GROUND-WATER HYDROCHEMISTRY IN THE SOUTHEASTERN HUECO BOLSON AND SOUTHWESTERN DIABLO PLATEAU, TRANS-PECOS TEXAS

by

R. Stephen Fisher and William F. Mullican III

Final Contract Report

Prepared for

Texas Low-Level Radioactive Waste Disposal Authority
Under Interagency Contract Number IAC(90-91)0268

by

Bureau of Economic Geology
W. L. Fisher, Director
The University of Texas at Austin
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EXECUTIVE SUMMARY

The hydrochemical history of ground water in the arid southeastern Hueco Bolson and southwestern Diablo Plateau was investigated by collecting soil-moisture samples from unsaturated siliciclastic bolson-fill sediments and ground-water samples from the Diablo Plateau aquifer, the Hueco Bolson silt and sand aquifer, and the Rio Grande alluvial aquifer. Major, minor, and trace solutes, stable isotopic compositions, and activities of tritium and carbon-14 were measured in ground-water samples; major solute concentrations were determined in soil-moisture samples. Soil samples were collected to determine the type and amount of material that could be readily dissolved by recharge water. Core samples of Cretaceous carbonate and bolson-fill material were analyzed to determine the mineralogy of sediment and aquifer matrix.

The Hueco Bolson and Diablo Plateau aquifers contain mainly sodium-sulfate ground water that derived solutes by calcite, dolomite, and gypsum dissolution, coupled with exchange of aqueous calcium and magnesium for sodium on clay minerals and other ion-exchange sites. Rio Grande ground water is dominated by sodium and chloride derived from dissolution of salts precipitated in irrigated fields during times of high evaporation. All ground waters are inferred to acquire major compositional characteristics early in the flow history, principally through reactions in the unsaturated zone.

Ages estimated from tritium and carbon-14 activities show that Rio Grande ground waters are youngest, reflecting the short flow paths from the river to sampled wells following irrigation and percolation. Young ground waters are also found in the Diablo Plateau aquifer at wells both on the plateau and near the toe of the plateau escarpment. These are inferred to be recharge waters that rapidly moved along fractures to the water table. Other ground-water samples from the Diablo Plateau and Hueco Bolson aquifers are as much as 28,000 yr old. Carbon-14 ages and tritium activities do not vary uniformly along a flow path. However, the oldest waters are found in wells near the center of the bolson pediment, and the distribution of carbon-14 ages

generally conforms to the salinity distribution, suggesting a systematic relation between residence time, chemical and isotopic composition of ground water, and regional hydrologic properties of the aquifers.

INTRODUCTION

Purpose and Scope

Geologic and hydrologic investigations in Trans-Pecos Texas were initiated in 1985 at the request of the Texas Low-Level Radioactive Waste Disposal Authority to characterize areas that were candidates for hosting a low-level radioactive waste repository. Results of the preliminary investigations (Kreitler and others, 1986, 1987) led the Authority to select an area of the southeastern Hueco Bolson near Fort Hancock, Texas, for more detailed studies. As part of these studies water samples from all accessible wells and springs were analyzed to determine hydrologic and hydrochemical factors that could impact the suitability of the area for hosting a radioactive waste repository. This investigation also was an opportunity to investigate the hydrology and ground-water geochemistry of arid land where the unsaturated zone is exceptionally thick. This report summarizes the results of an extensive ground-water-sampling program conducted in 1988 and 1989, combined with data derived from earlier studies and related work conducted during the same period.

Location and Geologic History

The Hueco Bolson (fig. 1) is a major basin in the southeastern Basin and Range physiographic province. It is located in northern Mexico, Trans-Pecos Texas, and southeastern New Mexico, extending along the Rio Grande from the Quitman Mountains near Sierra Blanca to the Franklin Mountains near El Paso and north into New Mexico. Major topographic and geographic features of the area are (1) the Rio Grande to the southwest, (2) Arroyo Alamo, Camp Rice Arroyo, Arroyo Campo Grande, Arroyo Madden, and Arroyo Diablo, which dissect the bolson surface, (3) Campo Grande Mountain, which rises more than 200 ft (61 m) above the bolson surface, and (4) the Diablo Plateau, which lies above the bolson surface and is separated from it by an escarpment of more than 400 ft (122 m). The Hueco Bolson lies within the northern Chihuahuan Desert and has a subtropical arid climate (Thornthwaite, 1931, as modified by Larkin and Bomar, 1983) characterized by high mean annual temperatures, marked temperature fluctuations over broad diurnal and annual ranges, low mean annual precipitation, and wide extremes in seasonal and annual precipitation (Orton, 1964). Table 1 summarizes selected climatic data from the nearest long-term recording station.

The bolson developed during regional east-northeast extension and normal faulting that began in the Trans-Pecos region approximately 24 Ma ago (Henry and Price, 1985). This tectonic activity resulted in topographically high ranges separated by low basins. The Hueco Bolson was filled by clastic sediments carried by the ancestral Rio Grande and by local drainages from adjacent highlands (Strain, 1973).

Major Aquifer Units

The oldest strata from which ground water is pumped are Cretaceous carbonate and clastic rocks of the Finlay, Cox, and Bluff Mesa Formations that underlie bolson sediments and form the Diablo Plateau. Water-bearing units in these strata are grouped together and designated the Diablo Plateau aquifer (Mullican and Senger, 1989). Whether there is one integrated aquifer system in the Cretaceous carbonate rocks or several unconnected or poorly connected carbonate aquifers is not resolved. In this report we group all samples from the Diablo Plateau aquifer because geochemical and hydrologic data are inadequate for distinguishing different aquifers.

Cenozoic bolson-fill sediments constitute a second major aquifer unit. Most wells that produce water from the Hueco Bolson silt and sand aquifer do so from sand lenses that are interstratified with clays and silty clays (Texas Department of Water Resources, 1984). Physical discontinuities are common within this aquifer both because of the lenticularity of the sand, silt, and clay deposits that characterize bolson fill and because of possible stratal offset by Basin and Range faults. Hydrologic discontinuities may also exist; however, the number of wells available for testing and sampling is insufficient for mapping separate aquifer units. The bolson fill is therefore considered a single aquifer unit for this investigation.

The third major aquifer is the Quaternary alluvium of the Rio Grande. This Rio Grande alluvial aquifer may be physically more homogeneous than the other two, but extensive pumping from wells and local recharge during times of high irrigation results in local hydrochemical variations in the ground-water system.

Piezometric Surface

A regional piezometric head map has been constructed on the basis of water-level measurements (fig. 2; Mullican and Senger, 1989). The general trend shows high levels on the Diablo Plateau that decrease toward the southwest. As a result of this gradient, ground-water flow should be from the Diablo Plateau toward the Rio Grande. Water depths in the study area are as great as 590 ft in the Hueco Bolson; the water table is shallower on the Diablo Plateau and near the Rio Grande (fig. 3).

INFORMATION SOURCES

Water Samples

Few sources of ground-water samples exist because the study area is semiarid, the water table is deep, and specific yields of wells are low. During 1988 and 1989, ground-water samples were collected from 16 wells and 1 spring. Two of these wells were drilled and completed specifically for this project, and several other abandoned wells were recompleted for hydrologic testing and sample collection. Nine wells and one spring were sampled repeatedly during the 12-mo period of investigation. This data set is increased to a total of 56 water samples by including 14 analyses from earlier investigations (Kreitler and others, 1986, 1987) and 3 analyses reported by the Texas Water Development Board and the Texas Department of Water Resources, all from sources that could not be sampled during the 1988–1989 period.

Two soil-moisture samplers were installed in each of three boreholes to collect water from the unsaturated zone. Samplers were placed at depths ranging from 23.5 to 110 ft (7.2 to 33.5 m) in strata that, on the basis of stratigraphic information derived from a nearby stratigraphic test borehole that was cored and geophysically logged, were considered most likely to yield water. The soil-moisture samplers consist of a porous ceramic cup attached to 1.5-inch-diameter (3.8-cm), high-temperature PVDC pipe. Two internal check valves are arranged such that the cup could be placed under vacuum to collect water, which could then be driven to the surface under pressure for collection (Wood, 1973). Prior to installation, the ceramic cups were thoroughly cleaned with acid and rinsed with distilled water to remove soluble ions that could contaminate water samples. The ceramic cups were then seated in 200-mesh silica flour to ensure good contact between cup and sediment and evacuated to a pressure of 20 inches (50.8 cm) of mercury after installation.

Soil Samples

Solutes derived from soils have been shown to affect significantly the composition of stream (Miller and Drever, 1977) and spring (Smith and Drever, 1976) waters in arid regions. Therefore, soil samples from the Diablo Plateau, the bolson pediment, and the Rio Grande alluvium were collected for chemical and mineralogic characterization to aid in interpreting the hydrochemical evolution of ground waters for this investigation.

The nature of soils in the southeastern Hueco Bolson can be inferred by correlating the general descriptions provided by the Texas Agricultural Experiment Station (1973) with the more detailed descriptions of soils to the northwest in El Paso County (Jaco, 1971). Soil on the Diablo Plateau is described as calcareous, gypsiferous loamy outwash and sediment, whereas soil on the bolson surface is sandy, loamy, alkaline, calcareous wind-laid deposits. Soil developed on the Rio Grande alluvium is calcareous loamy to clayey material that supports salt-tolerant grasses, salt cedar, and cottonwood trees.

METHODS OF COLLECTION AND ANALYSIS

Ground-Water Samples

Ground water from the three principal aquifers collected during 1988–1989 was analyzed for unstable constituents and treated at the collection site for subsequent laboratory analysis of major, minor, and trace inorganic components, selected organic constituents, and stable (^{18}O, D, ^{13}C, and ^{34}S) and cosmogenic (^{3}H and ^{14}C) isotopic compositions. Sampling procedures were described in a Specific Work Instruction prepared for this study (Fisher, 1989); the methods are briefly summarized in the following paragraphs.

All sample containers and equipment used for field testing of unstable species were thoroughly cleaned and rinsed before each sampling trip. At each collection site, pH, Eh, and water temperature were measured in a flow cell connected to the well such that the sample was not exposed to the atmosphere. Measurements were monitored until values stabilized, at which time final values were recorded and the water was considered suitable for sampling. Alkalinity was determined by potentiometric titration, and the resulting titration curves were examined to verify that bicarbonate was the source of alkalinity. A 300-mL BOD bottle was rinsed, the sample was added, and all air bubbles were dislodged. The sample was then preserved for subsequent determination of dissolved oxygen concentration, which was performed later the same day by titration with sodium thiosulfate.

Aliquots for measurement of major, minor, and trace cations and anions; stable isotopic compositions of oxygen, hydrogen, carbon, and sulfur; tritium activity; dissolved sulfide; total organic carbon; and cyanide were passed through a 0.45-µm filter and preserved. Three 50-L carboys were filled with sample, and 500 mL of saturated ammoniacal strontium chloride was added to raise the pH above 11 and precipitate dissolved carbon species as strontium carbonate. Later the same day the precipitate from each carboy was transferred to a 1-qt jar without exposing it to the atmosphere. The sealed jars were carried back to the Bureau of Economic Geology Mineral Studies Laboratory, where the precipitate was subsequently removed, rinsed, and dried without exposing it to the atmosphere, for carbon-14 analysis. Chemical analyses were performed at the Bureau of Economic Geology Mineral Studies Laboratory. Tritium activities were determined by the University of Miami Tritium Laboratory. Stable isotopic compositions and carbon-14 activities were measured at the University of Arizona Laboratory of Isotope Geochemistry. Total organic carbon, dissolved sulfide, and cyanide were analyzed at Core Laboratories, Corpus Christi, Texas.

Samples collected during 1988 and 1989 provide the primary data base for this report. Samples collected during earlier investigations (Kreitler and others, 1986, 1987) or reported by the Texas Water Development Board or the Texas Department of Water Resources have no field measurements of unstable constituents and thus are less complete analyses. However, data from these samples are included in the following discussions because they provide important information about wells that could not be sampled during the recent field investigations.

Water from the Unsaturated Zone

Water was drawn into the soil-moisture samplers under vacuum and raised to sample containers at the surface under moderate air pressure. Because pressure changes during sample collection result in partial loss of dissolved gases and because only small volumes of water were recovered, only the major and some minor constituents could be analyzed.

Soil Samples

Soils in the study area have a crust that is a fraction of an inch to a few inches thick and significantly better consolidated than underlying material. Paired samples of this crust were collected on the Diablo Plateau, on the Hueco Bolson, and on the Rio Grande alluvium. Each pair from the plateau and the bolson consists of one sample from a topographically high site where rainfall or surface runoff would quickly drain and one from a low site that could function as a drainage path or infiltration area. On the Rio Grande alluvium, one sample was collected from a field that had a long history of irrigation, and one sample was taken from an area that had never been cultivated, where surface runoff ponds during heavy rainfall or runoff events and subsequently evaporates.

Each of the six samples was homogenized and a 75-gram subsample was placed in a flask with 100 mL of distilled water. The soil and water mixture was shaken for 15 min, after which the leachate was removed by centrifugation and passed through a 0.45-µm filter. This process was repeated to give extraction times of 15, 240, and 360 min. Each leachate solution was analyzed to determine the amount of readily soluble ions that could be removed from surface soil samples.

Core Samples

Five samples of bolson fill from core in the Fort Hancock Formation were collected to aid interpretation of the chemical evolution of ground-water compositions. Mineralogic composition of the whole-rock sample and of the clay-size fraction was determined by standard X-ray diffraction (XRD) analysis. A representative split of each sample was leached in distilled water, and the leachate was analyzed using standard methods to determine water-soluble constituents. Exchangeable cations were displaced into solution from a second split of each sample (Thomas, 1982), and the composition of the exchangeable ion population was measured to evaluate the amount and composition of exchangeable cations and the total cation-exchange capacity.

RESULTS OF ANALYSES

Ground-Water Samples

Concentrations of major dissolved species and results of field analyses of ground water are listed in appendix 1; minor and trace species concentrations are shown in appendix 2. Ten additional trace metals were determined for all samples collected in 1988 and 1989 but were found to be below detection limits for all samples. These metals and their detection limits in mg/L are Cr (0.03), Cu (0.03), Ni (0.06), As (0.12), Cd (0.03), Pb (0.25), Sn (0.06), Co (0.03), Se (0.28), and Ag (0.0002). The mean charge balance (meq cations/meq anions) for samples collected in 1988 and 1989 is 0.96 ($1\sigma=0.15$).

Stable isotopic compositions (app. 3) are given in parts per thousand (‰) with respect to the standard SMOW (Standard Mean Ocean Water) for oxygen and hydrogen, PDB (*Belemnitella americana* from the Peedee Formation, South Carolina) for carbon, and CDT (troilite from the Canyon Diablo meteorite) for sulfur. Uncertainties (‰ 2σ) in stable isotopic data are <2.0 (δD), <0.4 ($\delta^{34}S$), and <0.2 ($\delta^{18}O$ and $\delta^{13}C$). Tritium activity is reported in tritium units (TU: 1 TU=$^3H/^1H$ ratio of 10^{-18}), with accuracy and precision stated to be 0.1 TU or 3.5 percent, whichever is larger for samples collected in 1988 and 1989. Tritium activities for samples collected in 1986 have a precision of about 1 TU. Carbon-14 activities are reported as percent modern carbon (pmc, app. 3), with analytical uncertainty as listed for each sample.

Several wells and one spring were sampled repeatedly for this investigation. These data permit evaluation of possible changes in water composition over time. Nine wells were sampled both in 1986 and in 1988–1989. Of these, four present valid comparisons of water chemistry over a 2-yr period. The other five ground waters include (1) spring waters that seep into a standing pool (No. 106), (2) water collected from a holding tank because the windmill-driven pump had not been operating for several weeks before the 1988 sampling (No. 107), (3) water from a well that had recently been completed and may have not yet been developed sufficiently to remove all drilling fluid (No. 126), and (4) water from the Rio Grande aquifer (Nos. 92 and 110), which typically shows seasonal variations in composition caused by variable irrigation and infiltration rates (app. 1). Table 2 summarizes the major ionic compositions of wells sampled in 1986 and again in 1988 or 1989. In most cases, 1986 compositions are slightly lower than 1988–1989 compositions. However, this relation does not hold for all ions, suggesting that systematic differences in sampling or analytical methods are not the cause of observed variations. Differences in concentrations of the major ions between samples collected in 1986 and those collected in 1988–1989 are generally within the uncertainty expected for separate sampling and analysis events, suggesting that compositional changes over a 2-yr period are insignificant.

Four wells and one spring were sampled quarterly from summer 1988 to spring 1989 (table 3). Comparison of major ionic compositions for these samples shows minor, nonsystematic variation attributable to random variations in sampling and analysis in three of the four samples (Nos. 97, 108, and 93). Well No. 110, an irrigation well in Rio Grande alluvium, shows marked compositional changes. These variations are attributed to the effects of irrigation, dissolution of salts on irrigated fields, and soil-water evaporation, as discussed in a later section. With this exception, the major ionic compositions of ground waters sampled quarterly for a 1-yr period remained essentially constant.

Salinity varies widely within each major aquifer. Mean, minimum, and maximum concentrations of total dissolved solids (mg/L) are 1,590, 800, and 2,900 for Diablo Plateau aquifer ground waters; 1,730, 1040, and 3,830 for Bolson aquifer ground waters; and 2,890, 940, and 5,703 for Rio Grande alluvium ground waters, respectively. The distribution of predominant cations and anions (fig. 4) shows that all samples from the Rio Grande alluvium have sodium and chloride as the predominant cation and anion, respectively. Most ground water from wells or springs on the bolson pediment or near the edge of the Diablo Plateau, whether from bolson or Diablo Plateau aquifers, has sodium and sulfate as the predominant cation and anion, respectively. Samples from the Diablo Plateau aquifer collected from wells away from the escarpment have sodium and bicarbonate as the major cation and anion, respectively. One well from the Diablo Plateau aquifer near the toe of the escarpment produces calcium-sulfate water.

Stable isotopic compositions of oxygen and hydrogen are between –6 and –11 ‰ and –45 to –85 ‰ SMOW, respectively (fig. 5), and cluster near the global meteoric water line (fig. 6). All samples from the bolson aquifer fall within the range of –6 to –11 ‰ and –45 to –85 ‰ SMOW for oxygen and hydrogen, respectively. The most depleted isotopic compositions are found in wells on the Diablo Plateau and in the Rio Grande alluvium, reaching values as low as $\delta^{18}O$ of about –11 ‰ and δD of –85 ‰ (figs. 5 and 6). Water from wells on the bolson pediment are less depleted regardless of whether the Bolson or the Diablo Plateau aquifer was sampled.

Water from the Unsaturated Zone

Sodium and bicarbonate are the major cation and anion, respectively, in all samples (table 4). The few measured dissolved silica values are higher than most concentrations observed either in ground-water samples (app. 1) or in leachate from soil samples (discussed in the following section). The high silica content of soil-moisture samples may be due partly to dissolution of some silica flour that was used to ensure contact between the ceramic cup of the soil-moisture sampler and the encasing sediment.

Soil Samples

The composition of leachate from the irrigated Rio Grande alluvium sample differs significantly from all other leachate compositions (table 5). Calcium and bicarbonate are the most abundant leachable ions in all samples except that from the irrigated Rio Grande alluvium; extremely high amounts of sodium, chloride, and nitrate are readily removed from the irrigated sample. Magnesium, calcium, and sulfate also are much more abundant in leachate from the irrigated Rio Grande sample than in other samples. Dissolved silica is high in all samples and is readily removed from the sediment even after only a 15-min exposure to water.

Core Samples

X-ray diffraction (XRD) patterns indicate that quartz is the predominant silt-sized or larger component of the bolson sediments; calcite and potassium feldspar are present in minor amounts in some samples. Although XRD analysis has not identified gypsum as a major or minor phase in the analyzed bolson sediments (Fuentes and others, 1987, 1988; this study), trace amounts of gypsum are common in surface sediments. Gypsum is also observed as discrete beds or as disseminated crystals in both the Fort Hancock and Camp Rice Formations (T. C. Gustavson, personal communication, 1989). The clay-size fraction contains an expandable clay tentatively identified as illite/smectite, kaolinite, and illite. The XRD patterns of clay-size material are complex, indicating that other clay minerals may be present in lesser amounts that cannot be identified in the presence of the more abundant kaolinite, expandable clay, and illite. Similar results have been reported by Daniel and Nelson (1987) and by Fuentes and others (1987).

ORIGIN OF SOLUTES

Two approaches were taken to investigate controls on the composition of ground waters. First, chemical compositions were evaluated to determine whether mineral solubilities limit the concentrations of dissolved constituents. Second, stoichiometric relations among major solutes were examined to evaluate which chemical reactions control the amount of dissolved material.

Mineral Saturation States

Ionic speciation and mineral saturation states of the ground waters were computed using the geochemical modeling program SOLMNEQ (Kharaka and Barnes, 1973). Samples that had no field pH or alkalinity measurements, that were collected from holding tanks because windmill-driven pumps were not functioning, or that were taken from springs of low discharge were not included because those water compositions would not reflect geochemical conditions in the aquifer. Calculated values for the ionic strength of the water samples range from 0.0155 to 0.1074 molal, corresponding to an activity of water of 0.9997 to 0.9974. These values indicate that the ground waters are dilute enough that SOLMNEQ can accurately compute thermodynamic activities of aqueous species.

The SOLMNEQ code (Kharaka and Barnes, 1973) reports the state of equilibria between water and minerals as saturation indices that essentially compare the amount of dissolved species in the water with the amount that would be present if the water were in equilibrium with a particular mineral at sample temperature. A saturation index of zero indicates chemical equilibrium between a mineral and the water sample; values greater than zero indicate oversaturation; and values less than zero indicate undersaturation. Because dissolution and precipitation-reaction rates may be slow or may have high activation energies, a state of oversaturation or undersaturation does not indicate that a particular mineral is being precipitated or dissolved, respectively. The indices do, however, show which reactions are thermodynamically impossible; water oversaturated with a particular phase cannot dissolve that phase, nor can water undersaturated with a certain phase precipitate that phase.

No attempt was made to collect and analyze water samples for aluminum species because of the low concentrations typically observed in ground water (Hem, 1985) and because of the difficulties in obtaining representative samples (Brown and others, 1974; Kennedy and others, 1974). Dissolved aluminum was set at 10^{-6} molal (0.027 mg/L) for the SOLMNEQ runs so that the saturation index of aluminosilicate minerals could be estimated despite the absence of aluminum analyses. This value was chosen because it is the approximate value expected for aluminum concentrations determined by equilibrium with bayerite or gibbsite (polymorphs of $Al[OH]_3$), the phases most likely to control aluminum concentrations in shallow siliciclastic sediments in neutral to slightly alkaline solutions (Hem, 1985).

Results of the SOLMNEQ computations show that all waters are highly oversaturated with most aluminosilicate and silicate minerals because of the high concentrations of dissolved silica. Most ground waters contain silica concentrations of as much as 17.6 mg/L Si (app. 1), with a mean value of 11.4. In comparison, values for saturation with quartz, cristobolite-A, and amorphous silica computed by SOLMNEQ are about 3, 8, and 51 mg/L Si, respectively. The high silica concentrations observed in ground-water samples and the ease with which silica is leached from soils (table 5) suggest that much of the silica in ground water is derived from the vadose zone. A likely source is the amorphous silica in phytoliths that can constitute as much as several percent by weight of the grasses and hardened spines that typify arid-climate vegetation (Iler, 1979). The high dissolved silica concentrations result in oversaturation with all common clay, feldspar, and quartz, the typical silicate minerals in the Diablo Plateau, Hueco Bolson, and Rio Grande aquifers. Therefore, the ground water is incapable of dissolving silicate minerals.

SOLMNEQ results (table 6) also show that ground water from the Hueco Bolson and Diablo Plateau aquifers is essentially saturated with calcite and possibly with dolomite as well, whereas water from the Rio Grande alluvium is slightly oversaturated with both these minerals. Despite high sulfate concentrations in many of the water samples, none are saturated with gypsum (table 6). None of the ground waters are saturated with celestite, the mineral that typically controls strontium concentrations in natural waters (Hem, 1985). Fluorite is at or near saturation in 13 ground waters, principally those from the Diablo Plateau aquifer; all ground waters sampled are saturated with barite. Fluorite and barite solubility probably controls fluoride and barium concentrations in most ground-water samples, although the presence of fluorite and barite has not been confirmed in the few sediment samples examined. Concentrations of other minor and trace elements are apparently not limited by mineral-water equilibrium.

Relations among Dissolved Ions

Two major compositional relations exist for most ground waters. First, all water samples except those from the Rio Grande alluvium show an excess of sodium relative to chloride (fig. 7) and proportionality between excess sodium (sodium minus chloride) and sulfate (fig. 8). Sodium and chloride are highly mobile in ground-water systems; once released from minerals, they are most likely to remain in solution. A sodium/chloride molal ratio approximately equal to unity is usually attributed to halite dissolution, whereas a ratio greater than unity is typically interpreted as reflecting sodium added from silicate weathering reactions (see, for example, Mackenzie and Garrels, 1966; Meybeck, 1987). This explanation does not appear valid for

Hueco Bolson and Diablo Plateau ground water because (1) water that derives solutes primarily by silicate weathering reactions should have bicarbonate as the most abundant anion, but bicarbonate is of secondary importance in all but one sample analyzed in this study, (2) water involved in typical silicate weathering reactions should have silica concentrations controlled by saturation with kaolinite or other clay minerals, if not by quartz (Mackenzie and Garrels, 1966), but all of the ground-water samples analyzed in this study are highly oversaturated with respect to all common silicate phases, and (3) few unstable silicate minerals that would be subject to weathering reactions have been identified in surface sediments or bolson fill.

Second, water samples from the Hueco Bolson and Diablo Plateau aquifers and from the unsaturated zone show a positive correlation between dissolved sodium and sulfate. The excess of molal sodium over chloride, even though silicate weathering reactions seem unimportant in controlling water compositions, and the proportionality between sodium and sulfate suggest that dissolution of gypsum, coupled with exchange of aqueous divalent cations for sodium on clay minerals, is the most likely explanation for the abundance of sodium and sulfate in most Hueco Bolson ground waters.

The results of mineral-water equilibria evaluations and the observed relations among concentrations of major dissolved species suggest that a fairly simple set of chemical reactions control ground-water compositions. Plausible reactions include

$$CaCO_3 + H^+ = Ca^{+2} + HCO_3^-, \tag{1}$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{+2} + Mg^{+2} + 2HCO_3^-, \tag{2}$$

$$CaSO_4 \bullet 2H_2O = Ca^{+2} + SO_4^{-2} + 2H_2O, \text{ and} \tag{3}$$

$$Na_2\text{-clay} + Ca^{+2} = Ca\text{-clay} + 2Na^+, \tag{4}$$

where Na_2-clay and Ca-clay represent ion exchange sites filled by either two Na^+ ions or by one Ca^{+2} ion. Dissolution of calcite and dolomite to saturation (equations [1] and [2]) is suggested by ground-water-saturation indices for these minerals (table 6), whereas dissolution of gypsum (equation [3]) is indicated by high dissolved sulfate concentrations. Ion exchange (equation [4] is indicated by the excess of Na relative to Cl and by the relation between Na and SO_4. The equilibrium constant (K) for reaction (4) is

$$K = \frac{(\alpha Na^+)^2 (\alpha Ca\text{-clay})}{(\alpha Ca^{+2})(\alpha Na_2\text{-clay})}, \tag{5}$$

where α denotes the thermodynamic activity of each species. As Ca^{+2} concentrations increase because of gypsum dissolution, ion-exchange reactions proceed between aqueous species and exchangeable ions on clay mineral surfaces. According to equation (5), as Ca^{+2} is added to solution by gypsum dissolution, the $(Na^+)^2/(Ca^{+2})$ activity ratio decreases. Therefore, the ratio of exchange sites occupied by Ca^{+2} to the number of exchange sites occupied by Na^+ must increase. No anions are added to solution as a result of cation exchange; therefore, the total positive charge of the solution remains constant. As ion exchange, driven by gypsum or carbonate dissolution, increases therefore, the sum $(2Na^+ + Ca^{+2})$ must increase in proportion to SO_4. These relations account for the observed relations in water from the Diablo Plateau and Hueco Bolson aquifers; they also account for the major ionic compositions in water from the unsaturated zone (fig. 9).

Given the major compositional differences between ground-water samples from the Rio Grande alluvium and water from the unsaturated zone, Hueco Bolson and Diablo Plateau aquifers must be understood in terms of the history of the Rio Grande and Upper Rio Grande Valley. A predominance of sodium and chloride over other cations and anions, respectively, is the most obvious difference between ground water from the Rio Grande alluvial aquifer and other ground waters in the study area (fig. 4). Rio Grande ground waters also have the highest mean concentrations of magnesium, calcium, and potassium. Furthermore, there is a deficiency of molal sodium relative to chloride in many Rio Grande samples (fig. 7), indicating that halite is not the sole contributor of chloride to Rio Grande ground water.

Intensive irrigation in the upper Rio Grande basin (north of Fort Quitman, Texas) began in the early 1880's; before that time the Pueblo Indians irrigated crops even before Spanish explorers came to the region (Young, 1981). Post-1880 irrigation, combined with a series of droughts in the 1940's and 1950's, resulted in serious degradation of river quality and deposition of large quantities of salts in irrigated fields (Young, 1981). Solutes in irrigation water become concentrated when the water evaporates on fields and in the shallow subsurface. The resulting saline water eventually returns to the shallow alluvial aquifer or to the river, where it is subsequently used to irrigate fields downstream. Thus, because of heavy irrigation, the Rio Grande has high sodium, chloride, and TDS concentrations (No. 105, app. 1), and large amounts of salts are precipitated on irrigated fields. For example, Young (1981) estimated that solutes in irrigation water added approximately 10 tons of salt per acre in the lower El Paso Valley and Hudspeth Valley in 1955 alone. These salts are readily soluble and can contribute significant amounts of sodium, calcium, magnesium, chloride, and sulfate to ground water (irrigated Rio Grande alluvium sample, table 5) when excess irrigation recharges the aquifer.

One soil sample does not adequately represent the amount and composition of soluble salts in irrigated fields, however, nor does our leaching experiment necessarily simulate the derivation of solutes from shallow sediments by recharge to the Rio Grande alluvial aquifer. Nevertheless, leachate from the soil sample shares many compositional characteristics with Rio Grande ground water. Leachate from the irrigated Rio Grande sediment sample has sodium and chloride as the dominant cation and anion, respectively, whereas all other soil leachates have calcium and bicarbonate as the dominant ions (table 5). Irrigated and nonirrigated Rio Grande soils also have higher leachable concentrations of potassium, magnesium, and sulfate than do any other surface sediments.

Oxygen and Hydrogen Isotopic Compositions

Comparisons of observed and predicted isotopic compositions indicate that ground waters are not in oxygen or hydrogen isotopic equilibrium with common sedimentary minerals. Carbonate minerals typically control oxygen isotopic compositions in ground waters. The isotopic composition of local carbonate can be reasonably estimated. Cretaceous marine carbonates such as that of the Diablo Plateau aquifer typically have oxygen isotopic compositions that range between 0 and –5 ‰ PDB (31 to 26 ‰ SMOW; Veizer, 1983), whereas local caliche has an isotopic composition of about –3 ‰ PDB (Rightmire, 1967). O'Neil and others (1969, as revised by Friedman and O'Neil, 1977) show that the equilibrium oxygen isotopic composition of calcite and water is related by the fractionation equation

$$10^3 \ln\alpha = 2.78 \times 10^6 T^{-2} - 2.89, \qquad (6)$$

where α is the isotope fractionation factor, T is degrees Kelvin, and $10^3\ln\alpha$ represents the difference between the isotopic composition of mineral and water. At 25°C, this equation predicts that water in oxygen isotopic equilibrium with calcite of $\delta^{18}O$ between 31 and 26 ‰ SMOW should be between 2.6 and –2.4 ‰, respectively. These calculated equilibrium values are much higher than the values observed in Hueco Bolson ground waters, indicating that the waters have not reacted with calcite extensively enough to attain isotopic equilibrium.

Clay minerals are the only significant hydrogen reservoir in the Hueco Bolson, and isotopic relations between water and clay minerals at surface temperatures are relatively well established (Lawrence and Taylor, 1971). Water equilibrated with kaolinite or smectite at surface temperatures in the Hueco Bolson would be expected to have hydrogen and oxygen isotopic compositions of about –50 to –80 ‰ and 15 to 20 ‰ SMOW, respectively, depending on the isotopic composition of local meteoric water. These hydrogen isotopic values are within the range observed in the ground waters, but the absence of such enriched oxygen isotopic compositions confirms that equilibration between water and clay minerals has not occurred.

AGE OF GROUND WATERS

Tritium and Carbon-14 in Ground Water

Tritium (^{3}H) and carbon-14 (^{14}C) are produced by the interaction of cosmic-ray neutrons with atmospheric nitrogen (Faure, 1986). Tritium is rapidly incorporated into water molecules and removed as precipitation, whereas carbon-14 quickly enters the natural carbon cycle and is incorporated into organic material, dissolved carbonate species, and carbonate minerals. Both tritium and carbon-14 are unstable; their activities decrease over time according to the standard radioactive decay equation

$$A = A_o e^{-\lambda t}, \qquad (7)$$

where A is the measured activity, t is the time since the sample was isolated from the source of radioactive material, A_o is the initial activity, and λ is the decay constant. Because the decay constant λ is related to the half-life ($t_{1/2}$, the time required for one half of a given number of radionuclides to decay) by the equation

$$t_{\frac{1}{2}} = \frac{\ln 2}{\lambda}, \qquad (8)$$

equation (8) can be substituted and equation (7) rearranged to solve for the time since the sample was isolated from the source of cosmogenic ^{3}H and ^{14}C,

$$t = -\left(\frac{t_{\frac{1}{2}}}{\ln 2}\right) \ln\left(\frac{A}{A_o}\right) \qquad (9)$$

The decay constants of tritium and carbon-14 are well established; therefore, if A_o can be determined, the age of a water containing tritium or carbon-14 can be determined from the measured activity, A. In the case of tritium this age represents the time since water was isolated from free exchange with the atmosphere. Carbon-14 ages obtained in this manner represent the time since dissolved carbonate species were isolated from sources of carbon-14. Typically in the hydrologic cycle, this is the time since the water was isolated from soil gas where decaying plants generate carbon dioxide that contains carbon-14. However, determining the age of ground-water samples is complicated by the fact that it is seldom possible to determine a precise value of A_o for either tritium or carbon-14 at the time and place of recharge.

Ages Interpreted from Tritium Activities

The short half-life of tritium (12.26 yr) should make this an ideal isotope for tracer studies and age determinations of water less than about 75 yr old (approximately 6 half-lives, the amount of time before tritium decays to levels too low for reliable detection [Gat, 1980]). However, two major problems exist. The first is that the tritium content of atmospheric water vapor and precipitation varies regionally and seasonally, so it is difficult to determine the initial activity of tritium in recharge. More important, massive amounts of tritium were produced during atmospheric nuclear testing in the 1950's to early 1960's, and atmospheric tritium levels exceeding 2,200 TU were reported in the northern hemisphere in 1964. Although approximately 2 half-lives have passed since atmospheric testing of nuclear devices ended, levels as high as several hundred TU could remain in some ground waters. Small amounts of tritium can also be produced by natural subsurface processes, so values in the range of 0.05 to 1 TU are possible in ancient ground water.

Sample 105 (Rio Grande river water) contains about 24 TU (app. 3). Assuming this value represents modern recharge in the southwest since atmospheric nuclear testing ended, 5 half-lives, or approximately 60 yr, are sufficient to reduce tritium activity to less than 1 TU. Therefore, samples that contain more than 1 TU are considered to be recent recharge, and no attempt is made to quantify these ages further.

Ages Interpreted from Carbon-14 Activity

The half-life of carbon-14 is 5,730 yr, making it suitable for resolving ages to about 35,000 yr. In ground-water investigations, however, dissolved carbonate is commonly derived from several sources and carbon-14 activity may be reduced by factors other than simple radioactive decay. These additional sources and sinks for carbon must be evaluated on the basis of the regional hydrology, as well as the chemical and stable isotopic compositions of ground-water samples, before ages can be estimated from carbon-14 activity (Pearson and White, 1967; Pearson and Hanshaw, 1970; Wigley, 1975; Mook, 1976; Reardon and Fritz, 1978; Wigley and others, 1978; Fontes and Garnier, 1979; Mook, 1980).

The main sources of dissolved carbonate in most ground waters are carbon dioxide dissolved from soil gas and carbonate minerals dissolved in either the unsaturated or saturated zones (Mook, 1980). Secondary sources of dissolved carbon are atmospheric carbon dioxide, bicarbonate produced by weathering of silicate minerals or by oxidation of organic material, carbonate produced by sulfate reduction, and carbon dioxide from volcanic or magmatic sources (Mook, 1980). Carbon-14 can be removed from ground water by precipitation of carbonate minerals; this reduces the carbon-14 activity of dissolved carbonate and thereby increases the apparent age of the water.

Typically not all of the possible sources and sinks of carbon are important in any particular region; therefore, interpretation of carbon-14 activities in ground waters usually does not require quantitative consideration of all possible sources and sinks. However, because numerous processes can affect calculated ground-water ages, carbon-14 activities must be interpreted within the framework of a hydrochemical and hydrologic model developed specifically for each study.

The geologic history of the region indicates that carbon-14 data can be interpreted within the framework of the present hydrologic system. Water levels now essentially reflect topographic relations and indicate gravity-driven flow potentials. This situation has existed for at least the last 24 Ma, since Basin and Range extension affected the area (Henry and Price, 1985). Caliche deposits in the southeastern Hueco Bolson have carbon-14 ages that are nearly as much as 23,000 yr (Rightmire, 1967), indicating that the climate has been hot and dry at least that long.

Two different approaches can be taken to determine the initial value of carbon-14 in recharge (summarized by Fontes and Garnier, 1979). One uses the concentration and isotopic composition of dissolved carbonate to correct measured carbon-14 activities for the contribution of mineral carbon to ground water. The second approximates the amount of mineral carbon added from changes in dissolved carbonate concentrations along ground-water flow paths. Either approach may be valid for the system under investigation; comparison of the results from each method gives not only ground-water ages but also estimates of the uncertainty involved.

Consideration of both the concentration and isotopic composition of dissolved carbonate has the advantage that the validity of the assumptions involved in determining a carbon-14 age can be evaluated. For the case of recharge acquiring carbon-14 from carbon dioxide in soil gas (carbon-14 activity of 100 pmc and $\delta^{13}C$ determined by vegetation type) and also dissolving marine carbonate minerals (carbon-14 activity of 0 pmc and $\delta^{13}C$ of approximately 0 ‰), mass balance requires that

$$\log C_T = -\log\left[\frac{\delta^{13}C_{sm}}{\delta^{13}C_{rc}}\right] + \log C_i\,, \tag{10}$$

where C_T is the measured total dissolved carbonate, $\delta^{13}C_{sm}$ is the measured carbon isotopic composition of the water sample, $\delta^{13}C_{rc}$ is the isotopic composition of recharge, C_i is the amount of carbon derived from soil gas, and $\delta^{13}C_{sm}/\delta^{13}C_{rc}$ gives the fraction of total dissolved carbon derived from soil gas in the recharge zone (Pearson and White, 1967). Plotting $\log C_T$ versus $\log[\delta^{13}C_{sm}/\delta^{13}C_{rc}]$ for a set of water samples provides a test of the assumptions involved in calculating carbon-14 ages. If soil carbon dioxide and marine carbonate minerals are the only sources of aqueous carbon species, the data will define a linear trend with a slope of –1 and a y-intercept equal to the amount of carbon derived from soil gas (Pearson and White, 1967). We use a value of $\delta^{13}C_{rc}$ = –17 ‰ to evaluate the data because this is the average value for soil carbon dioxide found in the southeastern Hueco Bolson (Rightmire, 1967) and should therefore best represent regional recharge.

Total carbonate could not be determined for ground-water samples collected in 1986 because pH was not measured. However, in all cases where pH was measured and carbonate speciation could be determined, titration alkalinity (HCO_3^- and CO^{-2}) accounts for more than 95 percent of total dissolved carbonate, as expected over the narrow, slightly alkaline pH range of the ground waters. Therefore, the linear relation predicted by equation (10) remains whether total carbonate or total alkalinity is plotted. Figure 10 shows the relation between alkalinity and the carbon isotopic composition of ground-water samples. With the exception of samples from Rio Grande irrigation well 110, the data fall within a linear band. Exclusion of data from well 110 from further consideration is justified because these samples contain more than 100 pmc (app. 3), reflecting a contribution of carbon-14 from atmospheric nuclear testing. Linear regression parameters for the relation (fig. 10) computed using the statistical package in a TI-60 programmable scientific calculator yield a slope of –0.966, correlation coefficient of –0.766, and y-intercept of log total carbonate = 2.11. The width of the band (fig. 10) undoubtedly reflects factors such as (1) local variability in the value of $\delta^{13}C_{rc}$ for recharge to different wells at different times (see, for example, Parada and others, 1983), (2) the likelihood that some carbonate was dissolved from caliche (carbon-14 from 0 to 12.6 pmc, $\delta^{13}C$ from –3.1 to –5.3 ‰; Rightmire, 1967), or (3) the possibility that some secondary carbonate was precipitated as gypsum dissolution added dissolved calcium to calcite- or dolomite-saturated ground water. The indicated value of C_i is about 130 mg/L HCO_3, which is in reasonable agreement with values predicted for soil-gas partial pressures typical of arid environments (CO_2 partial pressures approximately five to ten times atmospheric [Wallick, 1976]), carbonate solubility calculated by the method of Garrels and Christ, 1965) and observed by Wood and Low (1988).

Figure 10 provides one basis for adjusting measured carbon-14 activities to reflect initial activity in recharge before mineral carbon was added to the water (Pearson and White, 1967). The correction factor is simply

$$K_1 = \frac{C_i}{C_t}, \tag{11}$$

where C_i is the amount of carbon derived from soil gas (represented by the value of the y-intercept in fig. 10) and C_t is the total measured alkalinity of the sample. Values of K for ground-water samples of measured tritium and carbon-14 activities are listed in table 7. A value of C_i = 130 mg/L was used for all samples except that from well 126. Water from well 126 contains only 60 mg/L alkalinity and has a $\delta^{13}C$ value of –18 ‰, indicating that essentially all dissolved carbon was derived from soil gas. For this sample, C_i was set to 60 mg/L.

The second approach to correcting carbon-14 activities for the amount of dissolved mineral carbon is based on $\delta^{13}C$ mass balance rather than carbonate concentrations. The fraction of total dissolved carbon derived from soil gas can be expressed as

$$K_2 = \frac{\left(\delta^{13}C_{sm} - \delta^{13}C_{min}\right)}{\left(\delta^{13}C_{rc} - \delta^{13}C_{min}\right)}, \tag{12}$$

where $\delta^{13}C_{sm}$, $\delta^{13}C_{min}$, and $\delta^{13}C_{rc}$ refer to the stable carbon isotopic composition of water sample, dissolved carbonate minerals, and recharge (soil gas), respectively (after Pearson and White, 1967).

The $\delta^{13}C_{sm}$ can be measured (app. 3); however, appropriate values for $\delta^{13}C_{rc}$ and $\delta^{13}C_{min}$ must be estimated. The two main sources of mineral carbonate in the area are (1) the Cretaceous marine Finlay Limestone that outcrops on the Diablo Plateau and locally on the bolson plain and also is part of the Diablo Plateau aquifer system and (2) caliche deposits on and near ground surface. Carbonate dissolved from the Finlay Limestone would have a $\delta^{13}C$ value of about 0 ‰ because of its marine origin, whereas caliche in the southeastern Hueco Bolson has $\delta^{13}C$ values that average –4.5 ‰ (Rightmire, 1967). The value for $\delta^{13}C_{rc}$ is usually taken to be the composition of soil carbon dioxide (Pearson and White, 1967; Rightmire and Hanshaw, 1973). For the Hueco Bolson area, this would be best approximated by –17 ‰, the average value measured by Rightmire (1967). Equating the isotopic composition of soil gas with that of dissolved carbonate presumes that isotopic equilibrium between gaseous and aqueous carbon species is not achieved. This may be the case if recharge rapidly moves down to the saturated zone where most water is no longer in contact with soil gas. However, if carbon isotopes equilibrate between gaseous and aqueous phases, dissolved carbonate should be enriched relative to soil carbon dioxide; at 20 °C, this enrichment would result in a $\delta^{13}C_{rc}$ value of about –9 ‰ for dissolved carbonate (fractionation factor from Friedman and O'Neil, 1977, fig. 28).

Allowing $\delta^{13}C_{rc}$ and $\delta^{13}C_{min}$ to have values of either –17 or –9 ‰ and –4.5 or 0 ‰, respectively, results in four possible values of K_2 (equation 12) for most ground water. The sample from well 107 has a $\delta^{13}C$ value of –16.8 ‰, and thus contains essentially only carbon from soil gas that has not equilibrated isotopically with water. For all other samples, the combination of $\delta^{13}C_{rc}$ and $\delta^{13}C_{min}$ that yielded the best agreement between K_2 (equation 12) and K_1 (equation 11) is considered to best represent the primary source of recharge and mineral carbon. Note that equations (11) and (12) are independent, and therefore the values of K_1 and K_2 will agree only if they adequately reflect the sources and amounts of dissolved carbon contributed to the ground water.

Having developed appropriate factors that describe the types of dissolved carbon in a ground water, we can now adjust the measured carbon-14 activity for the amount of mineral-derived carbon and solve for the age of the sample. Equation (9) can be written as

$$t = 8{,}267 \ln\left(\frac{100\ K_1}{\mathrm{pmc}}\right), \qquad (13)$$

where 8,267 is the half-life of carbon-14 divided by the natural logarithm of 2, 100 is the initial percent modern carbon of soil carbon dioxide, and pmc is the measured carbon-14 activity of the ground water (after Pearson and White, 1967). Values of K_1, K_2, and resulting carbon-14 ages are given in table 7.

Discussion

Ground water that was probably recharged within the past 75 yr is found in wells completed in the Diablo Plateau aquifer both on the plateau (wells 96 and 112) and on the bolson plain near the edge of the plateau escarpment (wells 113 and 114; table 7 and fig. 11). The presence of recent recharge in wells as deep as several hundred feet on the Diablo Plateau and on the bolson plain near the toe of the escarpment suggests that recharge along fractures and fault planes locally results in short travel times between ground surface and water table. Well 114 is located near the toe of the fault-bounded escarpment (fig. 11) and contains tritium and carbon-14 activities that suggest a relatively young water. Recharge along the fault plane is likely because of the position and shallowness of the well (approximately 100 ft [30.5 m]). As previously discussed, this is the only example of a Ca-SO_4 water; it also has relatively low salinity and low silica content. All these characteristics signify a ground water that was recently recharged and one that has not undergone extensive water-rock interactions. Water containing more than 1 TU is also produced from the Rio Grande aquifer (wells 92 and 110). Recharge to the Rio Grande aquifer near the river probably results from irrigation. Some of the samples that contain cosmogenic tritium also have carbon-14 ages as much as about 3,000 yr, whereas the agreement between carbon-14 ages determined by two independent methods is generally better than 2,000 yr (table 7). These relations suggest that differences of less than about 3,000 yr in carbon-14 ages are probably insignificant.

A second group of ground waters containing less than 1 TU and having carbon-14 ages of less than about 3,000 yr is found in the Diablo Plateau aquifer at wells on the plateau (well 96), in the Hueco Bolson aquifer (well 108), and in the Rio Grande aquifer (well 93) (table 7 and fig. 11). These are interpreted to be old enough that tritium has decayed to background levels, but younger than a few thousand years.

The third group of samples contains no cosmogenic tritium and has carbon-14 ages of from 7,000 to 28,000 yr (table 7 and fig. 11). These oldest waters in the region are found in both the Diablo Plateau (wells 95, 97, 115, and 116) and Hueco Bolson (wells 107, 111, and 126) aquifers. The carbon-14 ages are considered to reflect actual time since recharge, with an uncertainty of about 3,000 yr.

One of the wells that contains very old water deserves special mention. Well 126 was initially sampled in 1986 and found to contain 3.6 ± 0.6 TU, 3.3 percent modern carbon, and to have a $\delta^{13}C$ ratio of –18.1 ‰. At the time, it was suspected that the tritium activity reflected some contamination from drilling fluid. Because it is extremely unlikely that the carbonate system could be contaminated in a way that would produce such low carbon-14 and $\delta^{13}C$ values, the estimated carbon-14 age of more than 28,000 yr is considered representative of the true age. Several aquifer tests were performed after 1986 and before a second sample was collected in 1989. Special attention was given to removing all drilling fluid before sampling in 1989. However, the sample collected in 1989 was found to have a $\delta^{13}C$ ratio of –9.1 ‰ and to contain 0 TU and 69.4 percent modern carbon. These data yield a much younger carbon-14 age of about 3500 yr. At this time we cannot explain the discrepancy between the compositions of ground water sampled at the different times. We consider the earlier data to best represent a true sample composition and suspect the 1989 sample was contaminated by atmospheric carbon dioxide ($\delta^{13}C$ of about –7 ‰ and 100 percent modern carbon).

Ground-water ages follow the general trend displayed by the distribution of total dissolved solids and the pattern of predominant cations and anions (compare figs. 4 and 12); older waters are relatively saline and have sodium and sulfate as the dominant dissolved species, whereas younger waters are relatively fresh and have calcium and sulfate (well 114) or sodium and bicarbonate (wells 95, 96, 97, and 115) as the dominant aqueous cation and anion, respectively.

SUMMARY

Ground-water samples from three major aquifer systems, water extracted from vadose zone sediments, soil leachates, and core samples were analyzed to investigate the regional hydrochemical system in the southeast Hueco Bolson and southwest Diablo Plateau, Trans-Pecos Texas. Repeated ground-water sampling over a 3-yr period and quarterly sampling of selected wells showed no significant short-term chemical or isotopic variability. Long-term monitoring of wells and springs may show systematic seasonal variations in ground-water compositions that could provide important information about the regional hydrologic system; however, such trends cannot be identified in the available data.

The major solute chemistry of Hueco Bolson and Diablo Plateau ground water is generally controlled by simple mineral dissolution and ion exchange. Calcite and dolomite are dissolved to saturation in most ground waters. Gypsum is also dissolved, but gypsum is apparently not present in sufficient quantities for saturation to be achieved. Dissolution of gypsum raises the calcium concentration in ground-water and soil-water samples, which drives exchange of aqueous calcium for sodium on ion exchange sites. This coupled process results in water compositions dominated by sodium and sulfate in most samples. Diablo Plateau ground waters that have bicarbonate as the most abundant anion occur only in wells on the Plateau. These waters have dissolved gypsum relative to calcite less than waters that have sulfate as the most abundant anion. The single ground-water sample from the Diablo Plateau aquifer that has calcium as the most abundant cation lies at the base of the plateau escarpment. This sample differs from other Diablo Plateau ground waters in that it has encountered little clay or other phases having ion-exchange capacity. The water from this well is also relatively young, suggesting that water-rock interactions may have not been extensive because the residence time of the water is short. Ground water from the Rio Grande alluvial aquifer is predominantly a sodium-chloride type. Dissolution of salts that precipitate in irrigated fields during times of high evaporation rates largely controls dissolved solutes in this aquifer.

The major ionic characteristics of ground waters are apparently established early in the flow history, largely by processes that occur at the sediment surface. Evidence to support this conclusion includes the observation that the composition of soil leachate and soil-moisture samples falls on the same compositional evolution trends as Diablo Plateau and Bolson ground water. Soil leachate contains the same major species as Bolson and Diablo Plateau ground water, but in proportions that reflect simple dissolution without ion exchange. Soil-moisture samples from bolson sediments well above the water table show the same major solutes as soil leachate and ground waters from the Hueco Bolson and Diablo Plateau aquifers and also show evidence that ion exchange of sodium on clay for calcium in solution has occurred. The fact that ground-water samples from carbonate strata sampled at wells on the Diablo Plateau where soil thickness ranges from zero to only a few tens of feet is compositionally similar to soil moisture and ground water from bolson siliciclastic strata is further evidence that geochemical processes in the vadose zone establish the major features of ground-water chemistry. Ground water in the Rio Grande alluvial aquifer also apparently derives most major solutes from dissolution of salts at the sediment surface. Alluvium from an irrigated field readily yields high concentrations of sodium and chloride, the most abundant solutes in Rio Grande ground water. Potassium, magnesium, calcium, silica, sulfate, and nitrate also are readily available in irrigated surface sediments.

Ground-water ages estimated from tritium and carbon-14 activities range from recent to nearly 28,000 yr. Water that was recently recharged is found along the Rio Grande, in wells on the Diablo Plateau, and in wells near the toe of the plateau escarpment. The three oldest waters (approximately 14,500 to 28,000 carbon-14 yrs) are produced from wells on the bolson pediment from both the Hueco Bolson and Diablo Plateau aquifers. Age distributions for water from the Diablo Plateau and Hueco Bolson show a pattern similar to those of total dissolved solids and predominant aqueous cation and anion, suggesting that ground-water hydrochemistry largely reflects hydrologic properties of the aquifers.

ACKNOWLEDGMENTS

Funding for this research was provided by the Texas Low-Level Radioactive Waste Disposal Authority under Interagency Contract No. 90-008 IAC(90-91)0268. Conclusions of the authors are not necessarily endorsed by the Authority. This investigation could not have been completed without the kind help of many residents of Hudspeth County. In particular we express our appreciation to Mr. and Mrs. Scott Wilkey, Mr. and Mrs. Dennis Walker, Mr. E. Franklin, and Mr. J. Gavin. We also sincerely thank Doug Ratcliff for purchasing and outfitting the Bureau of Economic Geology field vehicle for hydrologic and hydrochemical studies. Bernd Richter and Rainer Senger assisted with sample collection; Bernd Richter provided unpublished chemical analyses of soil-moisture samples. Alan Dutton and Tucker Hentz reviewed and improved draft versions of this report.

Melissa Snell and Susan Lloyd did the word processing for the report under the supervision of Susann Doenges. Figures were drafted by Richard L. Dillon, as well as by Joel Lardon and David Ridner under the direction of Richard L. Dillon. Lana Dieterich was the editor; Jamie H. Coggin, the designer.

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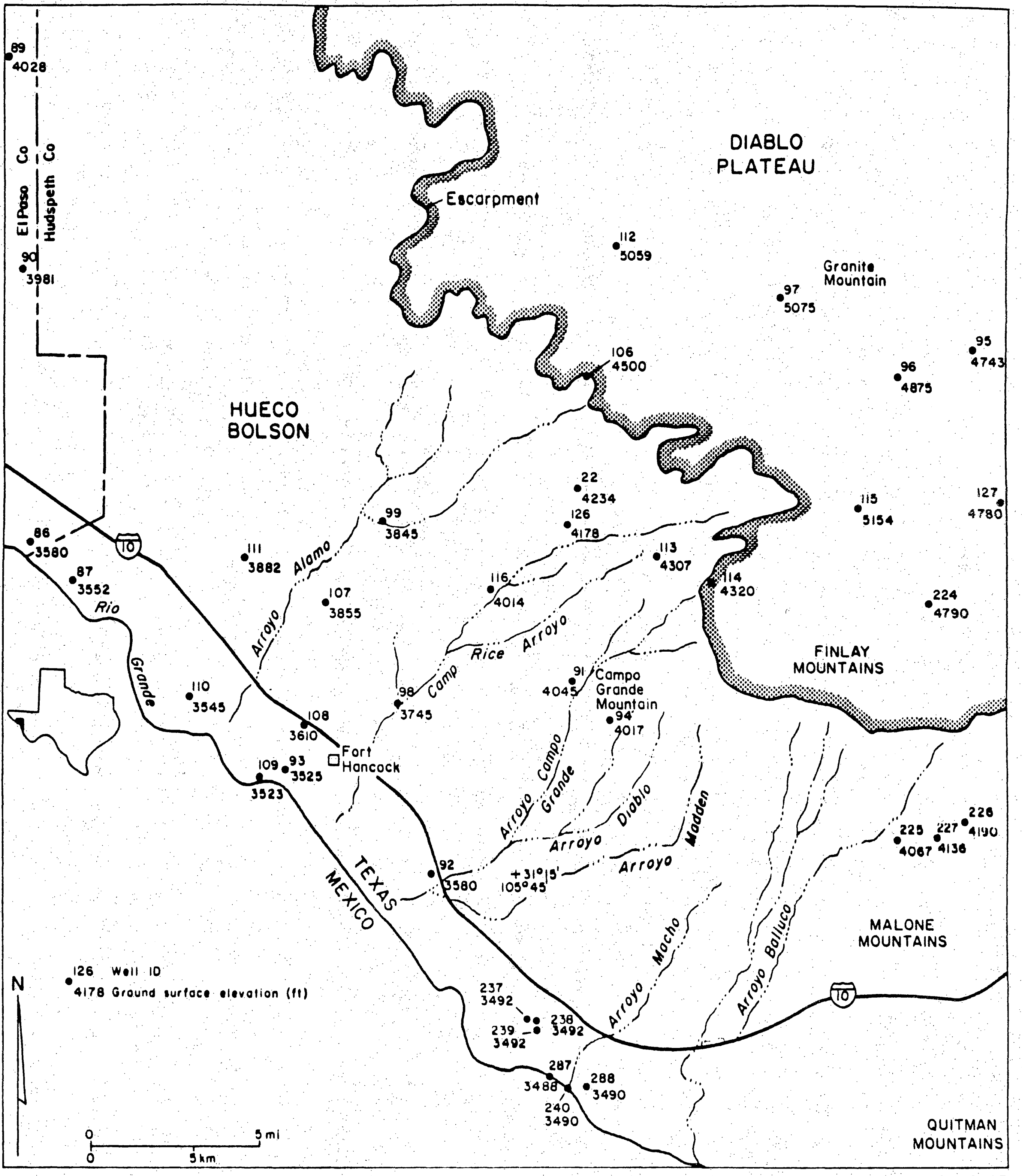

Figure 1. Location map showing major geographic features, well locations and identification numbers, and ground-surface elevations of southeastern Hueco Bolson and southwestern Diablo Plateau. Cross section A–A′ shown in figure 3.

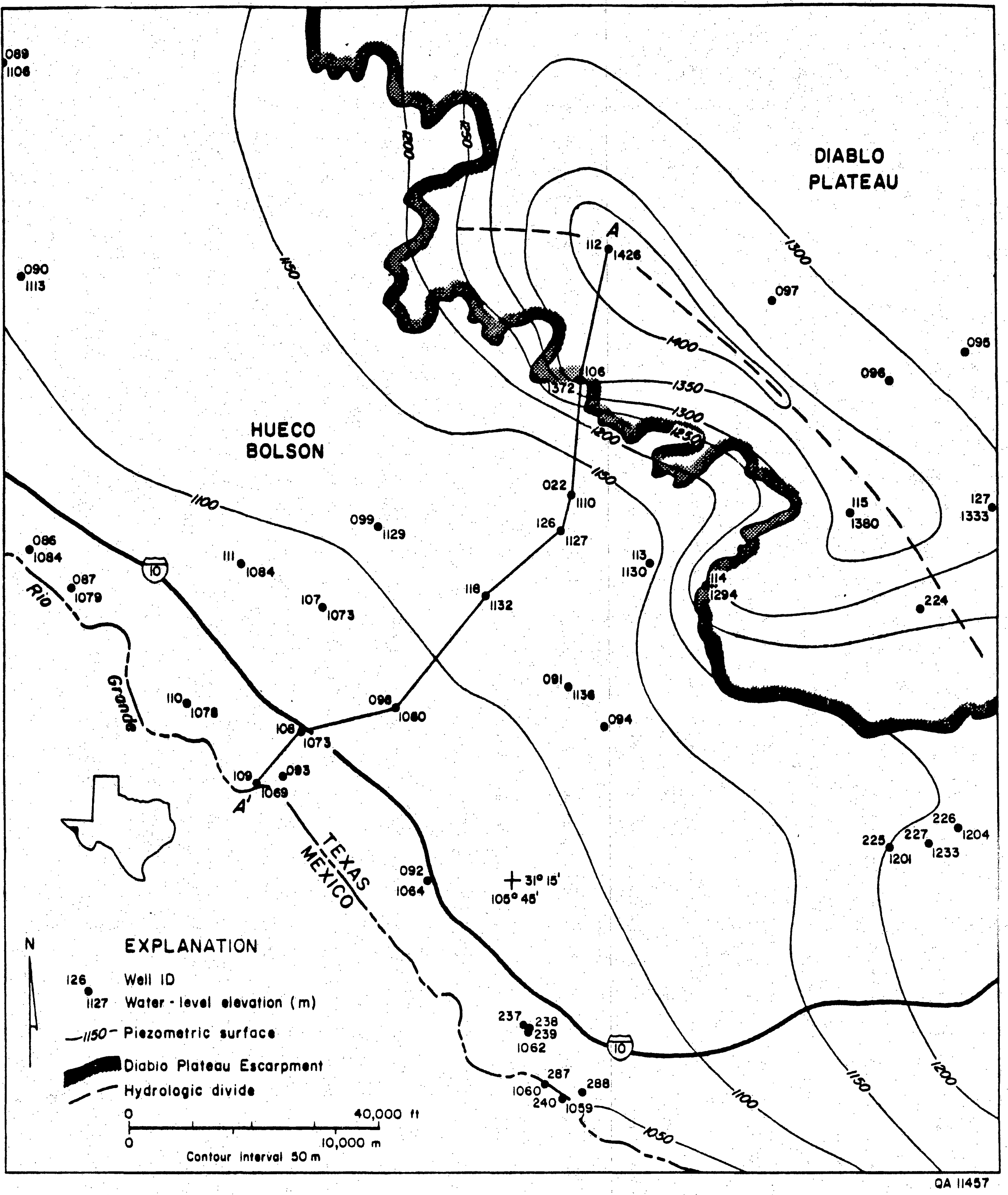

Figure 2. Map of piezometric surface as determined from water-level measurements (after Mullican and Senger, 1989). The closed potentiometric high and resulting hydrologic divide on the Diablo Plateau are interpreted on the basis of water-level measurements to the north, northeast, and east that are not shown on this map. Cross-section A–A′ shown in figure 3.

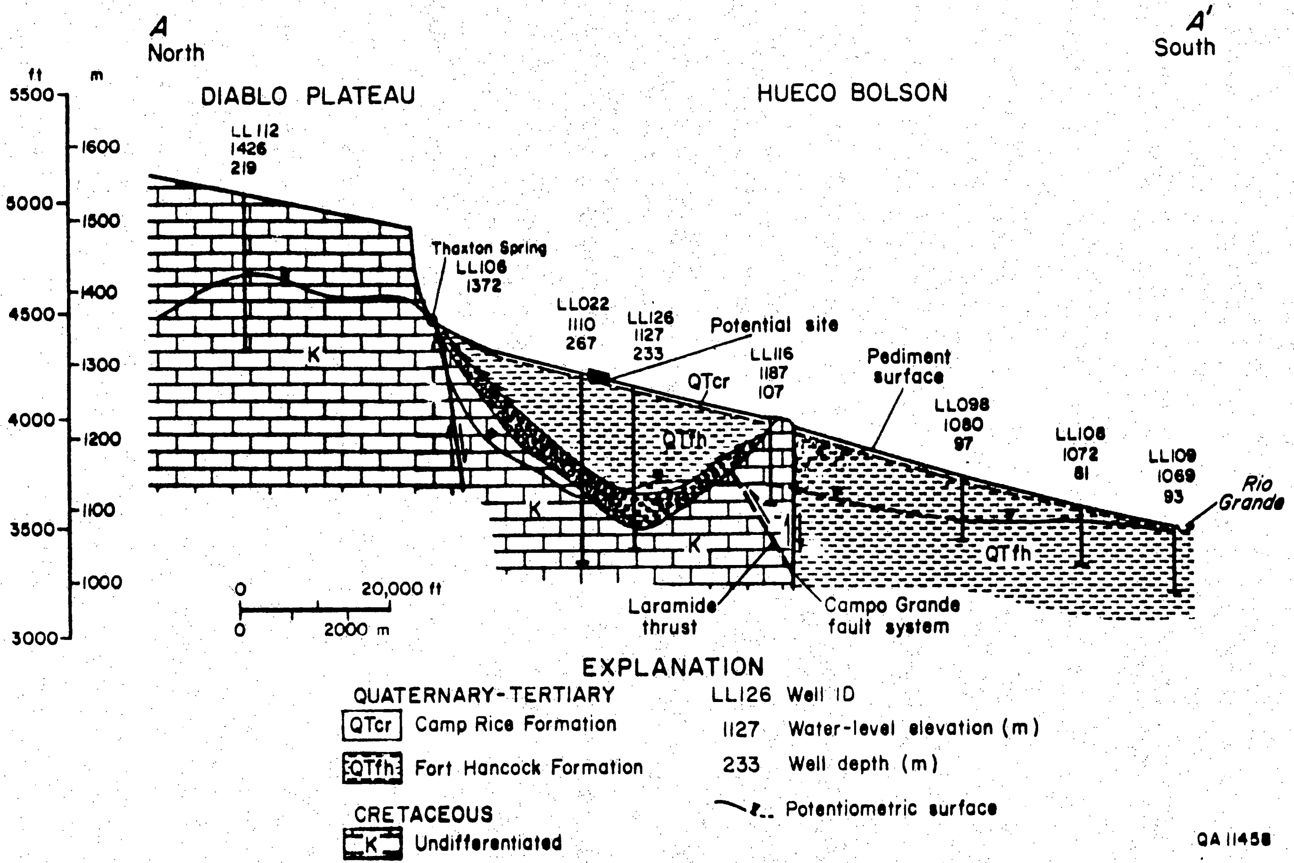

Figure 3. North-south hydrologic cross section A–A′ showing vertical relations between Diablo Plateau and Hueco Bolson aquifers and depth to water (after Mullican and Senger, 1989). Line of section shown in figures 1 and 2.

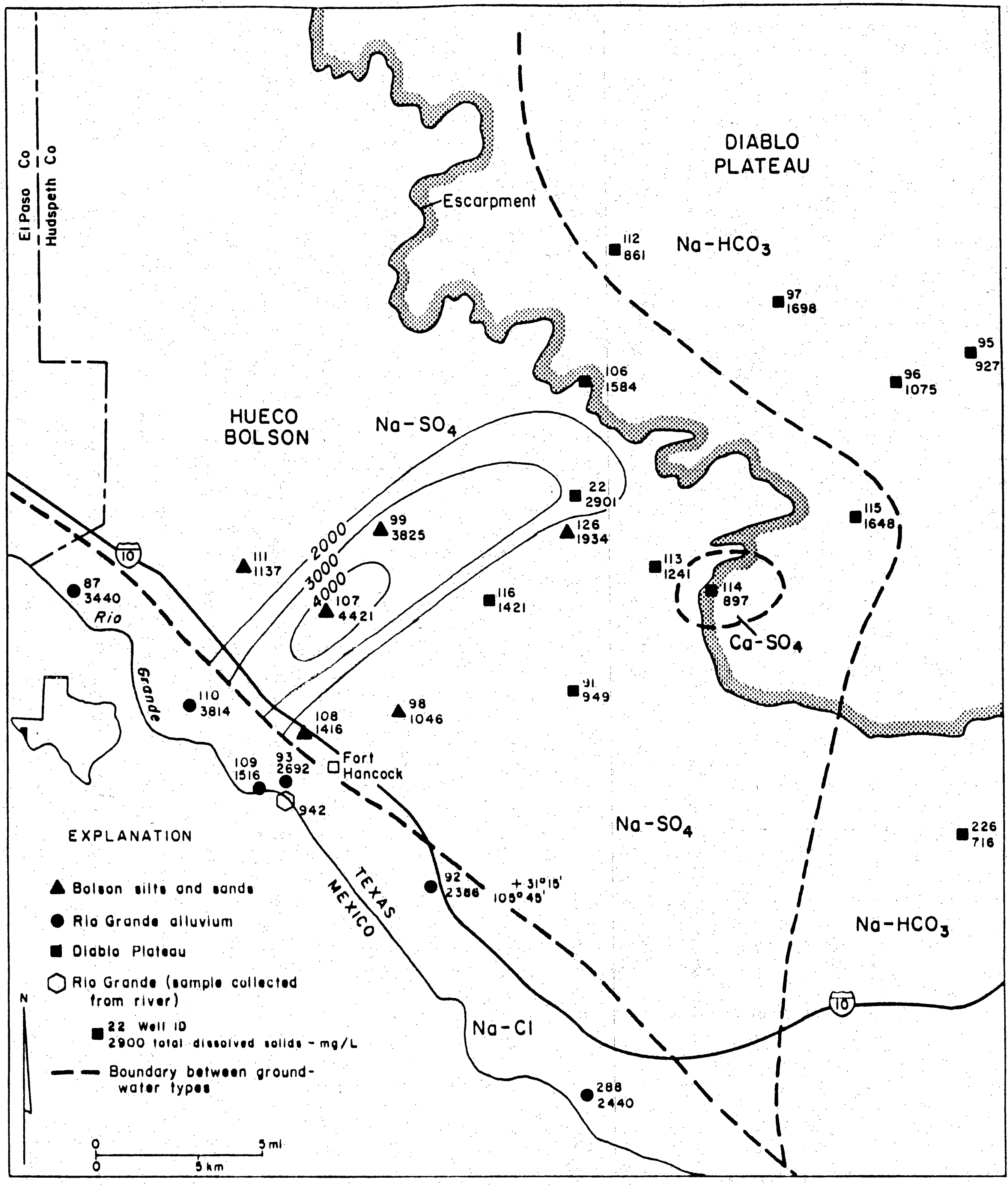

Figure 4. Map of total-dissolved-solids concentrations and predominant cations and anions in ground-water samples. Contour interval for total dissolved solids is 1,000 mg/L; contours are not extended into the Rio Grande aquifer because the salinity of the Rio Grande ground waters varies with irrigation and evaporation rates.

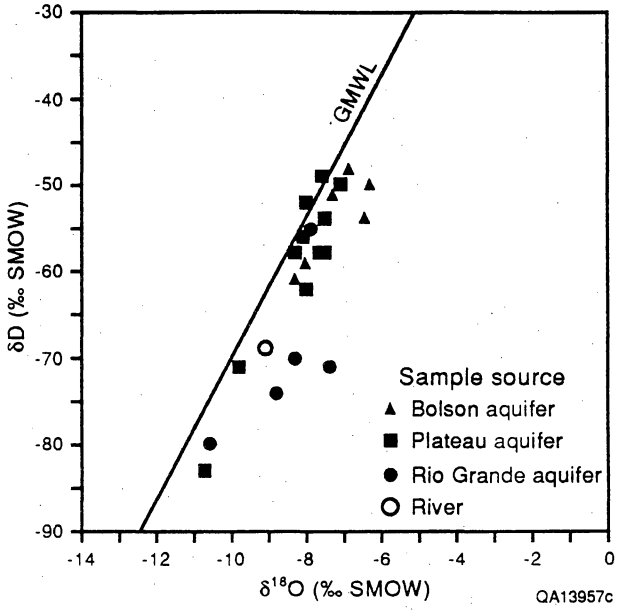

Figure 5. Plot of $\delta^{18}O$ versus δD (‰ SMOW) for ground waters. Line GMWL is the global meteoric water line (Craig, 1961).

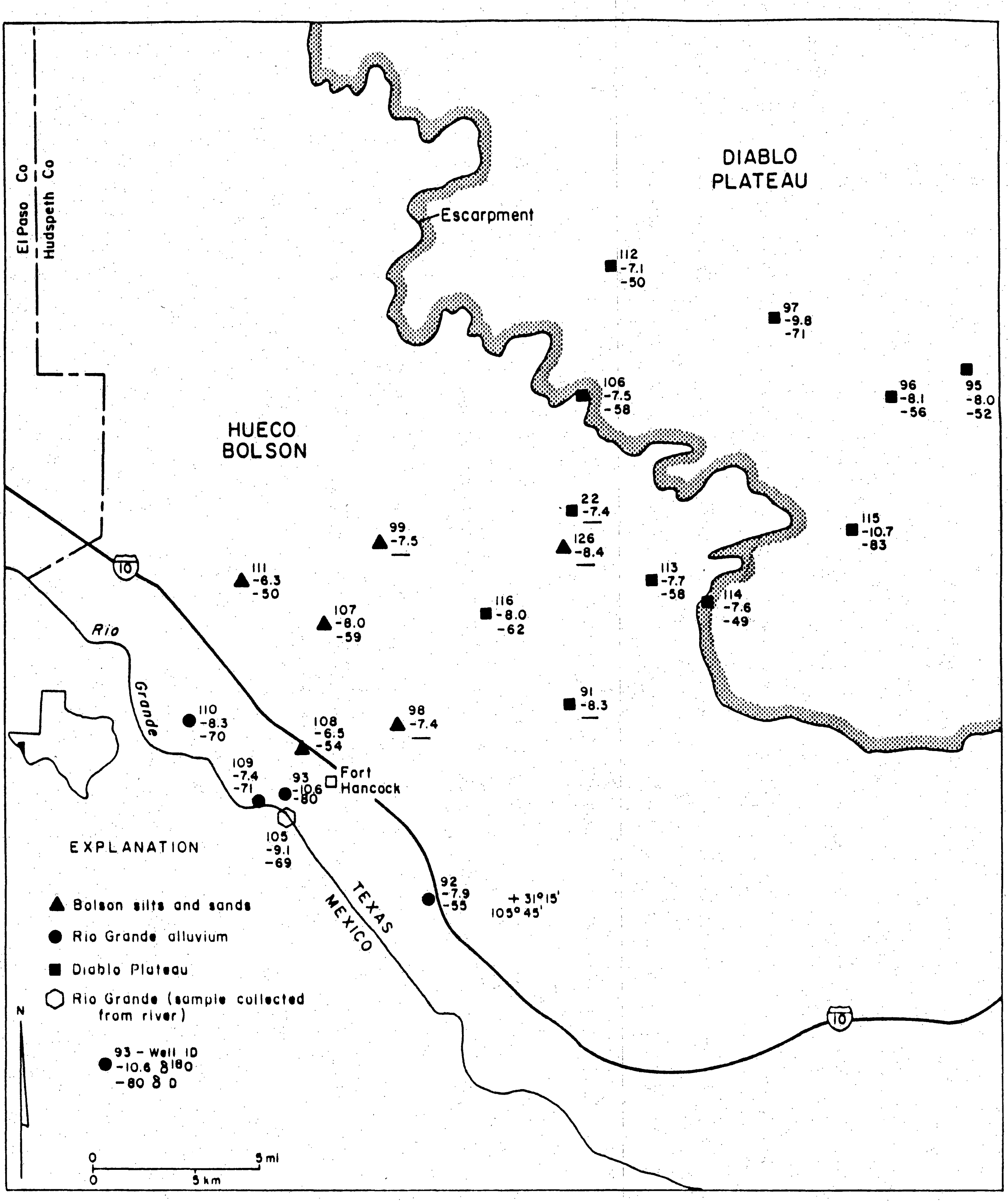

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Figure 6. Map showing distribution of $\delta^{18}O$ and δD in ground waters.

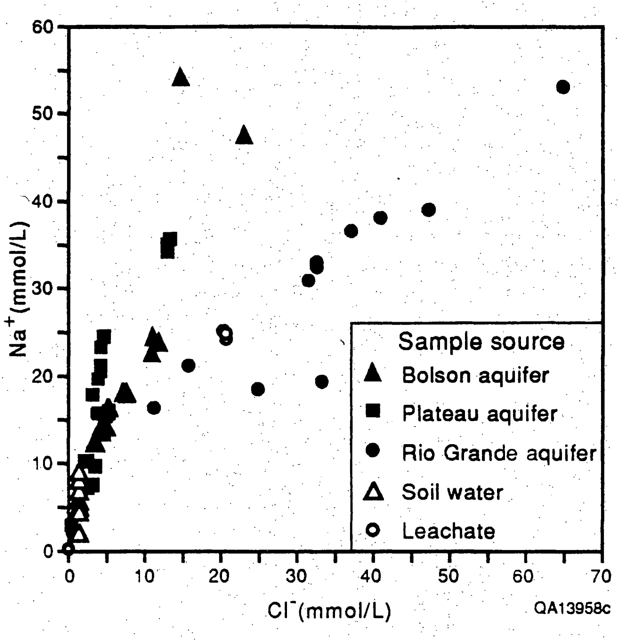

Figure 7. Plot of Na^+ versus Cl^- in ground waters, soil-moisture samples, and soil leachates.

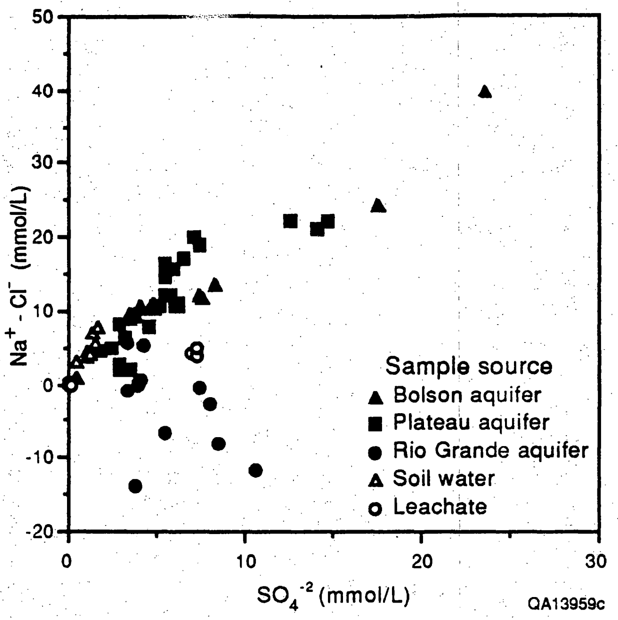

Figure 8. Plot of Na^+-Cl^- versus SO_4^{-2} in ground waters, soil-moisture samples, and soil leachates.

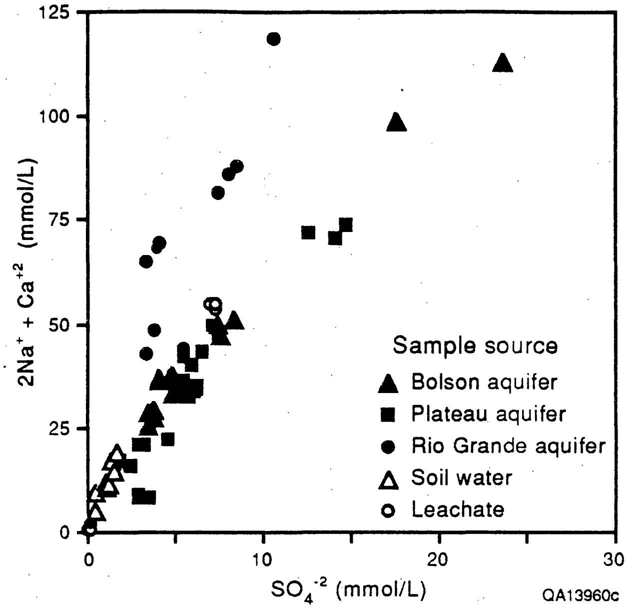

Figure 9. Plot of $2Na^{+}+Ca^{+2}$ versus SO_4^{-2} in ground waters, soil-moisture samples, and soil leachates.

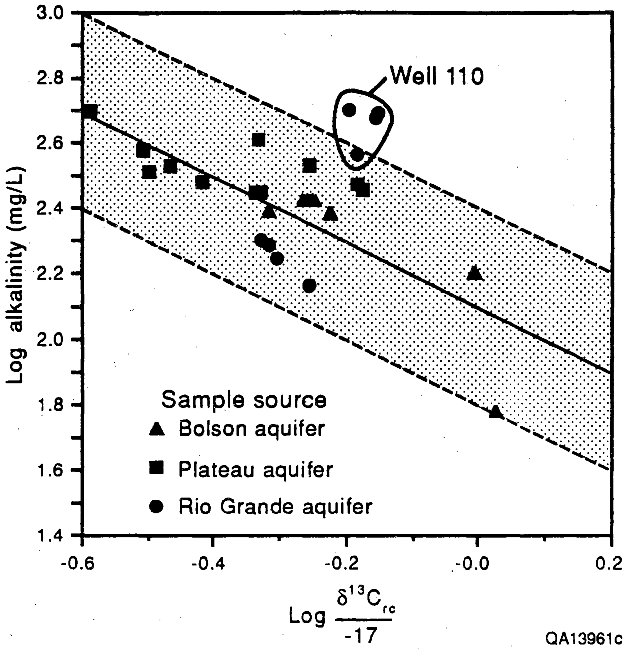

Figure 10. Plot of log alkalinity versus log ($\delta^{13}C_{rc}$/-17) for ground waters. Solid line is result of linear regression analysis; dashed lines indicate envelope of data trend.

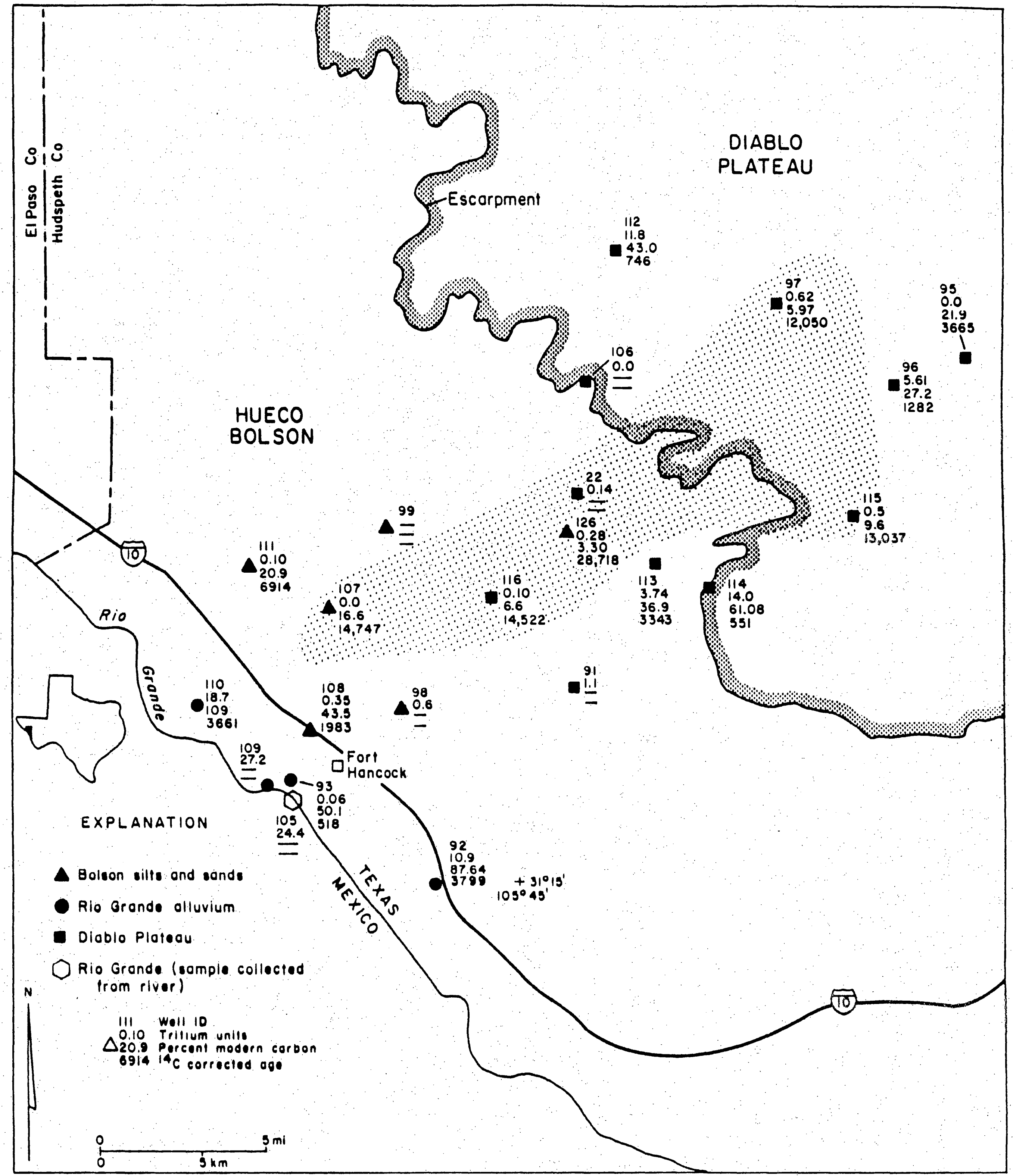

Figure 11. Map showing distribution of representative tritium activities and carbon-14 ages in ground-water samples. Carbon-14 ages in excess of 10,000 yr are found in a band (shaded area) that extends from well 97 (Diablo Plateau aquifer) to well 107 (Hueco Bolson aquifer).

Table 1. Summary of climatic data for El Paso County, Texas (after Orton, 1969, p. 33, 39; National Climatic Data Center, 1985, p. 15).

Temperature	
Maximum (1960)	109° F (43° C)
Minimum (1962)	–8° F (–22° C)
Mean (1951–1980)	63.4° F (17° C)
Precipitation	
Mean (1951–1980)	7.82 inches (20 cm)

Table 2. Comparison of major ion compositions (mg/L) for wells sampled in 1986 and 1988 or 1989, or both.

Well	Date	Na	Ca	HCO_3	SO_4	Cl
114	2/12/86	55	131	284	275	10
	7/06/88	56	145	297	340	12
	10/06/88	68	112	304	280	7
116	2/13/86	362	48.4	278	525	128
	1/18/89	365	53.8	303	530	131
	5/03/89	360	50.3	292	556	127
108	1/21/86	410	34.7	263	395	259
	7/01/88	412	36.2	263	320	269
	10/04/88	415	36.3	265	450	261
	1/17/89	417	38.9	263	460	274
	5/01/89	419	36.0	264	469	260
111	1/22/86	327	26.8	242	360	168
	7/06/88	310	28.7	248	360	155
	10/05/88	373	25.1	279	460	189
	5/02/89	321	27.6	248	340	155

Table 3. Major ionic compositions (mg/L) of samples collected quarterly from summer 1988 through spring 1989.

Well	**Season**	**Na**	**Ca**	**HCO_3**	**SO_4**	**Cl**
97	Summer	355	104	498	500	173
	Fall	361	106	379	580	181
	Winter	371	113	497	600	183
	Spring	363	106	496	602	177
108	Summer	412	36.2	263	400	269
	Fall	415	36.3	265	450	261
	Winter	417	38.9	263	460	274
	Spring	419	36.0	264	469	260
93	Summer	710	132	193	320	1120
	Fall	748	129	177	380	1150
	Winter	747	143	202	380	1153
	Spring	757	136	194	397	1150
110	Summer	842	342	473	720	1320
	Fall	899	383	366	820	1670
	Winter	1220	502	501	1020	2290
	Spring	379	116	347	414	397

Table 4. Results of chemical analyses of soil-moisture samples (mg/L).

Sample	Depth	Date	Ca	Mg	Na	K	HCO_3	SO_4	Cl	Si
17a-1	54	10/24/88	35.6	6.5	117	7.7	237	102	44	NA
17a-2	54	10/24/88	35.6	6.4	123	7.7	223	110	43	NA
17a-3	54	12/06/88	34.4	6.7	129	7.9	260	107	43	36
17a-4	54	1/28/89	34.2	8.0	157	12.0	220	150	46	29
16a-1	78	10/24/88	23.5	5.3	190	4.7	359	132	48	NA
16a-2	78	12/06/88	25.2	5.9	210	5.2	370	154	53	40
16b-3	110	10/24/88	21.1	6.9	102	5.2	230	49	48	NA

Depths in feet
NA = not analyzed

Table 5. Results of leaching surface sediments in distilled water for 15, 240, and 360 min. Concentrations in milligrams solute per gram sediment.

Aquifer	Time	Na	K	Mg	Ca	Fe	Si	SO_4	Cl	HCO_3	NO_3
Diablo Plateau high area	15	0.8	14.3	4.5	42.8	2.5	22.2	10.8	1.4	130	9.4
	240	0.8	21.7	6.9	76.7	0.3	17.8	9.9	1.8	245	8.1
	360	0.6	24.3	7.9	85.3	0.5	19.8	11.7	1.7	281	9.2
Diablo Plateau low area	15	0.1	5.2	2.9	57.2	0.5	10.9	6.1	5.7	120	7.0
	240	bd	7.4	3.9	59.9	0.2	13.3	9.9	1.7	162	7.5
	360	bd	8.2	4.5	65.9	0.1	14.2	9.7	1.4	175	9.4
Bolson arroyo	15	0.3	21.6	7.0	61.2	9.1	57.7	5.8	2.7	170	5.8
	240	0.3	24.0	3.4	48.4	0.5	15.6	6.9	2.5	173	7.0
	360	0.1	26.5	3.5	46.4	0.2	15.3	6.9	2.2	169	5.6
Bolson interarroyo	15	1.0	19.6	10.0	33.9	16.5	92.4	4.3	1.4	965	1.8
	240	1.4	17.8	3.5	48.2	1.3	20.2	6.8	1.3	166	0.1
	360	1.6	19.5	3.6	53.8	0.5	16.6	9.2	2.6	178	1.0
Rio Grande irrigated	15	726	29.6	43.5	262.6	0.1	10.9	900	949	92	188
	240	744	29.1	43.3	257.3	0.5	14.3	876	949	112	170
	360	750	30.8	43.0	257.0	0.1	13.0	913	937	119	181
Rio Grande not irrigated	15	7.5	48.9	30.1	37.4	42.4	220	7.9	5.8	122	6.8
	240	10.8	44.2	8.7	68.8	0.2	15.7	10.9	5.8	295	7.1
	360	9.7	46.5	9.6	72.9	1.0	20.8	10.4	4.5	289	6.0

bd = below detection

Table 6. Mean values and standard deviations (1δ) of saturation indices for ground waters from each principal aquifer. Saturation index values were computed by geochemical modeling program SOLMNEQ (Kharaka and Barnes, 1973).

	Aquifer					
Mineral	**Bolson**		**Diablo Plateau**		**Rio Grande**	
Calcite	–0.022	(0.329)	0.034	(0.200)	0.360	(0.311)
Dolomite	–0.397	(0.583)	–0.216	(0.473)	0.356	(0.579)
Gypsum	–1.432	(0.342)	–1.174	(0.260)	–0.941	(0.296)

Table 7. Results of carbon-14 age calculations.

BEG ID	Date	Alkalinity (mg/L)	Carbon-14 (pmc)	$\delta^{13}C$ ‰	K_1	Age(K_1) (yr)	K_2	Age (K_2) (yr)
				Diablo Plateau Aquifer				
107	1/22/86	161	16.1	−16.8	0.807	13,078	0.988[a]	14,748
108	1/21/86	263	61.0	−9.6	0.494	neg	0.565[a]	neg
108	7/1/88	263	43.5	−9.4	0.494	1,056	0.533[a]	1,983
108	1/17/89	263	56.3	−9.2	0.494	neg	0.541[a]	neg
111	1/22/86	242	21.8	−10.1	0.537	7,456	0.594[a]	8,288
111	7/6/88	248	20.9	−8.2	0.524	7,602	0.482[a]	6,914
126	4/23/86	60	3.3	−18.1	1.000	28,201	1.065[a]	28,719
				Hueco Bolson Aquifer				
95	6/30/88	336	21.9	−5.8	0.387	4,705	0.354[a]	3,665
96	6/30/88	325	27.2	−5.4	0.400	3,188	0.318[a]	1,283
97	6/30/88	498	6.0	−4.4	0.261	12,197	0.256[a]	12,051
97	10/6/88	379	7.4	−5.3	0.343	12,679	0.312[a]	11,889
97	1/26/89	497	6.6	−4.4	0.262	11,384	0.259[a]	11,297
112	2/13/86	282	43.0	−8.0	0.461	575	0.471[a]	746
113	2/11/86	336	36.9	−9.4	0.387	392	0.363[b]	neg
114	2/12/86	284	60.0	−11.3	0.458	neg	0.504[b]	neg
114	7/6/88	297	61.1	−11.1	0.438	neg	0.489[b]	neg
115	2/14/86	411	9.6	−7.9	0.316	9,857	0.252[b]	7,973
116	2/13/86	278	8.9	−7.8	0.468	13,715	0.459[a]	13,558
116	1/18/89	303	6.6	−6.5	0.429	15,475	0.382[a]	14,523
				Rio Grande Aquifer				
92	6/28/88	145	87.6	−9.4	0.897	188	1.046[b]	1,459
93	7/5/88	193	51.9	−8.2	0.674	2,163	0.480[a]	neg
93	10/4/88	177	52.9	−8.4	0.734	2,713	0.993[c]	4,694
93	1/17/89	202	50.1	−8.0	0.644	2,070	0.471[a]	neg

K_1 from equation (11)

K_2 from equation (12):

[a] $=\delta^{13}C_{min} = 0$ ‰ , $\delta^{13}C_{rc} = -17$ ‰

[b] $=\delta^{13}C_{min} = -4.5$ ‰, $\delta^{13}C_{rc} = -9$ ‰

[c] $=\delta^{13}C_{min} = 0$ ‰, $\delta^{13}C_{rc} = -9$ ‰

neg = calculated age has negative value

Ages calculated from equation (13)

APPENDICES

Appendix 1. Results of field measurements of unstable parameters and concentrations of major ions (mg/L) in ground waters.

BEG ID	TWC ID	Date	T (°C)	Field pH	Lab pH	Eh (mv)	Dissolved oxygen	Na	Mg	Ca	K	Si	Field alkalinity	Lab alkalinity	Cl	SO_4	NO_3	TDS
Diablo Plateau Aquifer																		
22	48-35-4	10/5/88	NA	NA	7.49	NA	NA	805	13.6	73.7	6.8	6.4	NA	72	456	1210	23.9	2653
22	48-35-4	3/16/89	25.0	8.25	7.54	30	3.00	784	16.0	100.0	5.7	7.2	54	64	461	1360	10.9	2806
22	48-35-4	4/24/89	20.0	7.85	7.69	240	4.70	820	16.0	103.0	5.2	7.5	56	56	473	1410	7.6	2901
22	48-35-4	11/17/89	22.9	8.19	8.22	–120	1.9	875	13.3	57.9	7.0	2.3	61	68	452	1390	4.1	2895
91	48-43-1	4/28/89	32.0	7.60	8.14	290	3.60	234	12.4	32.9	3.0	7.7	290	311	71	270	4.4	949
95	48-36-3	6/30/88	20.0	7.60	8.15	NA	NA	166	26.9	62.6	3.0	7.9	344	336	88	230	32.7	927
96	48-36-2	6/30/88	27.0	7.40	8.18	NA	NA	221	28.0	64.0	2.6	9.7	336	325	118	300	23.9	1075
97	48-28-7	6/30/88	27.0	7.00	8.09	NA	NA	355	45.1	104.0	4.4	11.1	512	498	173	500	10.8	1698
97	48-28-7	10/6/88	20.0	7.20	8.12	400	5.00	361	49.0	106.0	5.1	11.6	512	379	181	580	7.2	1680
97	48-28-7	1/26/89	14.0	6.70	7.89	NA	3.60	371	52.1	113.0	5.3	11.9	495	497	183	600	0.4	1842
97	48-28-7	5/2/89	21.0	7.06	8.09	300	4.00	363	48.2	106.0	5.0	11.1	488	496	177	602	<0.8	1816
97	48-28-7	8/17/89	26.2	7.02	8.13	147	NA	362	46.7	105.0	5.7	12.4	488	496	182	549	<0.8	1784
106	48-35-401	1/22/86	9.0	NA	8.61	NA	NA	475	22.9	26.8	4.6	NA	NA	501	148	520	11.3	1718
106	48-35-401	6/29/88	26.0	8.50	8.59	NA	NA	411	19.8	34.7	3.8	7.4	466	454	117	530	17.3	1584
106	48-35-401	10/5/88	23.0	8.30	8.63	NA	NA	562	25.6	28.2	11.4	8.7	701	579	158	680	10.3	2061
106	48-35-401	1/26/89	11.5	8.15	8.28	NA	6.60	535	28.3	37.2	5.3	10.1	561	510	147	720	4.6	2004
106	48-35-401	5/3/89	12.0	8.70	8.11	NA	3.24	490	24.9	32.0	7.5	8.5	NA	542	147	629	10.8	1888
106	48-35-401	8/15/89	27.3	8.47	8.38	NA	NA	359	17.7	30.1	4.5	8.2	436	434	108	433	<0.8	1415
106	48-35-401	11/18/89	16.8	8.44	8.38	NA	9.66	394	18.8	31.5	4.7	8.5	458	434	101	428	9.9	1450
112	48-27-801	2/13/86	14.0	NA	8.14	NA	NA	177	19.3	61.6	5.4	NA	NA	282	116	168	26.3	862
113	48-35-801	2/11/86	20.0	NA	8.01	NA	NA	237	43.1	77.1	3.4	NA	NA	336	88	438	11.8	1241
114	48-35-901	2/12/86	11.0	NA	7.61	NA	NA	55	24.6	131.0	1.5	NA	NA	284	10	275	11.3	801
114	48-35-901	7/6/88	25.0	7.20	8.06	NA	NA	56	28.0	145.0	2.1	7.9	306	297	12	340	14.0	897
114	48-35-901	10/6/88	21.0	7.20	8.48	90	2.32	68	27.8	112.0	1.8	8.2	323	304	7	280	11.8	818
115	48-36-801	2/14/86	19.0	NA	7.92	NA	NA	454	22.1	37.3	7.4	NA	NA	411	137	570	<0.5	1649

Appendix 1. (continued)

BEG ID	TWC ID	Date	T (°C)	Field pH	Lab pH	Eh (mv)	Dissolved oxygen	Na	Mg	Ca	K	Si	Field alkalinity	Lab alkalinity	Cl	SO_4	NO_3	TDS
116	48-34-901	2/13/86	14.0	NA	7.90	NA	NA	362	15.3	48.4	3.5	NA	NA	278	128	525	<0.5	1369
116	48-34-901	1/18/89	23.0	7.50	8.02	NA	0.60	365	17.1	53.8	3.4	8.5	274	303	131	530	0.3	1421
116	48-34-901	5/3/89	23.0	NA	8.00	NA	1.04	360	16.0	50.3	3.4	7.9	NA	292	127	556	<0.8	1419
116	48-34-901	8/23/89	23.2	7.66	8.14	–163	<1	325	14.5	46.9	7.91	7.9	288	288	130	467	<0.8	1308

Hueco Bolson Aquifer

BEG ID	TWC ID	Date	T (°C)	Field pH	Lab pH	Eh (mv)	Dissolved oxygen	Na	Mg	Ca	K	Si	Field alkalinity	Lab alkalinity	Cl	SO_4	NO_3	TDS
98	48-42-5	5/11/89	32.0	7.93	7.84	260	5.30	288	7.2	20.8	3.8	11.8	336	252	125	335	7.4	1046
98	48-42-5	8/17/89	26.9	8.02	8.16	167	NA	243	6.7	18.5	4.0	11.0	124	253	106	245	<0.8	967
98	48-42-5	11/18/89	25.8	7.99	7.97	–37	2.50	265	6.1	18.1	3.8	11.8	317	250	99	282	5.0	961
99	48-34-8	12/5/88	20.5	8.95	7.33	–150	0.00	1094	24.7	151.0	6.9	0.6	27	29	818	1690	7.8	3825
107	48-42-101	1/22/86	24.5	NA	7.50	NA	NA	1250	35.3	169.0	7.7	NA	NA	161	520	2270	1.3	4422
107	48-42-101	6/29/88	26.0	8.70	8.44	NA	NA	1200	23.1	88.7	8.2	8.5	231	212	533	1870	0.6	3951
107	48-42-101	9/26/89	27.1	7.64	7.71	70	<1	1430	35.7	173	11.7	14.0	117	122	474	2660	<0.8	4950
108	48-42-404	1/21/86	22.5	NA	7.97	NA	NA	410	11.9	34.7	4.5	NA	NA	263	259	395	5.1	1388
108	48-42-404	7/1/88	26.0	7.50	8.11	NA	NA	412	11.5	36.2	4.0	15.8	273	263	269	400	6.4	1416
108	48-42-404	10/4/88	24.0	7.90	8.48	350	1.75	415	12.1	36.3	4.6	16.6	277	265	261	450	5.5	1465
108	48-42-404	1/17/89	18.0	7.96	7.88	120	3.30	417	13.1	38.9	4.6	16.5	244	263	274	460	5.4	1493
108	48-42-404	5/1/89	24.0	7.82	8.04	280	2.42	419	11.9	36.0	4.4	16.9	256	264	260	469	3.3	1486
108	48-42-404	8/16/89	24.4	7.85	7.96	224	NA	395	11.3	34.7	5.1	16.6	284	261	269	354	1.0	1373
108	48-42-494	11/17/89	23.8	7.75	7.97	146	2.78	435	12.1	36.2	5.0	17.3	265	262	254	446	<0.8	1495
111	48-33-901	1/22/86	21.0	NA	8.09	NA	NA	327	10.5	26.8	4.2	NA	NA	242	168	360	11.4	1154
111	48-33-901	7/6/88	26.0	7.70	8.14	NA	NA	310	11.6	28.7	4.2	14.5	256	248	155	360	12.8	1137
111	48-33-901	10/5/89	18.0	8.50	8.34	NA	NA	373	13.5	25.1	4.9	17.4	294	279	189	460	7.5	1364
111	48-33-901	5/2/89	27.0	7.60	8.00	300	2.54	321	11.5	27.6	4.3	14.8	233	248	155	340	10.9	1126
111	48-33-901	8/22/89	26.2	7.84	7.99	80	1.80	298	10.9	27.1	4.24	14.4	233	240	166	330	2.39	1116
126	48-35-701	4/23/86	17.0	NA	7.69	NA	NA	549	6.9	70.7	4.4	NA	NA	60	416	710	18.3	1850
126	48-35-701	1/19/89	21.0	8.24	7.65	NA	1.70	523	8.2	62.5	4.1	10.2	62	70	386	730	16.7	1805
126	48-35-701	4/27/89	20.0	8.23	7.90	260	1.98	567	7.9	67.2	4.0	10.0	51	64	398	804	6.6	1934
126	48-35-701	8/23/89	23.4	8.24	7.67	142	1.90	518	7.1	63.0	16.9	9.6	54	59	420	735	7.7	1857
126	48-35-701	11/19/89	21.1	8.26	7.92	105	2.20	584	7.6	66.2	4.9	10.7	177	58	402	749	12.3	1925

Rio Grande Aquifer

BEG ID	TWC ID	Date	T (°C)	Field pH	Lab pH	Eh (mv)	Dissolved oxygen	Na	Mg	Ca	K	Si	Field alkalinity	Lab alkalinity	Cl	SO_4	NO_3	TDS
92	48-50-2	5/6/86	24.0	NA	7.79	NA	NA	445	114.0	403.0	15.7	NA	NA	119	1180	371	28.0	2683
92	48-50-2	6/28/88	25.0	6.80	7.84	NA	NA	422	87.2	280.0	11.7	17.4	164	145	881	530	26.8	2386

Appendix 1. (continued)

BEG ID	TWC ID	Date	T (°C)	Field pH	Lab pH	Eh (mv)	Dissolved oxygen	Na	Mg	Ca	K	Si	Field alkalinity	Lab alkalinity	Cl	SO_4	NO_3	TDS
93	48-42-4	7/5/88	24.0	7.55	7.97	NA	NA	710	35.7	132.0	6.5	12.6	197	193	1120	320	0.7	2534
93	48-42-4	10/4/88	25.0	7.70	8.15	340	0.60	748	37.2	129.0	7.0	13.3	206	177	1150	380	<0.2	2646
93	48-42-4	1/17/89	13.0	7.69	7.82	NA	3.08	747	41.2	143.0	7.3	13.5	178	202	1153	380	4.1	2692
93	48-42-4	4/27/89	21.0	7.67	8.03	290	3.96	757	38.6	136.0	7.3	12.8	201	194	1150	397	<0.8	2697
93	48-42-4	8/16/89	25.1	7.55	7.86	–85	NA	782	34.9	123.0	8.2	13.9	191	198	1180	315	<0.8	2679
93	48-42-4	11/16/89	17.3	7.58	7.86	–109	1.88	792	35.6	122.0	8.2	14.2	201	199	1090	351	<0.8	2636
105	Rio Grande	1/21/86	11.0	NA	7.80	NA	NA	186	18.5	86.9	7.8	NA	NA	214	185	234	6.6	942
109	48-41-618	1/21/86	NA	NA	8.07	NA	NA	486	23.9	23.8	14.6	NA	NA	96	555	315	<0.5	1517
110	48-41-624	1/21/86	19.0	NA	7.69	NA	NA	881	91.7	387.0	12.8	NA	NA	495	1450	770	<0.5	3604
110	48-41-624	7/5/88	28.0	7.20	7.85	NA	NA	842	78.5	342.0	11.4	17.5	495	473	1320	720	14.0	3814
110	48-41-624	10/5/88	21.0	7.20	7.81	–30	NA	899	91.8	383.0	12.4	17.6	516	366	1670	820	<0.2	4271
110	48-41-624	1/18/89	19.5	6.93	7.89	NA	0.70	1220	137.0	502.0	14.8	17.4	508	501	2290	1020	2.0	5719
110	48-41-624	5/1/89	20.0	7.42	7.83	–80	0.78	379	27.1	116.0	7.3	16.3	329	347	397	414	<0.8	1707
110	48-41-624	8/16/89	20.9	7.43	7.92	–180	NA	230	16.1	72.7	5.9	16.4	259	263	228	242	<0.8	1098
110	48-41-624	11/16/89	23.1	7.33	7.75	–162	4.40	281	19.7	86.4	6.8	18.1	281	270	240	307	<0.8	1256
72		11/17/89	22.7	8.84	8.79	204	2.82	639	18.1	76.6	7.7	10.5	51	69	505	841	4.3	1696
73		11/19/89	25.4	7.97	8.06	–4	2.30	474	13.0	48.7	5.6	7.5	141	143	272	630	1.7	1614
94		10/3/89	28.5	7.51	8.03	–39	<1	245	12.5	34.6	4.3	6.3	302	312	74	273	2.0	980

NA = not analyzed

Appendix 2. Concentrations of minor and trace species (mg/L) in ground waters.

BEG ID	Date	Sr	Ba	Fe	Mn	Zn	Li	B	Br	I	F	NH_4	Cs	Hg	U (µg/L)	Cyanide	Sulfide	TOC
Diablo Plateau Aquifer																		
22	10/5/88	3.58	0.02	<0.02	0.02	0.05	0.15	1.08	2.20	0.1	3.60	0.2	NA	NA	NA	NA	NA	NA
22	3/16/89	3.59	0.03	0.05	0.05	0.11	0.15	1.68	2.50	0.2	1.70	<0.2	P	P	P	NA	NA	NA
22	4/24/89	4.28	<0.01	<0.02	0.04	<0.03	0.12	1.24	2.70	0.3	3.10	<0.2	0.5	<2	4.3	<0.01	<0.05	9.6
22	11/17/89	3.66	0.02	0.09	0.02	0.15	0.20	2.33	3.10	<0.1	3.57	1.07	NA	NA	NA	NA	NA	NA
91	4/28/89	1.54	0.02	0.27	0.03	0.44	0.05	0.49	0.50	0.1	4.70	<0.2	0.5	<2	11.9	<0.01	<0.05	<0.1
95	6/30/88	1.79	0.02	<0.02	<0.02	0.05	0.11	0.55	0.70	0.1	4.00	<0.2	0.9	<2	13.3	NA	NA	NA
96	6/30/88	1.81	0.02	<0.02	<0.02	0.32	0.12	0.65	0.90	0.1	4.50	<0.2	0.5	<2	16.4	NA	NA	NA
97	6/30/88	3.34	0.02	<0.02	<0.02	0.07	0.16	0.84	1.40	0.2	2.80	<0.2	1.1	<2	29.4	NA	NA	NA
97	10/6/88	3.62	0.02	<0.02	<0.02	0.06	0.11	0.88	1.40	0.1	2.51	<0.2	1.2	<2	29.8	NA	NA	NA
97	1/26/89	3.40	0.02	0.03	<0.02	0.05	0.11	0.93	1.60	0.3	3.85	0.6	1.2	<2	29.8	NA	NA	NA
97	5/2/89	3.42	0.02	<0.02	<0.02	0.04	0.10	0.82	1.60	0.8	2.70	<0.2	P	P	P	<0.01	<0.05	13.1
106	1/22/86	1.63	0.02	0.02	NA	NA	0.13	NA	1.34	NA	5.57	NA	NA	NA	NA	NA	NA	NA
106	6/29/88	1.60	0.02	<0.02	<0.02	0.03	0.17	1.28	0.70	0.3	4.30	0.4	0.4	<2	26.6	NA	NA	NA
106	10/5/88	1.97	0.03	0.08	<0.02	<0.03	0.16	1.99	1.00	0.5	5.03	0.4	0.4	8	29.8	NA	NA	NA
106	1/26/89	1.89	0.02	0.03	<0.02	<0.03	0.15	1.62	1.00	0.1	8.59	<0.4	0.4	<2	31.6	NA	NA	NA
106	5/3/89	1.78	0.03	0.15	<0.02	<0.03	0.13	1.42	0.90	0.9	4.70	<0.2	P	P	P	<0.01	<0.05	29.2
106	11/18/89	1.61	0.02	0.02	<0.02	0.10	0.13	1.88	0.79	0.4	4.53	<0.2	NA	NA	NA	NA	NA	NA
112	2/13/86	1.72	0.02	0.10	NA	NA	0.06	NA	1.14	NA	2.79	NA	NA	NA	NA	NA	NA	NA
113	2/11/86	3.90	0.03	0.71	NA	NA	0.05	NA	0.77	NA	1.60	NA	NA	NA	NA	NA	NA	NA
114	2/12/86	7.50	0.03	<0.02	NA	NA	0.03	NA	0.44	NA	0.90	NA	NA	NA	NA	NA	NA	NA
114	7/6/88	7.49	0.04	0.04	<0.02	0.28	0.12	<0.23	0.20	<0.1	0.80	0.2	<0.2	<2	3.8	NA	NA	NA
114	10/6/88	8.59	0.04	0.02	<0.02	0.32	0.06	0.31	<0.10	0.4	0.80	<0.2	<0.2	9	5	NA	NA	NA
115	2/14/86	3.32	0.03	2.15	NA	NA	0.12	NA	1.15	NA	3.10	<0.5	NA	NA	NA	NA	NA	NA
116	2/13/86	2.87	0.12	0.20	NA	NA	0.07	NA	1.10	NA	4.30	NA	NA	NA	NA	NA	NA	NA
116	1/18/89	2.79	0.01	0.63	<0.02	0.30	0.07	0.84	0.80	0.2	5.03	<0.4	<0.2	<2	14.2	NA	NA	NA

Appendix 2. (continued)

BEG ID	Date	Sr	Ba	Fe	Mn	Zn	Li	B	Br	I	F	NH_4	Cs	Hg	U (µg/L)	Cyanide	Sulfide	TOC
116	5/3/89	2.90	0.01	0.70	<0.02	0.35	0.07	0.75	0.80	0.2	2.20	<0.2	0.5	<2	14.4	<0.01	<0.05	0.1
Hueco Bolson Aquifer																		
98	5/11/89	0.45	0.03	0.05	0.04	0.12	0.11	1.14	0.70	1.6	1.10	<0.2	0.5	<2	21.5	<0.01	<0.05	20.9
98	11/18/89	0.56	0.03	0.15	0.04	0.20	0.11	1.29	0.41	0.31	2.73	<0.2	NA	NA	NA	NA	NA	NA
99	12/5/88	4.65	0.06	0.02	0.14	0.07	0.23	1.52	3.30	0.2	2.51	<0.4	<0.4	<4	<0.4	NA	NA	NA
107	1/22/86	3.20	0.02	0.04	NA	NA	0.26	NA	2.66	NA	1.05	NA	NA	NA	NA	NA	NA	NA
107	6/29/88	2.07	0.02	0.03	<0.02	0.07	0.35	1.66	2.60	0.3	2.80	0.4	<0.2	<2	15.2	NA	NA	NA
107	9/26/89	3.49	0.03	0.04	0.14	0.17	0.39	4.18	2.17	0.4	0.95	<0.2	NA	NA	NA	NA	NA	NA
108	1/21/86	1.01	0.04	0.05	NA	NA	0.10	NA	1.25	NA	2.37	NA	NA	NA	NA	NA	NA	NA
108	7/1/88	1.37	0.02	0.02	<0.02	<0.03	0.17	0.59	0.90	0.1	2.20	0.4	<0.2	<2	20	NA	NA	NA
108	10/4/88	1.10	0.02	<0.02	<0.02	<0.03	0.12	0.63	1.00	0.2	1.90	0.3	<0.2	<2	24.6	NA	NA	NA
108	1/17/89	1.05	0.03	<0.02	<0.02	<0.03	0.11	0.66	1.70	<0.1	2.77	<0.4	<0.2	<2	22.6	NA	NA	NA
108	5/1/89	1.07	0.02	0.02	<0.02	<0.03	0.11	0.63	1.00	2.4	2.30	0.5	<0.2	<2	21.1	<0.01	<0.05	1.3
108	11/17/89	1.14	0.03	0.13	<0.02	0.04	0.14	1.27	0.99	0.17	2.13	<0.2	NA	NA	NA	NA	NA	NA
111	1/22/86	0.81	0.02	0.49	NA	NA	0.10	NA	1.01	NA	2.03	NA	NA	NA	NA	NA	NA	NA
111	7/6/88	0.78	0.02	0.03	0.03	0.11	0.15	0.54	0.60	0.1	3.20	0.2	<0.2	<2	15.8	NA	NA	NA
111	10/5/99	0.88	0.02	<0.02	<0.02	0.04	0.11	0.71	0.60	0.1	0.68	<0.2	<0.2	6	20.6	NA	NA	NA
111	5/2/89	0.80	0.01	0.02	0.02	0.05	0.09	0.54	0.80	0.1	2.60	<0.2	0.5	<2	16.7	<0.01	<0.05	19.5
126	4/23/86	8.30	0.19	0.13	NA	NA	0.10	NA	2.10	NA	4.30	NA	NA	NA	NA	NA	NA	NA
126	1/19/89	5.40	0.03	0.03	<0.02	<0.03	0.10	1.02	1.70	0.1	4.37	<0.4	<0.2	<2	2.9	NA	NA	NA
126	4/27/89	7.35	0.03	<0.02	<0.02	0.06	0.09	1.01	2.20	<0.1	2.00	<0.2	<0.2	<2	2.4	<0.01	<0.05	1.4
126	11/19/89	7.76	0.03	0.02	<0.02	0.05	0.13	1.72	3.43	<0.1	4.26	<0.2	NA	NA	NA	NA	NA	NA
Rio Grande Aquifer																		
92	5/6/86	9.70	0.42	5.07	NA	NA	0.22	NA	1.90	NA	1.40	NA	NA	NA	NA	NA	NA	NA
92	6/28/88	8.54	0.05	<0.02	<0.02	0.99	0.23	0.27	1.50	<0.1	1.40	0.2	<0.2	<2	10.0	NA	NA	NA
93	7/5/88	2.22	0.07	<0.02	0.04	0.03	0.28	0.35	0.90	<0.1	1.20	0.2	<0.2	<2	<0.2	NA	NA	NA
93	10/4/88	2.30	0.07	<0.02	0.02	0.03	0.20	0.43	0.90	<0.1	0.86	0.2	<0.2	<2	<0.2	NA	NA	NA
93	1/17/89	2.24	0.07	<0.02	0.03	<0.03	0.19	0.44	1.00	0.1	1.78	0.4	<0.2	<2	<0.2	NA	NA	NA

Appendix 2. (continued)

BEG ID	Date	Sr	Ba	Fe	Mn	Zn	Li	B	Br	I	F	NH_4	Cs	Hg	U (µg/L)	Cyanide	Sulfide	TOC
93	4/27/89	2.42	0.06	<0.02	0.03	<0.03	0.19	0.37	1.00	0.8	1.10	<0.2	<0.2	<2	<0.2	<0.01	<0.05	41.4
93	11/16/89	2.24	0.07	0.16	0.31	0.09	0.24	1.55	0.77	0.23	1.09	<0.20	NA	NA	NA	NA	NA	NA
105	1/21/86	1.36	0.06	0.69	NA	NA	0.11	NA	0.22	NA	0.66	NA	NA	NA	NA	NA	NA	NA
109	1/21/86	1.43	0.01	0.02	NA	NA	0.21	NA	0.59	NA	0.39	NA	NA	NA	NA	NA	NA	NA
110	1/21/86	6.69	0.06	1.35	NA	NA	0.26	NA	2.27	NA	0.61	NA	NA	NA	NA	NA	NA	NA
110	7/5/88	5.56	0.05	1.78	1.62	0.03	0.36	0.48	1.20	0.2	0.80	0.2	<0.2	<2	2.8	NA	NA	NA
110	10/5/88	6.99	0.05	2.31	1.82	0.03	0.28	0.57	1.40	0.2	0.45	0.2	<0.4	<4	3.4	NA	NA	NA
110	1/18/89	10.60	0.06	2.74	0.99	<0.03	0.33	0.69	2.00	0.2	0.80	<0.4	<0.2	<2	2.2	NA	NA	NA
110	5/1/89	1.93	0.02	0.51	0.52	<0.03	0.15	0.30	0.50	0.4	0.80	<0.2	<0.2	<2	0.3	<0.01	<0.05	19.2
110	11/16/89	1.40	0.03	0.66	0.46	0.05	0.16	0.86	0.37	0.13	0.83	<0.2	NA	NA	NA	NA	NA	NA
72	11/17/89	4.40	0.03	0.05	0.02	0.07	0.17	2.21	2.39	<0.10	2.13	1.07	NA	NA	NA	NA	NA	NA
73	11/19/89	3.26	0.03	<0.02	<0.02	0.07	0.11	1.53	1.26	0.42	2.88	<0.20	NA	NA	NA	NA	NA	NA
94	10/3/89	1.51	0.02	0.05	0.08	0.70	0.08	1.17	0.26	0.34	4.53	0.57	NA	NA	NA	NA	NA	NA

NA = not analyzed
P = analysis pending

Appendix 3. Isotopic compositions of ground waters.

BEG ID	Date	Modern carbon (%)	δ^{13}C (‰)	Tritium (TU)	δ^{18}O (‰)	δD (‰)	δ^{34}S (‰)
Diablo Plateau Aquifer							
22	10/5/88	NA	NA	NA	NA	NA	NA
22	3/16/89	P	P	0.14	–7.9	P	4.6
22	4/24/89	P	P	0.00	–7.4	P	4.5
22	11/17/89	P	–12.9	–0.09	P	P	4.4
91	4/28/89	13.40 ± 0.7	–5.30	1.10	–8.3	P	6.5
94	10/3/89	P	–6.50	1.22	P	P	7.6
95	6/30/88	21.90 ± 1.10	–5.80	0.00	–8.0	–52.0	3.3
96	6/30/88	27.20 ± 0.40	–5.40	5.61	–8.1	–56.0	3.4
97	6/30/88	5.97 ± 0.28	–4.36	0.62	–9.8	–71.0	4.9
97	10/6/88	7.40 ± 0.40	–5.30	0.53	NA	NA	NA
97	1/26/89	6.60 ± 0.30	–4.40	0.59	–10.5	P	5.1
97	5/2/89	10.10 ± 0.70	–4.80	0.51	–10.3	P	5.1
97	8/17/89	NA	NA	NA	P	P	NA
106	1/22/86	NA	NA	<0.80	–7.5	–58.0	–1.8
106	6/29/88	NA	NA	NA	–8.3	–58.0	–1.4
106	10/5/88	NA	NA	NA	NA	NA	NA
106	1/26/89	NA	NA	2.64	–6.8	P	–3.5
106	5/3/89	NA	P	2.85	–7.0	P	–2.4
106	8/15/89	NA	NA	NA	P	P	NA
106	11/18/89	NA	NA	NA	P	P	NA
112	2/13/86	43.00	–8.00	11.80	–7.1	–50.0	5.8
113	2/11/86	36.90 ± 0.37	–9.40	3.74	–7.7	–58.0	5.2
114	2/12/86	60.00 ± 0.42	–11.30	20.67	–7.5	–54.0	10.9
114	7/6/88	61.08 ± 0.80	–11.10	14.00	–7.6	–49.0	11.4
114	10/6/88	61.80 ± 1.8	–10.80	11.60	NA	NA	NA
115	2/14/86	9.60 ± 0.36	–7.90	0.50	–10.7	–83.0	–0.5
116	2/13/86	8.90 ± 0.36	–7.80	1.52	–8.0	–62.0	7.0
116	1/18/89	6.60 ± 0.30	–6.50	0.00	–9.0	P	7.5
116	5/3/89	11.90 ± 0.70	–6.50	0.40	–9.4	P	7.2
116	8/23/89	NA	NA	NA	P	P	NA
Hueco Bolson Aquifer							
72	11/17/89	P	–9.10	–0.04	P	P	6.5
73	11/19/89	P	–6.30	0.02	P	P	3.2
98	5/11/89	24.50 ± 0.70	–8.70	0.60	–7.4	P	5.5
98	8/17/89	NA	NA	NA	P	P	NA
98	11/18/89	NA	NA	NA	P	P	NA
99	12/5/88	P	P	NA	–7.5	P	8.4
107	1/22/86	16.60	–16.80	<0.80	–8.0	–59.0	1.0
107	6/29/88	NA	NA	NA	–0.5	–28.5	3.9
107	9/26/89	P	–13.0	–0.03	P	P	1.8

Appendix 3. (continued)

BEG ID	Date	Modern carbon (%)	$\delta^{13}C$ (‰)	Tritium (TU)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{34}S$ (‰)
108	1/21/86	61.00 ± 0.42	–9.60	<0.80	–6.9	–48.0	3.8
108	7/1/88	43.50 ± 1.80	–9.40	0.35	–6.5	–54.0	5.3
108	10/4/88	52.30 ± 1.3	–9.20	<0.08	NA	NA	NA
108	1/17/89	56.30 ± 1.00	–9.20	NA	–7.0	P	5.7
108	5/1/89	63.20 ± 0.70	–8.90	0.18	–7.0	P	5.7
108	8/16/89	NA	NA	NA	P	P	NA
108	11/17/89	NA	NA	NA	P	P	NA
111	1/22/86	21.80	–10.10	<0.80	–7.3	–51.0	7.2
111	7/6/88	20.90 ± 0.80	–8.20	0.10	–6.3	–50.0	8.2
111	10/5/99	NA	NA	NA	NA	NA	NA
111	5/2/89	25.90 ± 0.70	–7.90	0.00	–7.3	P	8.3
111	8/22/89	NA	NA	NA	P	P	NA
126	4/23/86	3.30	–18.10	3.30	–8.3	–61.0	4.1
126	1/19/89	P	P	0.28	–8.0	P	4.8
126	4/27/89	P	P	0.25	–8.4	P	4.8
126	8/23/89	NA	NA	NA	P	P	NA
126	11/19/89	NA	NA	NA	P	P	NA
Rio Grande Aquifer							
92	5/6/86	NA	NA	NA	NA	NA	NA
92	6/28/88	87.64 ± 1.04	–9.41	10.90	–7.9	–55.0	5.5
93	7/5/88	51.85 ± 1.08	–8.16	0.00	–10.6	–80.0	5.5
93	10/4/88	52.90 ± 0.70	–8.40	0.00	NA	NA	NA
93	1/17/89	50.10 ± 0.60	–8.00	0.06	–11.1	P	NA
93	4/27/89	51.0 ± 0.60	–8.00	0.11	–11.0	P	6.7
93	8/16/89	NA	NA	NA	P	P	NA
93	11/16/89	NA	NA	NA	P	P	NA
105	1/21/86	NA	NA	24.40	–9.1	–69.0	1.1
109	1/21/86	NA	NA	27.20	–7.4	–71.0	16.9
110	1/21/86	116.00 ± 0.72	–12.00	21.80	–8.8	–74.0	4.7
110	7/5/88	109.00 ± 1.00	–11.90	18.70	–8.3	–70.0	6.0
110	10/5/88	112.70 ± 0.70	–11.10	18.70	NA	NA	NA
110	1/18/89	107.60 ± 0.50	–10.80	NA	–9.2	P	6.2
110	5/1/89	112.80 ± 0.70	–11.20	19.10	–9.2	P	3.5
110	8/16/89	NA	NA	NA	P	P	NA
110	11/16/89	NA	NA	NA	P	P	NA

NA = not analyzed
P = analysis pending