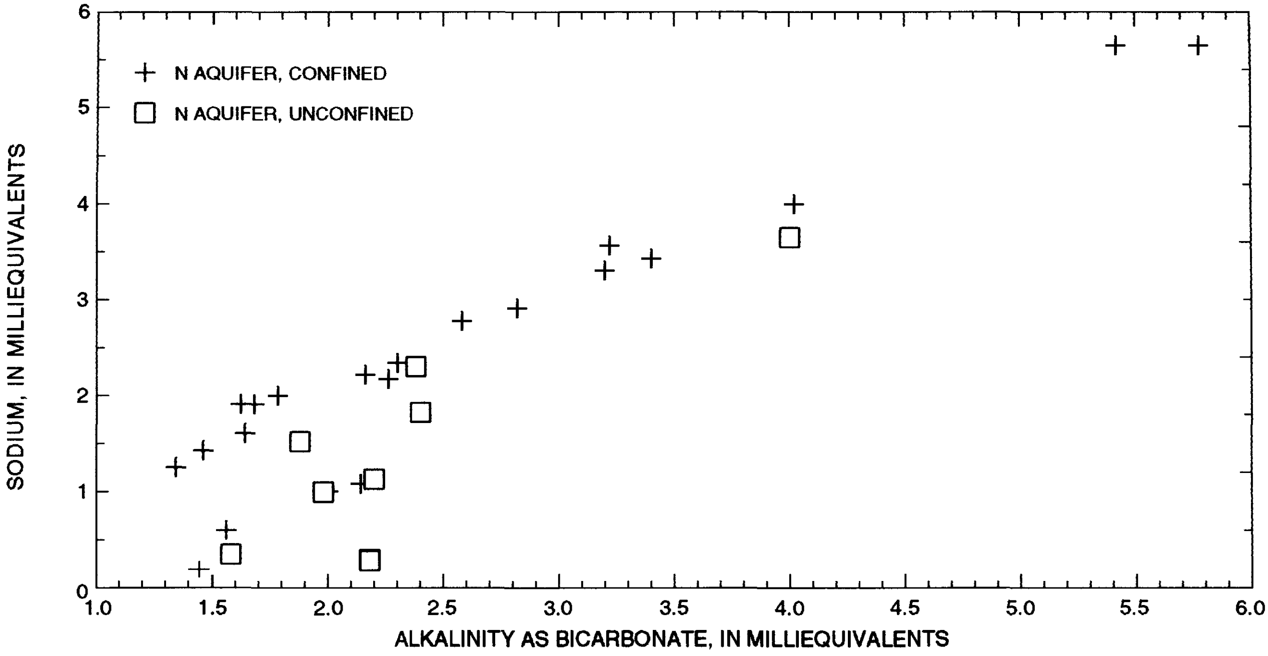


Figure 10. Sodium as a function of alkalinity north of the leakage boundary, Black Mesa area, Arizona.

of water at a downgradient site. Isotopic composition of minerals and gases also can be used to check the validity of reaction models by comparing isotopic values computed from the reaction model with the observed values. Rainwater (Hem, 1985, p. 36) was reacted with phases to determine how water chemistry at Shonto and Tuba City evolves; Shonto PM4 was used as the upgradient well to calculate reaction models for flow paths from the recharge area into the confined part of the N aquifer.

Phases used to estimate the net-mass transfer along flow paths (table 2) were included on the basis of previous studies of the N-aquifer mineralogy (Harshbarger and others, 1957; Geotrans, Inc., 1993). Possible weathering products of these minerals (Drever, 1988) were added to maintain mass balance, but are not important in estimating ground-water ages because calcite and carbon dioxide are the only phases that could affect the carbonate chemistry and ^{14}C activities. Although aluminum was not analyzed in water samples, it was constrained at 10 µg/L in all mass-balance calculations to prevent unrealistic concentrations from occurring. Carbon, silica, calcium, magnesium, sodium, and potassium also were constrained by specifying their upgradient and downgradient concentrations. Sulfur and chloride were not constrained for reaction models between Shonto and the confined aquifer because sulfur- and chloride-bearing minerals have not been found in the N aquifer; evaporative concentration, however, could cause the precipitation of these minerals in the unsaturated zone of the recharge area. Concentrations of sulfur and chloride in the confined aquifer north of the leakage boundary are small, and ground waters are undersaturated with sulfate and chloride minerals. NETPATH could calculate precipitation of sulfur and chloride minerals because of these small differences in sulfate and chloride concentrations, but precipitation is not thermodynamically possible. Differences in concentration of sulfur and chloride are likely due to variations in the composition of recharge. Solid-phase samples collected during this study and by Geotrans, Inc. (1993) indicate the mean $\delta^{13}C$ of calcite in the N aquifer is about -3.2°/$_{oo}$. $\delta^{13}C$ of carbon dioxide in soils from southeastern Arizona is about -19.9°/$_{oo}$ today (Robertson, 1992) and is similar to values from other arid areas of the West (Parada, 1981; Wood and Petraitis, 1984; Thorstenson and others, 1990). This value was assumed to be the mean $\delta^{13}C$ for carbon dioxide. Calculated $\delta^{13}C$ values from reaction models were compared with observed values to determine if the models were plausible.

No unique reaction models were found that can account for the difference in chemistry along any of the flow paths. Only certain models, however, resulted in a $\delta^{13}C$ value similar to the observed value at the downgradient well (table 3). These reaction models are variations of similar combinations of reactions because only two carbonaceous phases can affect carbon-isotope values; reaction models that calculated $\delta^{13}C$ values similar to the observed value also calculated similar mass balances of carbonaceous phases. Positive values of moles reacted (table 3) indicate dissolution and negative values indicate precipitation.

GROUND-WATER AGES

NETPATH (Plummer and others, 1994) also was used to estimate ground-water ages and traveltimes along flow paths. NETPATH has several adjustment methods for calculating the initial ^{14}C activity, adjusts ^{14}C activities for water-rock reactions between the initial and final well in a flow path, and estimates ground-water

Table 2. Phases used to model evolution of ground-water chemistry, Black Mesa area, Arizona

[Ca, calcium; Na, sodium; K, potassium; Mg, magnesium]

Albite	Anorthite	Calcite	Carbon dioxide	Ca-Na exchange
Gibbsite	Illite	K-montmorillonite	Kaolinite	Mg-Na exchange
Na-montmorillonite	Potassium feldspar	Silica		

Table 3. Example results of reaction models in the unconfined and confined parts of the N aquifer, Black Mesa area, Arizona

Reaction model	Phase	Moles reacted	Phase	Moles reacted	Phase	Moles reacted	Computed $\delta^{13}C$	Observed $\delta^{13}C$
Initial water, rain: Final water, Shonto PM4								
1	Calcite	1.43	Potassium feldspar	0.023	Gibbsite	-0.023	-7.2 (At Shonto PM4)	-7.7 (At Shonto PM4)
	SiO_2	.18	Mg/Na exchange	-.23	CO_2 gas	.74		
	Ca/Na exchange	.36						
2	Calcite	1.43	Potassium feldspar	.031	Illite	-.014	-7.2 (At Shonto PM4)	-7.7 (At Shonto PM4)
	SiO_2	.20	Mg/Na exchange	-.23	CO_2 gas	.74		
	Ca/Na exchange	.36						
Initial water (upgradient), Shonto: Final water (downgradient), Peabody #9								
1	Calcite	-.87	Anorthite	.24	Mg/Na exchange	.22	-8.3 (At Peabody #9)	-8.7 (At Peabody #9)
	SiO_2	-.26	Gibbsite	-.39				
	Ca/Na exchange	.35	Illite	-.038				
2	Calcite	-.87	Anorthite	.23	Gibbsite	-.30	-8.3 (At Peabody #9)	-8.7 (At Peabody #9)
	SiO_2	-.12	Potassium montmorillonite	-.070	Mg/Na exchange	.23		
	Ca/Na exchange	.34						
Initial water (upgradient), Shonto: Final water (downgradient), Piñon								
1	Calcite	.56	Anorthite	.62	Potassium montmorillonite	1.6	-6.8 (At Piñon)	-7.1 (At Piñon)
	SiO_2	-3.7	Gibbsite	-2.9				
	Ca/Na exchange	2.2	Illite	-.94				
2	Calcite	.56	Ca/Na exchange	2.0	Mg/Na exchange	.22	-6.8 (At Piñon)	-7.1 (At Piñon)
	SiO_2	-.42	Gibbsite	-.69				
	Anorthite	.40	Illite	-.047				

Table 4. Ranges in isotopic composition of carbonaceous phases used in correcting ^{14}C activities

[--, no data]

Isotope	Carbon dioxide			Calcite		
	Maximum	Mean	Minimum	Maximum	Mean	Minimum
Unconfined part of the aquifer						
$\delta^{13}C$, in per mil	-15.0	-19.9	-25.0	0.05	-3.2	-6.9
^{14}C, in percent modern carbon	100	100	100	97	71	45
Confined part of the aquifer						
$\delta^{13}C$, in per mil	--	--	--	.05	-3.2	-6.9
^{14}C, in percent modern carbon	--	--	--	20	10	0

ages from equation 2. The isotopic composition of carbonaceous phases must be known or estimated to make the corrections.

The isotopic composition of carbonaceous phases is variable, so ranges in the isotopic compositions (table 4) were used to determine how this variability affects estimated ages in the unconfined and confined parts of the aquifer. Solid-phase samples collected during this study and by Geotrans, Inc. (1993) indicate the mean $\delta^{13}C$ of the N aquifer is about -3.2‰ with a standard deviation of about 3.7‰. Carbonates in two soil samples collected during the study in the unconfined part of the aquifer near Tuba City and Red Lake had ^{14}C values of 45 and 97 pmc, respectively. The mean $\delta^{13}C$ of carbon dioxide in the unconfined part of the aquifer was assumed to be -19.9‰ (Robertson, 1992) and was varied by 25 percent for the maximum and minimum values. A ^{14}C value of 100 pmc also was assumed for carbon dioxide in all calculations. The confined part of the aquifer is a closed system; therefore, reactions involving carbon dioxide were not considered. ^{14}C of carbonates in the confined part of the aquifer has not been measured, therefore, values were varied between 0 and 20 pmc.

The initial ^{14}C activity of recharge and ground-water ages at Shonto and Tuba City were estimated using several correction methods (Ingerson and Pearson, 1964; Tamers, 1975; Fontes and Garnier, 1979; and Eichinger, 1983). These models are most appropriate in recharge areas where calcite is dissolving (Plummer and others, 1994), such as in the unsaturated zone of the unconfined aquifer. The initial ^{14}C activity of recharge also was estimated from reaction models of rain and phases that evolved the chemistry at Shonto. The ^{14}C activity of rain was varied between 87 and 150 pmc, which are the ranges found in rain during atmospheric testing (Fritz and Fontes, 1980), to evaluate the potential bias from bomb-related ^{14}C.

The Fontes and Garnier (1979) and Ingerson and Pearson (1964) models are the most commonly used adjustment methods. Results of these methods and of the reaction model were virtually identical (table 5), and results were most affected by uncertainty in the ^{14}C activity of calcite. The Tamers model is unaffected by varying $\delta^{13}C$ values and results were similar to the other methods at higher ^{14}C activities of calcite. The Eichinger model gave negative ages for all cases and was not used. Adjustment methods using mean-isotope values indicate the initial activity of recharge at Shonto is about 80 pmc. Estimated ages from the methods using ranges in isotopic composition of carbonaceous phases provide an estimate of the uncertainty in the initial ^{14}C activity and ground-water age at Shonto; the bias due to bomb-related ^{14}C is negligible in comparison to the uncertainty in age. Estimated ages in the unconfined part of the aquifer varied by about 50 to about 300 percent. The large uncertainty in estimated ages is due mostly to the large variance in the ^{14}C activity of the two soil samples. Additional data are needed to better characterize recharge processes near Shonto, the ^{14}C activity of calcite, and the age of ground water in the Black Mesa area.

Table 5. Sensitivity analysis of the initial ^{14}C activity of recharge and ground-water age at Shonto PM4, Black Mesa area, Arizona

[The ^{14}C activity of carbon dioxide was 100 percent modern carbon (pmc) in all calculations; $\delta^{13}C$, in per mill; A_o, initial ^{14}C activity at Shonto]

Calcite		Ingerson and Pearson (1964)		Fontes and Garnier (1979)		Tamers (1975)		Reaction model			
								Rain with 87 pmc		Rain with 150 pmc	
^{14}C	$\delta^{13}C$	A_o	Age, in years	A_o	Age, in years	A_o	Age, in years	A_o	Age, in years	A_o	Age, in years
$\delta^{13}C$ of carbon dioxide = -19.9											
97	0.05	98.2	4,100	98.2	4,100	98.6	4,200	98.1	4,100	99.5	4,200
	-3.2	97.8	4,100	97.8	4,100	98.6	4,200	97.8	4,100	99.2	4,200
	-6.9	97.2	4,000	97.1	4,000	98.6	4,200	96.8	4,000	98.2	4,100
71	.05	82.3	2,700	82.2	2,700	85.9	3,000	84.0	2,800	85.4	3,000
	-3.2	78.8	2,300	78.6	2,300	85.9	3,000	81.0	2,500	82.4	2,700
	-6.9	72.3	1,600	72.4	1,600	85.9	3,000	71.4	1,500	72.7	1,600
45	.05	66.4	890	66.2	870	73.3	1,700	64.5	650	65.9	830
	-3.2	59.8	28	59.5	-14	73.3	1,700	64.3	630	65.7	800
	-6.9	48.4	-1,700	47.7	-1,800	73.3	1,700	45.9	-2,200	47.3	-1,900
$\delta^{13}C$ of carbon dioxide = -25											
97	.05	97.9	4,100	97.9	4,100	98.6	4,200	98.4	4,100	99.2	4,200
	-3.2	97.6	4,100	97.6	4,100	98.6	4,200	97.4	4,100	99.2	4,200
	-6.9	97.1	4,000	97.1	4,000	98.6	4,200	96.4	4,000	98.2	4,100
71	.05	80.0	2,400	80.0	2,400	85.9	3,000	80.6	2,500	82.4	2,700
	-3.2	77.0	2,100	76.8	2,100	85.9	3,000	80.5	2,500	82.3	2,700
	-6.9	72.3	1,600	72.0	1,600	85.9	3,000	70.9	1,600	72.7	1,500
45	.05	62.0	320	61.8	310	73.3	1,700	63.8	560	65.6	790
	-3.2	56.4	-460	56.1	-500	73.3	1,700	63.8	560	65.6	790
	-6.9	47.4	-1,900	46.9	-2,000	73.3	1,700	45.5	-2,200	47.3	-1,900
$\delta^{13}C$ of carbon dioxide = -15											
97	.05	98.5	4,200	98.5	4,200	98.6	4,200	97.8	4,100	99.7	4,200
	-3.2	98.1	4,100	98.1	4,100	98.6	4,200	97.4	4,100	99.1	4,200
	-6.9	97.3	4,000	113	5,300	98.6	4,200	96.4	4,000	98.2	4,100
71	.05	85.9	3,000	85.9	3,000	85.9	3,000	85.3	3,000	87.1	3,100
	-3.2	82.1	2,600	81.9	2,600	85.9	3,000	80.6	2,500	82.4	2,700
	-6.9	73.9	1,800	181	9,200	85.9	3,000	70.9	1,400	72.7	1,600
45	.05	73.3	1,700	73.3	1,700	73.3	1,700	72.8	1,600	74.6	1,800
	-3.2	66.0	840	65.8	810	73.3	1,700	64.4	640	66.2	870
	-6.9	50.4	-1,400	249	11,800	73.3	1,700	45.5	-2,200	47.3	-1,900

The ^{14}C activity measured in ground water at Shonto (59.6 pmc) was used as the initial activity of water that enters the confined part of the aquifer because sensitivity analysis indicated that bias due to bomb-related ^{14}C is negligible. Traveltimes for ground water that flows from Shonto to wells in the confined part of the aquifer were estimated by correcting the measured ^{14}C activity at Shonto for water-rock reactions, then using this corrected value and measured ^{14}C activities in the confined part of the aquifer directly in equation 2. Most of the ground water in the confined part of the N aquifer is saturated with calcite, and reaction models indicate precipitation of calcite is likely along flow paths. Precipitation of calcite would not affect ^{14}C activities and estimated ground-water ages; however, isotopic fractionation can occur during precipitation (Turner, 1982). Plummer and others (1994) note that isotopic fractionation should only be considered when evidence indicates fractionation is occurring. Isotopic fractionation was not included because of the lack of evidence.

Although reaction models were not unique, estimated traveltimes from Shonto to wells in the confined aquifer were found to be robust because only two carbonaceous phases can affect carbon-isotope values; reaction models that resulted in a $\delta^{13}C$ value similar to the observed value (table 3) also calculated similar traveltimes. Few reactions affect the carbonate chemistry of the N aquifer north of the leakage boundary; therefore, differences in ^{14}C activities are due mostly to radioactive decay and not to reactions with carbonaceous material.

A mean age of 2,700 years was used for ground water in the Shonto area; the uncertainty in this age is about 2,000 years. Mean ages in the confined part of the aquifer are the sum of traveltimes and the mean age of ground water at Shonto (table 6). Ages in the confined part of the N aquifer were consistent with $^{36}Cl/Cl$ ratios, which indicated an age of less than 100,000 years. All ages are given to two significant figures because of the large uncertainties. The uncertainty in traveltimes from Shonto to wells in the confined part of the aquifer was assumed to be 1,000 years because, relative to estimates of ground-water age at Shonto, fewer factors can affect traveltime estimates. Uncertainty of ages in the confined part of the aquifer was estimated as the sum of uncertainty in ground-water age at Shonto and uncertainty in traveltimes for a total uncertainty of 3,000 years.

Ground water at Red Lake NTUA1 and Kayenta NTUA4 had not mixed with water from another source, but ^{3}H was detected at Red Lake NTUA1 and heavy $\delta^{18}O$ and $\delta^{2}H$ values were measured at Kayenta NTUA4. The ^{3}H and heavy $\delta^{18}O$ and $\delta^{2}H$ values indicated that ground water at these wells had mixed with younger water of the N aquifer. The estimates for Red Lake NTUA1 and Kayenta NTUA4, therefore, represent minimum ages (table 6).

GROUND-WATER FLOW DIRECTIONS

^{3}H data indicate that rain and snowmelt recharge the N aquifer along the periphery of Black Mesa where the Navajo Sandstone is exposed and that recent recharge to the east, west, and south of Black Mesa mixes with older ground water that

Table 6. Estimated ground-water ages at wells in the Black Mesa area, Arizona

Well name	Mean age,[1] in years	Uncertainty, in years	Well name	Mean age,[1] in years	Uncertainty, in years
Shonto PM4	2,700	2,000	Tuba City #3	2,500	2,000
Red Lake NTUA1[2]	9,800	3,000	Peabody #6	17,400	3,000
Peabody #9	20,000	3,000	Kayenta NTUA4[2]	29,000	3,000
Chilchinbito NTUA1	34,000	3,000	Forest Lake	34,000	3,000
Piñon	35,000	3,000	Hard Rocks	28,000	3,000
Rocky Ridge	28,000	3,000			

[1] Represents traveltime from Shonto plus 2,700 years (does not apply to Shonto or Tuba City).

[2] Represents a minimum age because isotope data indicate ground water at these wells had mixed with younger water of the N aquifer.

discharges from the confined part of the aquifer and flows away from Black Mesa. Ground water younger than about 45 years occurs only in the unconfined parts of the N aquifer or in the margins of the confined part of the aquifer (near Red Lake and Rough Rock). ^{3}H activities were greater than the minimum detection level in 4 of 12 samples from the N aquifer; the activities in the four samples ranged from 0.4 to 1.1 pCi/L. Current recharge rates and ground-water velocities are too small for ^{3}H to be detected in all but the margins of the confined part of the N aquifer. Isochrons (fig. 11) and equipotentials (Eychaner, 1983; fig. 3) indicate that recharge to the confined part of the aquifer occurs north of Black Mesa.

Ground-water ages, estimated at 11 wells, increase gradually from a few thousand years near Shonto to about 35,000 years in the confined part of the aquifer in the south-central and eastern parts of Black Mesa (fig. 11). A sufficient number of wells were sampled in the central and eastern areas of the confined part of the aquifer to interpolate isochrons. The isochron patterns are similar to equipotentials in these areas (Eychaner, 1983). Data, however, are sparse in the area of Moenkopi Wash. Isochron patterns around Moenkopi Wash were extrapolated on the basis of ground-water levels (Eychaner, 1983). Although ^{14}C data were collected from wells on the Hopi Indian Reservation and at Rough Rock, ground-water ages were not estimated because chemical data indicated that ground water had mixed with ground water from another source. Data from Hard Rocks and Forest Lake also could be affected by mixing with this source, and water at Red Lake and Kayenta NTUA4 has mixed with younger water from the N aquifer. Improved estimates of ages at Red Lake and Kayenta NTUA4 could change the locations of the 10,000- and 30,000-year isochrons. The estimated ages of ground water at Hard Rocks and Forest Lake are shown in figure 11, but were not used in locating the 30,000-year isochron. Additional data are needed to accurately estimate ground-water ages at these wells.

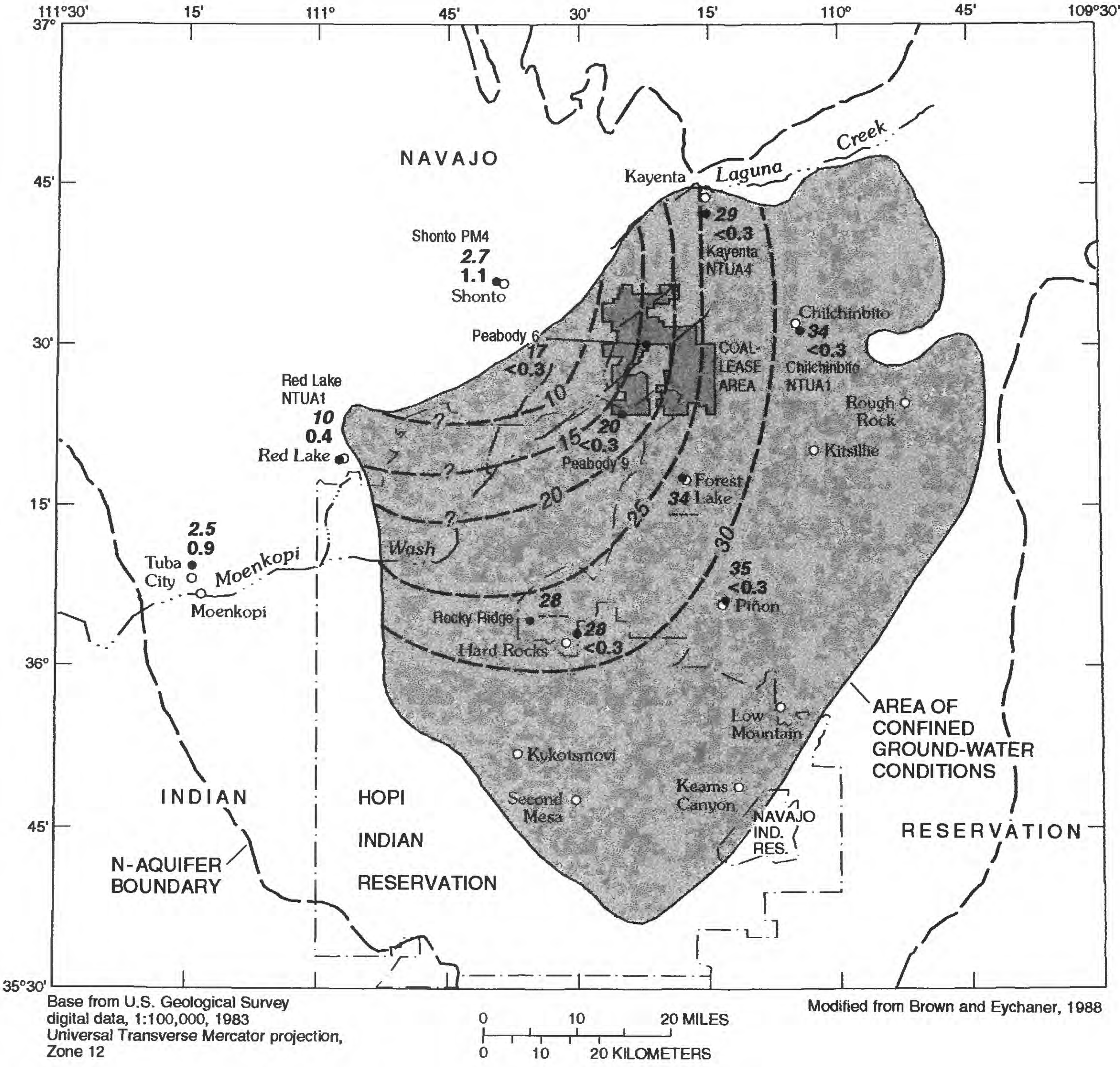
Most recharge occurs in an area near Shonto where the Navajo Sandstone is exposed at elevations above 6,300 ft (fig. 3, *B–B′*; and fig. 4). Ground water flows in a south-southeastward direction from the recharge area and into the confined part of the aquifer underneath the mesa. Isochrons and equipotentials (Eychaner, 1983) indicate that ground-water flow paths diverge to the northeast and southwest in the confined part of the aquifer, which results in a ground-water divide. The axis of the ground-water divide was approximated by a straight line that is perpendicular to all of the isochrons. The discontinuity of the Navajo Sandstone could force ground water to diverge. Ground water discharges from the confined part of the aquifer into Laguna Creek and Moenkopi Wash and from springs near the contact between the Kayenta and Chinle Formations southwest of Kykotsmovi and southeast of Rough Rock.

From isochrons (fig. 11), cross sections (fig. 3), and an equal-thickness map of the N aquifer (Eychaner, 1983, fig. 4), it was estimated that about 94 percent of the water in the confined part of the aquifer is older than 10,000 years (table 7). δ^{18}O and δ^2H data indicate that this older water was recharged during glacial periods (at least 10,000 years before present) when the climate was much colder than today. Mean values of δ^{18}O and δ^2H in 35 ground-water samples from the confined part of the aquifer are 3.3 and 20.1$^\circ/_{oo}$ lighter, respectively, than mean values in 11 samples from the unconfined part of the aquifer (fig. 12*A*). The heavier composition of recent recharge may be due, at least in part, to climatic warming since the last glacial period. The observed average shift of about 3.3$^\circ/_{oo}$ in δ^{18}O indicates that glacial period temperatures were about 5.9°C cooler than present temperatures (L. Niel Plummer, hydrologist, U.S. Geological Survey, written commun., 1996). In addition, other paleoclimate studies have found a 5°C shift in recharge temperature for glacial-age water from the Southwest (Anderson, 1993). The shift to precipitation that is enriched with heavier isotopes is demonstrated by the changes in δ^{18}O and δ^2H values along the ground-water flow path from Shonto to Kitsillie (fig. 12*B*).

The relation between δ^{18}O and δ^2H in meteoric water is represented by:

$$\delta^2\mathrm{H} = 8\delta^{18}\mathrm{O} + d\ , \qquad (7)$$

where *d* is the deuterium-excess parameter. Craig (1961) found that the global mean value of *d* for



Base from U.S. Geological Survey digital data, 1:100,000, 1983
Universal Transverse Mercator projection, Zone 12

Modified from Brown and Eychaner, 1988

EXPLANATION

—20— LINE OF EQUAL GROUND-WATER AGE IN THOUSANDS OF YEARS—Age estimated from geochemical data and water-level data (Eychaner, 1983, fig. 3). Queried where uncertain. Interval 5,000 years

28 ● <0.3 WELL—Upper number is ground-water age, in thousands of years, estimated from ^{14}C analysis; lower number is ^{3}H, in picocuries per liter with dashes indicating no data

Figure 11. Ground-water age in the N aquifer, Black Mesa area, Arizona. Ground-water ages have an uncertainty of 2,000 years in the unconfined area and an uncertainty of 3,000 years in the confined area.

freshwater sources is +10‰; however, the value of d may differ significantly from area to area and may differ over geologic time (Coplen, 1993). For instance, the cooler and more humid conditions during the Pleistocene glaciation were characterized by ^{2}H-depleted waters (Merlivat and Jouzel, 1979) resulting in a d value less than +10‰. The slope of $\delta^{18}O$ and $\delta^{2}H$ data from the confined part of the aquifer is similar to the slope of the global meteoric water line (Craig, 1961) but is depleted in ^{2}H (fig. 12A) with a d value of about 4‰. The slope, however, indicates that recharge occurred

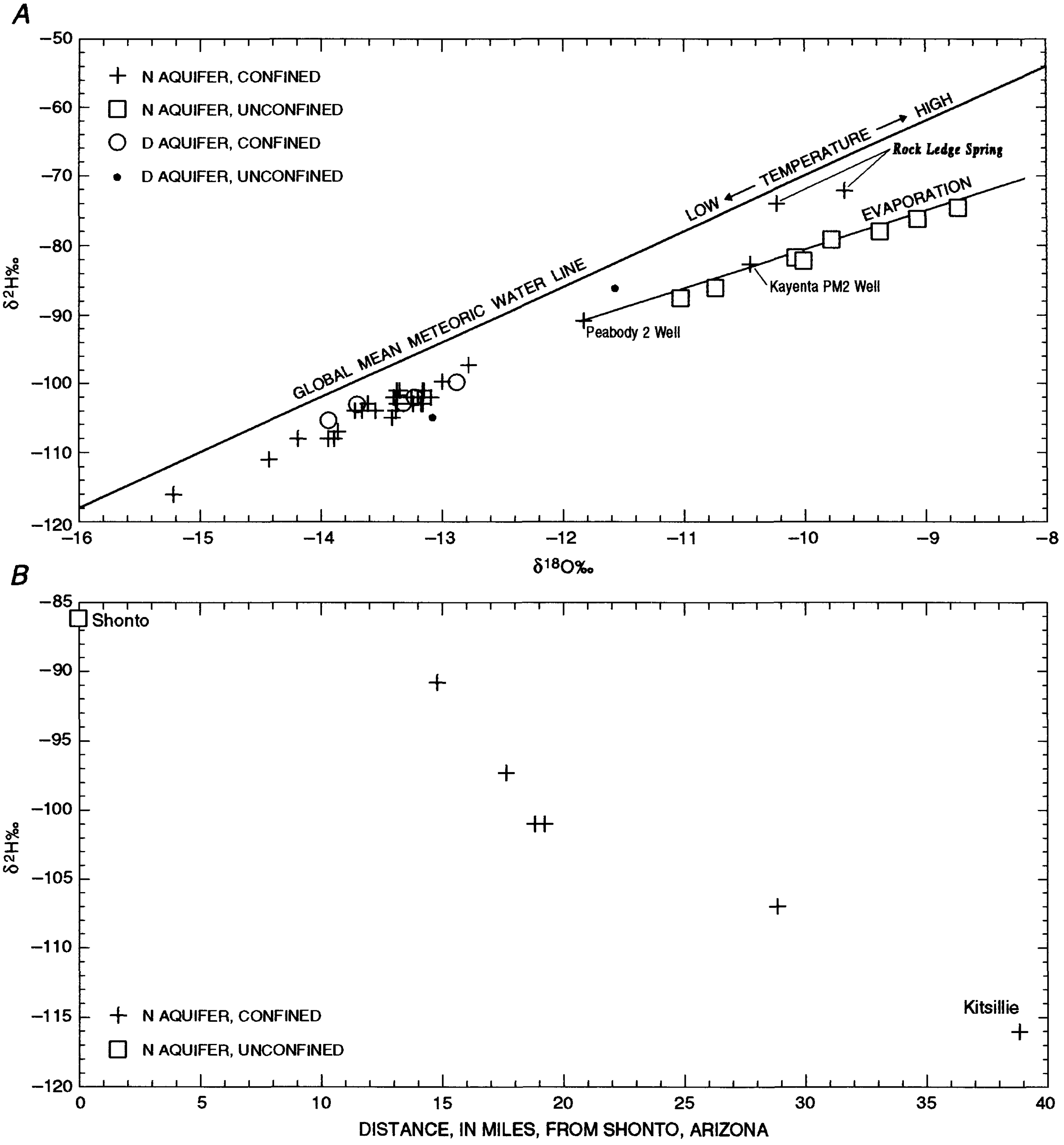


Figure 12. Oxygen and hydrogen isotopes in ground water, Black Mesa area, Arizona. *A*, Relation between δ^2H and $\delta^{18}O$ composition. *B*, Relation between δ^2H and distance from Shonto, Arizona.

under temperate conditions without intense evaporation.

The heavy isotopic composition of water from the unconfined part of the aquifer and deviation of the slope from the global meteoric water line are due to the high evaporation rates of the current semiarid and arid climate (Gat, 1981). One sample from the confined part of the aquifer, at Kayenta PM2, has a heavy isotopic composition similar to that of samples from the unconfined part of the aquifer. The similarity suggests that this well is capturing ground water from the unconfined part of the N aquifer that had been recently recharged.

RECHARGE RATES AND HYDRAULIC CONDUCTIVITY

The small percentage of water younger than 10,000 years in the confined part of the aquifer (fig. 11) and $\delta^{18}O$ and $\delta^{2}H$ data (fig. 12) indicate that recharge is occurring at a lower rate than during the last glacial period. Changes in recharge rates owing to climate change were estimated from the volume of water stored in the aquifer between consecutive isochrons (table 7). The volume of water in storage was estimated from the area between isochrons, average aquifer thickness (fig. 11, this report; Eychaner, 1983, fig. 4), and effective porosity. Ranges in recharge rates were estimated by using effective porosities between 0.25 and 0.35, which is the range in 24 samples from the Navajo Sandstone (Cooley and others, 1969, p. A47). Porosity measured in five samples of the Navajo Sandstone (Geotrans, Inc., 1993) had a similar range and did not change significantly with increasing confining stress. The estimation of recharge rates depends on the amount of data available to interpolate isochrons, and few data exist to control the position of the 10,000-year isochron. The age of ground water at Shonto was assumed to be the youngest water in the confined part of the aquifer and was used to estimate average annual recharge during the last 10,000 years.

Estimates of average annual recharge in the northwestern part of the study area during the glacial periods was about four times the average annual rate of the past 10,000 years (table 7). Although uncertainties exist in the estimated values of recharge rate, the greater recharge rate for the glacial periods is well outside the level of uncertainty for the recharge calculation and coincides with known climatic changes. A wetter climate and corresponding higher recharge rates in the southwestern United States have been hypothesized on the basis of numerous paleoclimate studies (see for example, Galloway, 1970; Van Devender, 1977; Brakenridge, 1978; Van Devender and Spaulding, 1979; Wells, 1979; Van Devender, 1990; and Anderson, 1993). Eychaner (1983) assumed annual recharge to be about 4,800 acre-ft for the Shonto area, which is more than the maximum value of 3,500 acre-ft for the period 10,000 to 2,700 years ago determined in this study. The estimated annual recharge rate for the period 10,000 to 2,700 years ago may be underestimated because of the unknown age of the ground water at the boundary between unconfined and confined ground-water conditions. This study assumed a ground-water age of 2,700 years at the boundary on the basis of the ground-water age estimated at the Shonto well, which is 6 mi from the boundary. A ground-water age at the boundary of about 5,500 years would result in an estimated recharge rate

Table 7. Estimated ranges in recharge rates for ground water of different ages in the confined part of the N aquifer, Black Mesa area, Arizona

Age range of ground water, in years before present	Area, in square miles	Average thickness of aquifer, in feet[1]	Average volume of ground water in storage, in acre-feet[2]	Recharge rate, in acre-feet per year		
				Effective porosity		
				0.25	0.3	0.35
2,700–10,000	104	1,100	22,000,000	2,500	3,000	3,500
10,000–15,000	219	1,000	40,700,000	6,800	8,100	9,500
15,000–20,000	234	833	37,400,000	6,200	7,500	8,700
20,000–25,000	347	750	50,000,000	8,300	10,000	11,700
25,000–30,000	601	600	69,200,000	11,500	13,800	16,200
Greater than 30,000	1,929	200	74,100,000			
Totals	3,434		293,400,000			

[1] From Eychaner (1983); and figure 3.

[2] A porosity of 0.3 was used in estimating average volume in storage.

equivalent to that estimated by Eychaner (1983). Although estimates are approximate and average annual recharge rates for this period may not be equivalent to current recharge rates, the actual recharge in the Shonto area could be less than what Eychaner (1983) assumed. Given the uncertainties of the ground-water age at the boundary, the location of the 10,000-year isochron, and thickness and porosity of the aquifer, it is not certain that recharge estimates for the past 10,000 years differ from those of earlier studies. A lower actual recharge rate than was used in numerical models, however, could explain the differences between calculated and observed water-level declines in the Kayenta area (Littin, 1992). Differences in rates for 25,000 to 10,000 years are not significant for the accuracy of this estimation technique.

Total volume of ground water in the saturated N aquifer is estimated to be about 293 million acre-ft (table 6). Eychaner (1983, p. 11) conservatively estimated storage in the N aquifer to be about 180 million acre-ft. The difference between these estimates is due, at least in part, to the use of a specific yield of 0.10 by Eychaner and a porosity of 0.3 in this report.

Hydraulic-conductivity values were estimated from average linear velocity ($q_{\bar{x}}$), effective porosity, and from Darcy's Law (equation 8), which describes flow through a porous medium.

$$q_d = K \times I, \qquad (8)$$

where

q_d = specific discharge,
K = horizontal-hydraulic conductivity, and
I = hydraulic gradient.

The specific discharge is related to the average linear velocity by:

$$q_d = q_{\bar{x}} \times n, \qquad (9)$$

where

n = effective porosity.

Average linear velocities were estimated from ground-water ages by dividing the distance along northeast and southwest flow paths by the difference in age between the isochrons. The average linear velocity does not describe the actual velocity because a water molecule travels along a tortuous path through an aquifer. Average linear velocities along the northeast and southwest flow paths are about 5.4 and 7.3 ft/yr, respectively. Hydraulic gradients estimated from the water-level map of 1964 (Eychaner, 1983) are 0.0038 for the northeast flow path and 0.0043 for the southwest flow path (fig. 4). Hydraulic conductivity of the N aquifer was calculated by rearranging equation 8 and substituting equation 9 for q_d so that

$$K = q_{\bar{x}} \times n / I. \qquad (10)$$

Using effective porosities from 0.25 to 0.35, hydraulic conductivities varied from 0.95 ft/d for the northeast flow path to 1.16 ft/d for the southwest flow path. These values are similar to hydraulic-conductivity values calculated from more than 40 aquifer tests, which ranged from 0.05 to 2.1 ft/d and averaged 0.65 ft/d (Eychaner, 1983). A hydraulic conductivity of 0.65 ft/d was used for most of the study area in the numerical models developed for the Black Mesa area (Eychaner, 1983; Brown and Eychaner, 1988).

SUMMARY

The Black Mesa area in Arizona, home of The Navajo Nation and Hopi Tribe, is an arid to semiarid region with sparse water supplies. Most of the water demands are met by pumping from the N aquifer, and increasing pumpage has raised concerns about the adequacy of the N aquifer to meet tribal and industrial needs without causing adverse effects on the water resources of the region. Geochemical techniques were used as an independent means of improving the conceptual-flow model in the N aquifer and estimating recharge rates and hydraulic conductivities.

Dissolved-ion and dissolved-gas concentrations; ratios of dissolved ions; and ^{3}H, ^{36}Cl, and ^{13}C data indicate that water from the D aquifer may be leaking into the southeastern part of the confined part of the N aquifer. The boundary between the leaking and nonleaking zones is defined roughly by a line from Rough Rock to Second Mesa and separates ground waters that have significantly different chemistries. Few data exist on the chemistry of the ground water in the D aquifer; therefore, the amount of leakage cannot be quantified.

Estimated ground-water ages increase gradually from recent age in the recharge area near Shonto to at least 35,000 years old in the confined part of the aquifer in the south-central and eastern parts of Black Mesa. Ground water flows south-southeastward from the recharge area and into the confined part of the aquifer underneath the mesa. A ground-water divide results as ground water flows either northeastward or southwestward in the confined part of the aquifer. Ground water discharges from the confined part of the aquifer into Laguna Creek and Moenkopi Wash and from springs southwest of Kykotsmovi and southeast of Rough Rock. Recent recharge along the periphery of Black Mesa mixes with older ground water that discharges from the confined part of the aquifer and flows away from Black Mesa.

Ground-water ages and $\delta^{18}O$ and $\delta^{2}H$ data indicate that more than 90 percent of the water in the confined part of the aquifer is older than 10,000 years and was recharged during glacial periods. Estimates of average annual recharge in the northwestern part of the study area during the glacial periods was about four times the average annual rate of the past 10,000 years. Recent (2,700–10,000 years before present) recharge rates are estimated to be between 2,500 and 3,500 acre-ft/yr in the Shonto area. Estimated hydraulic conductivities were 0.95 and 1.16 ft/d for the northeast and southwest flow paths, respectively. These values are within the range of hydraulic conductivities calculated from aquifer tests, which ranged from 0.05 to 2.1 ft/d and averaged 0.65 ft/d.

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BASIC DATA

Tables 8–10

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Table 8. Selected properties of ground water, Black Mesa area, Arizona

[°C, degrees Celsius; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25°C; --, no data; IT, incremental titration; FE, fixed end-point method]

Well or spring identifier (See fig. 1)	Local well name	Site identification number	Date	Aquifer name	Temperature (°C)	Oxygen, dissolved (mg/L)	pH, field	Specific conductance, field (µS/cm)	Solids, residue at 180°C, dissolved (mg/L)	Solids, sum of constituents, dissolved (mg/L)	Alkalinity, water, dissolved total, IT, field (mg/L as $CaCO_3$)	Alkalinity, water, dissolved, FE, field (mg/L as $CaCO_3$)	Alkalinity, water, dissolved, laboratory (mg/L as $CaCO_3$)	Carbonate (CO_3)	Bicarbonate (HCO_3)
1	Rock Ledge Spring	354011110331501	04–15–93	N	14.0	1.5	7.9	1,290	3,030	2,550	152	--	150	0	185
2	Burro Spring	354156110413701	03–18–93	N	19.0	--	8.5	595	368	380	--	200	183	--	--
	Do.		12–08–94		8.0	--	8.1	597	368	362	--	--	184	--	--
3	Unknown	354226109571501	06–27–95	D	19.0	5.0	7.8	300	182	183	144	150	147	--	176
4	Whisky Spring	354446110562001	04–15–93	N	12.0	--	8.2	660	464	446	120	--	118	0	145
	Do.		12–07–94		11.5	--	8.1	649	458	446	--	--	120	--	--
5	Unknown	354524110495801	09–27–94	D	19.0	6.6	8.7	1,400	--	899	245	240	257	9	281
6	Unknown	354545110343101	06–28–95	D	30.0	5.0	9.8	574	328	323	253	250	251	77	152
7	2nd Mesa PM2	354749110300101	05–11–93	N	20.5	.1	9.5	630	350	346	289	--	283	83	184
	Do.		11–29–94		19.5	--	10.0	605	342	337	271	270	284	72	184
	Do.		08–28–95		21.5	.4	10.1	610	357	353	284	290	282	88	168
8	Unknown	354824109522201	06–27–95	D	24.0	1.1	7.5	3,350	2,700	2,660	580	570	485	--	707
9	NPID	354827110293701	07–27–94	N	--	--	[1]9.5	[1]617	--	345	--	--	283	--	--
10	Polacca 2	354848110243401	07–25–94	D	19.5	.2	9.3	1,470	--	797	315	--	330	32	319
	Do.		06–28–95		19.5	4.7	8.4	2,750	1,740	1,710	351	350	348	2	424
	Do.		08–23–95		20.0	.5	8.5	2,920	1,740	1,730	344	350	348	13	393
11	Hopi HS-1	354856110183201	03–19–93	N	20.5	.2	9.0	2,240	1,340	1,360	--	300	283	--	--
12	Hopi HS-2	354910110182201	05–11–93	N	21.5	.2	8.6	1,850	1,060	1,020	313	--	309	19	343
13	Polacca	354950110231501	10–14–93	N	22.0	.1	9.5	755	422	431	323	--	324	72	249
14	Keams Canyon PM2	355023110182701	02–04–93	N	19.5	.1	9.2	1,040	590	585	351	--	349	47	333
	Do.		11–29–94		19.0	--	9.4	975	562	544	333	330	346	42	321
15	Keams Canyon PM3	355034110183001	07–27–94	N	22.0	--	9.3	907	--	499	329	--	343	41	318

Table 8. Selected properties of ground-water, Black Mesa area, Arizona—Continued

Well or spring identifier (See fig. 1)	Local well name	Site identification number	Date	Aquifer name	Temperature (°C)	Oxygen, dissolved (mg/L)	pH, field	Specific conductance, field (μS/cm)	Solids, residue at 180°C, dissolved (mg/L)	Solids, sum of constituents, dissolved (mg/L)	Alkalinity, water, dissolved total, IT, field (mg/L as $CaCO_3$)	Alkalinity, water, dissolved, FE, field (mg/L as $CaCO_3$)	Alkalinity, water, dissolved, laboratory (mg/L as $CaCO_3$)	Carbonate (CO_3)	Bicarbonate (HCO_3)
16	Hopi Civic Center	355200110340701	07–25–94	N	--	--	[1]9.6	[1]411	--	243	--	--	183	--	--
17	Kykotsmovi PM2	355215110375001	11–28–94	N	22.0	--	10.0	365	212	213	160	160	164	55	83
18	Oraibi	355236110364501	07–26–94	N	22.5	4.2	9.9	388	--	223	161	--	169	54	87
19	Unknown	355250110175401	06–28–95	D	18.0	.5	8.5	1,870	1,270	1,220	390	390	387	11	454
20	Unknown	355507110395201	07–26–93	N	--	--	[1]9.5	[1]308	--	186	--	--	139	--	--
21	Hotevilla	355518110400301	10–14–93	N	25.5	5.4	9.7	305	180	188	141	--	139	47	77
	Do.		11–28–94		18.0	--	10.0	307	166	174	129	130	140	41	74
22	Hard Rocks	360309110301301	05–12–93	N	29.5	3.8	9.2	653	386	394	182	--	180	41	139
23	Unknown	360351110074101	08–10–95	D	20.0	1.4	8.5	2,050	1,480	1,440	312	--	311	9	363
24	Rocky Ridge	360422110353501	03–25–93	N	27.0	5.6	9.5	254	146	158	115	--	112	29	83
	Do.		11–29–94		21.0	--	9.6	248	152	149	108	110	112	20	90
25	Piñon	360614110130801	03–18–93	N	26.5	4.3	10.2	488	287	295	238	--	228	--	--
	Do.		03–18–93		26.5	4.3	10.2	488	--	--	--	240	--	95	94
	Do.		11–29–94		20.0	--	10.1	477	262	274	218	220	227	76	112
26	Moenkopi School Spring	360632111131101	04–07–93		16.0	6.9	7.5	313	--	--	--	110	--	--	--
	Do.		04–07–93		16.0	6.9	7.5	313	204	195	110	--	100	--	131
	Do.		09–23–93		18.5	6.8	7.5	286	--	178	99	--	97	--	121
	Do.		12–07–94		17.5	--	7.4	305	182	183	--	--	97	--	--
27	Tuba City #3	360924111142201	02–25–93	N	16.5	6.6	7.9	188	113	112	79	--	77	0	96
28	Sand Spring	361011110554401	10–13–93	N	21.0	--	7.5	358	212	215	94	--	93	--	113
29	Burnt Corn Spring Well	361208110064401	08–10–95	D	19.0	4.7	8.9	3,030	2,120	2,030	212	--	213	16	225
30	Forest Lake	361737110180301	04–07–93	N	28.5	3.0	9.3	693	352	369	--	150	147	--	--
	Do.		11–30–94		28.0	--	9.4	734	430	427	163	160	166	23	153

Table 8. Selected properties of ground-water, Black Mesa area, Arizona—Continued

Well or spring identifier (See fig. 1)	Local well name	Site identification number	Date	Aquifer name	Temperature (°C)	Oxygen, dissolved (mg/L)	pH, field	Specific conductance, field (µS/cm)	Solids, residue at 180°C, dissolved (mg/L)	Solids, sum of constituents, dissolved (mg/L)	Alkalinity, water, dissolved total, IT, field (mg/L as $CaCO_3$)	Alkalinity, water, dissolved, FE, field (mg/L as $CaCO_3$)	Alkalinity, water, dissolved, laboratory (mg/L as $CaCO_3$)	Carbonate (CO_3)	Bicarbonate (HCO_3)
30	Forest Lake—Cont.	361737110180301	08–09–95		29.0	5.1	9.4	470	274	274	128	--	132	29	98
31	Red Lake NTUA1	361920110573001	03–24–93	N	17.0	6.8	8.4	185	102	105	78	--	79	6	83
32	Red Lake PM1	361933110565001	10–19–93	N	16.5	7.8	8.2	156	84	90	72	--	74	0	80
	Do.		08–07–95		18.5	7.3	8.1	157	92	96	73	--	74	0	90
33	Kitsillie	362035110032201	10–22–93	N	24.0	.2	8.8	1,580	994	1,030	224	--	224	2	268
	Do.		08–29–95		24.0	.2	8.7	1,570	1,020	992	225	220	225	12	250
34	Peabody #9	362333110250001	04–21–93	N	32.0	5.5	8.8	157	94	109	73	--	73	13	62
35	Rough Rock	362418109514601	03–10–93	N	21.0	.3	8.8	1,040	614	629	226	--	220	19	237
	Do.		11–30–94		21.0	--	9.0	1,070	626	610	214	210	220	8	244
36	Peabody #7	362456110242301	10–21–93	N	31.5	6.8	7.2	228	128	150	89	--	90	15	77
	Do.		12–01–94		32.5	--	9.4	225	130	143	84	84	89	10	81
37	Peabody #4	362647110243501	12–02–93	N	31.5	--	9.3	214	124	141	81	--	84	12	75
38	Peabody #2	363005110250901	12–02–93		30.0	--	8.9	163	124	117	67	--	70	5	72
39	Peabody #6	363007110221201	04–21–93	N	33.5	4.8	8.9	181	126	125	82	--	82	8	83
40	Chilchinbito NTUA1	363122110042701	03–10–93	N	21.0	5.2	9.5	418	244	242	201	--	193	49	145
41	Shonto PM2	363558110392501	12–16–93	N	13.5	--	7.8	324	197	193	109	--	109	0	133
42	Shonto PM4	363604110390801	02–25–93	N	13.5	6.9	7.9	291	174	178	109	--	107	0	133
	Do.		08–08–95	N	16.0	6.2	8.1	306	182	181	115	--	112	0	141
43	Kayenta NTUA4	364217110151401	02–11–93	N	18.0	6.4	9.1	259	152	164	113	--	106	7	118
	Do.		08–08–95		20.0	5.6	9.1	245	148	153	108	--	104	8	116
44	Kayenta PM2	364344110151201	10–18–93	N	16.0	6.5	8.1	374	232	244	107	--	104	0	131
	Do.		12–01–94		16.0	--	8.1	371	236	232	100	100	103	0	122
45	Dennehotso PM2	365045109504001	10–20–93	N	16.0	7.8	9.1	298	164	181	119	--	121	12	121

Table 9. Selected chemical constituents of ground water, Black Mesa area, Arizona

[μg/L, micrograms per liter. Constituents are dissolved and are reported in milligrams per liter unless otherside noted. -- no data; <, less than]

Local well name	Site identification number	Date	Aquifer name	Calcium, (Ca)	Magnesium (Mg)	Potassium (K)	Chloride (Cl)	Sodium (Na)	Sulfate (SO_4)	Fluoride (F)	Boron (μg/L as B)	Silica (SiO_2)
Rock Ledge Spring	354011110331501	04–15–93	N	200	120	1.2	74	320	1,700	0.60	230	17
Burro Spring	354156110413701	03–18–93	N	44	3.1	.50	30	84	85	.40	80	12
Do.		12–08–94		47	3.3	.50	26	81	80	.40	70	13
Unknown	354226109571501	06–27–95	D	3.9	1.2	1.6	5.4	65	9.0	.40	140	10
Whisky Spring	354446110562001	04–15–93	N	68	16	2.8	9.1	42	220	.30	50	16
Do.		12–07–94		74	17	2.9	8.4	45	210	.30	40	16
Unknown	354524110495801	09–27–94	D	2.4	.38	1.3	17	310	410	1.6	360	8.4
Unknown	354545110343101	06–28–95	D	.58	.08	.40	9.4	120	20	.20	60	19
2nd Mesa PM2	354749110300101	05–11–93	N	.47	.03	.40	7.5	130	15	.30	100	19
Do.		11–29–94		.51	.04	.40	7.6	130	15	.30	100	20
Do.		08–28–95		.47	.03	.30	7.2	140	14	.30	90	20
Unknown	354824109522201	06–27–95	D	140	57	9.9	18	680	1,400	.10	340	9.8
NPID	354827110293701	07-27-94	N	.48	.04	.40	8.3	130	15	.30	100	19
Polacca 2	354848110243401	07–25–94	D	2.1	.44	1.0	160	300	130	1.6	430	12
Do.		06–28–95		5.9	1.3	2.4	460	640	380	3.5	820	8.4
Do.		08–23–95		5.4	1.2	1.9	450	650	400	3.1	760	8.7
Hopi HS-1	354856110183201	03–19–93	N	3.2	.80	1.8	460	510	190	2.4	11,500	11
Hopi HS-2	354910110182201	05–11–93	N	2.0	.43	1.3	320	370	120	2.7	1,400	10
Polacca	354950110231501	10–14–93	N	.62	.07	.30	27	170	23	.60	270	15
Keams Canyon PM2	355023110182701	02–04–93	N	.80	.15	.80	92	230	36	1.5	670	12
Do.		11–29–94		.74	.14	.80	86	210	32	1.3	610	12
Keams Canyon PM3	355034110183001	07–27–94	N	.67	.12	.60	61	200	26	1.0	440	12
Hopi Civic Center	355200110340701	07–25–94	N	.28	.01	.30	3.6	88	8.8	.20	40	26

Table 9. Selected chemical constituents of ground water, Black Mesa area, Arizona—Continued

Local well name	Site identification number	Date	Aquifer name	Calcium, (Ca)	Magnesium (Mg)	Potassium (K)	Chloride (Cl)	Sodium (Na)	Sulfate (SO_4)	Fluoride (F)	Boron (µg/L as B)	Silica (SiO_2)
Kykotsmovi PM2	355215110375001	11–28–94	N	0.51	0.02	0.60	3.6	76	8.5	0.30	30	23
Oraibi	355236110364501	07–26–94	N	.34	.02	.30	4.7	82	9.0	.20	40	24
Unknown	355250110175401	06–28–95	D	3.9	.81	1.9	65	430	470	4.4	1,200	8.7
Unknown	355507110395201	07–26–93	N	.54	.02	.40	1.9	65	5.8	.20	30	23
Hotevilla	355518110400301	10–14–93	N	.68	.02	.30	1.2	67	5.5	.10	30	23
Do.		11–28–94		.67	.03	.50	1.4	64	4.8	.10	20	20
Hard Rocks	360309110301301	05–12–93	N	.76	.06	.70	40	140	74	1.4	190	23
Unknown	360351110074101	08–10–95	D	4.9	.95	.30	25	490	720	3.5	1,000	9.2
Rocky Ridge	360422110353501	03–25–93	N	.41	.02	.40	1.3	54	5.5	<.10	20	21
Do.		11–29–94		.51	.03	.40	1.4	51	5.5	.10	20	20
Do.		12–13–94		--	--	--	1.3	--	--	--	--	--
Piñon	360614110130801	03–18–93	N	.55	.01	.40	3.6	110	4.5	.20	40	28
Do.		11–29–94		.54	.02	.40	3.9	100	4.7	.20	50	27
Do.		12–13–94	N	--	--	--	3.3	--	--	--	--	--
Moenkopi School Spring	360632111131101	04–07–93	N	29	6.1	1.4	17	26	27	.20	50	14
Do.		09–23–93		28	5.8	1.2	15	23	22	.20	40	13
Do.		12–07–94		29	6.3	1.3	17	24	23	.10	40	14
Tuba City #3	360924111142201	02–25–93	N	23	4.1	1.0	4.4	8.0	7.5	<.10	20	11
Sand Spring	361011110554401	10–13–93	N	32	3.2	.20	4.4	35	69	.40	130	14
Burnt Corn Spring Well	361208110064401	08–10–95	D	12	2.7	3.1	29	650	1,200	1.6	560	4.8
Forest Lake	361737110180301	04–07–93	N	1.2	.12	.80	35	130	88	.70	230	20
Do.		11–30–94		1.5	.15	1.0	56	150	100	1.1	350	17
Do.		06–29–95		--	--	--	43	--	--	--	--	--
Do.		08–09–95		1.1	.12	.70	13	98	60	.40	110	21

Table 9. Selected chemical constituents of ground water, Black Mesa area, Arizona—Continued

Local well name	Site identification number	Date	Aquifer name	Calcium, (Ca)	Magnesium (Mg)	Potassium (K)	Chloride (Cl)	Sodium (Na)	Sulfate (SO_4)	Fluoride (F)	Boron (µg/L as B)	Silica (SiO_2)
Red Lake NTUA1	361920110573001	03–24–93	N	16	3.4	1.1	1.6	14	2.7	0.20	20	13
Red Lake PM1	361933110565001	10–19–93	N	19	5.2	1.7	1.6	4.4	2.1	.20	20	11
Do.		08–07–95		19	5.1	2.0	1.6	4.6	2.0	.20	30	11
Kitsillie	362035110032201	10–22–93	N	3.7	.55	2.1	8.5	350	520	.70	200	12
Do.		08–29–95		3.5	.53	2.1	9.1	330	500	.60	210	11
Peabody #9	362333110250001	04–21–93	N	3.7	.03	.60	1.6	33	2.9	.20	30	20
Do.		12–14–94		--	--	--	1.7	--	--	--	--	--
Rough Rock	362418109514601	03–10–93	N	2.0	.26	1.4	130	230	110	1.6	40	13
Do.		11–30–94		1.9	.25	1.5	130	220	110	1.7	420	12
Do.		11–30–94		--	--	--	120	--	--	--	--	--
Peabody #7	362456110242301	10–21–93	N	3.7	.03	.60	3.8	46	16	.20	20	23
Do.		12–01–94	N	3.5	.03	.70	3.8	44	16	.20	30	21
Peabody #4	362647110243501	12–02–93	N	5.1	.04	.60	3.0	44	12	.20	20	23
Peabody #2	363005110250901	12–02–93	N	8.9	.14	.70	1.7	29	8.9	.10	20	23
Peabody #6	363007110221201	04–21–93	N	3.9	.03	.70	1.9	37	6.6	.20	30	23
Chilchinbito NTUA1	363122110042701	03–10–93	N	.70	.04	.50	2.5	92	3.8	.20	50	17
Shonto PM2	363558110392501	12–16–93	N	47	6.1	2.0	17	6.4	16	<.10	130	16
Shonto PM4	363604110390801	02–25–93	N	43	5.7	1.5	11	6.8	15	<.10	10	15
Do.		08–08–95		44	5.8	1.6	11	6.4	14	<.10	20	15
Kayenta NTUA4	364217110151401	02–11–93	N	5.1	1.1	1.3	4.9	50	21	.20	40	13
Do.		08–08–95		5.5	1.2	1.2	3.3	49	13	.20	40	13
Kayenta PM2	364344110151201	10–18–93	N	43	6.8	1.1	3.7	25	78	.20	20	17
Do.		12–01–94		40	6.3	1.3	4.2	23	77	.10	30	16
Dennehotso PM2	365045109504001	10–20–93	N	9.3	2.2	.60	8.2	53	16	.20	30	13

Table 10. Selected isotopic data for ground water, Black Mesa area, Arizona

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

Local well name	Site identification number	Date	Aquifer name	δ^2H (per mil)	$\delta^{18}O$ (per mil)	$\delta^{13}C$ (per mil)	$^{36}Cl/Cl$ ($x10^{-15}$)	^{14}C (percent modern)	^3H total, (pCi/L)
Rock Ledge Spring	354011110331501	04–15–93	N	-72.2	-9.67	--	--	--	--
Do.		06–15–93		-74.0	-10.23	--	--	--	--
Burro Spring	354156110413701	03–18–93	N	-74.6	-8.73	--	--	--	--
Unknown	354226109571501	06–27–95	D	-102.0	-13.37	--	--	--	<1.0
Whisky Spring	354446110562001	09–15–93	N	-81.7	-10.08	--	--	--	--
Unknown	354524110495801	09–27–94	D	-105.0	-13.08	--	--	--	--
Unknown	354545110343101	06–28–95	D	-99.8	-12.88	--	127	--	<1.0
2nd Mesa PM2	354749110300101	05–11–93	N	-102.0	-13.40	--	--	--	<.3
Unknown	354824109522201	06–27–95	D	-86.2	-11.57	--	--	--	<1.0
NPID	354827110293701	07–27–94	N	-103.0	-13.17	--	--	--	--
Polacca 2	354848110243401	07–25–94	D	-102.0	-13.24	--	--	--	--
Do.		06–28–95		-103.0	-13.32	--	10	--	<1.0
Hopi HS-1	354856110183201	03–19–93	N	-102.0	-13.20	--	--	--	--
Hopi HS-2	354910110182201	05–11–93	N	-103.0	-13.37	--	--	--	<.3
Polacca	354950110231501	10–14–93	N	-101.0	-13.15	--	--	--	--
Keams Canyon PM2	355023110182701	12–16–92	N	-101.0	-13.37	--	--	--	--
Do.		11–29–94		--	--	--	16,200	--	--
Keams Canyon PM3	355034110183001	07–27–94	N	-103.0	-13.24	--	--	--	--
Hopi Civic Center	355200110340701	07–25–94	N	-102.0	-13.09	--	--	--	--
Kykotsmovi PM2	355215110375001	12–10–92	N	-104.0	-13.72	--	--	--	--
Do.		11–28–94		--	--	--	64	--	--
Oraibi	355236110364501	07–26–94	N	-105.0	-13.41	--	--	--	--
Unknown	355250110175401	06–28–95	D	-105.0	-13.94	--	--	--	<1.0
Unknown	355507110395201	07–26–93	N	-108.0	-13.89	--	--	--	--
Hotevilla	355518110400301	10–14–93	N	-108.0	-13.94	--	--	--	--
Hard Rocks	360309110301301	05–12–93	N	-104.0	-13.66	-6.8	--	1.9	<.3
Unknown	360351110074101	08–10–95	D	-103.0	-13.70	--	--	--	<1.0

Table 10. Selected isotopic data for ground water, Black Mesa area, Arizona—Continued

Local well name	Site identification number	Date	Aquifer name	δ^2H (per mil)	$\delta^{18}O$ (per mil)	$\delta^{13}C$ (per mil)	$^{36}Cl/Cl$ ($x10^{-15}$)	^{14}C (percent modern)	^3H total, (pCi/L)
Rocky Ridge	360422110353501	12–16–92	N	-108.0	-14.19	--	--	--	--
Do.		03–25–93		--	--	-8.8	--	2.7	--
Do.		12–13–94	N	--	--	--	840	--	--
Piñon	360614110130801	03–18–93	N	-99.7	-13.00	-7.1	--	.9	<0.3
Do.		12–13–94		--	--	--	308	--	--
Moenkopi School Spring	360632111131101	04–06–93	N	-76.2	-9.07	--	--	--	--
Tuba City #3	360924111142201	02–25–93	N	-78.0	-9.38	-7.5	--	62.4	.9
Sand Spring	361011110554401	10–13–93	N	--	--	--	--	--	--
Do.		10–13–93		-79.2	-9.78	--	--	--	--
Burnt Corn Spring Well	361208110064401	08–10–95	D	--	--	--	--	--	<1.0
Forest Lake	361737110180301	04–06–93	N	-107.0	-13.86	--	--	--	--
Do.		06–29–95		--	--	--	27	--	--
Do.		08–09–95		--	--	-8.1	--	1.1	--
Red Lake NTUA1	361920110573001	03–24–93	N	-103.0	-13.16	-7.9	--	24.8	.4
Red Lake PM1	361933110565001	10–19–93	N	-104.0	-13.38	--	--	--	--
Kitsillie	362035110032201	10–22–93	N	-116.0	-15.22	--	--	--	--
Peabody #9	362333110250001	04–21–93	N	-101.0	-13.35	-8.7	--	7.0	<.3
Do.		12–14–94	N	--	--	--	653	--	--
Rough Rock	362418109514601	03–10–93	N	-103.0	-13.61	--	2	--	.5
Peabody #7	362456110242301	10–21–93	N	-101.0	-13.16	--	--	--	--
Peabody #4	362647110243501	12–02–93	N	-97.3	-12.78	--	--	--	--
Peabody #2	363005110250901	10–21–93	N	-90.8	-11.83	--	--	--	--
Peabody #6	363007110221201	04–21–93	N	-104.0	-13.55	-9.1	--	9.8	<.3
Chilchinbito NTUA1	363122110042701	03–10–93	N	-102.0	-13.25	-6.6	--	.9	<.3
Shonto PM2	363558110392501	12–16–93	N	-86.1	-10.74	--	--	--	--
Shonto PM4	363604110390801	02–25–93	N	-87.6	-11.03	-7.7	--	59.6	1.1
Kayenta NTUA4	364217110151401	02–11–93	N	-111.0	-14.43	-9.5	882	2.4	<.3
Kayenta PM2	364344110151201	10–18–93	N	-82.7	-10.45	--	--	--	--
Dennehotso PM2	365045109504001	10–20–93	N	-82.2	-10.01	--	--	--	--