Report of Investigations No. 191

Identification of Sources and Mechanisms of Salt-Water Pollution Affecting Ground-Water Quality: A Case Study, West Texas

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Bureau of Economic Geology • W. L. Fisher, Director

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Abstract

Occurrences of ground-water and soil salinization are numerous in the Concho River watershed and its confluence with the Colorado River in West Texas and in other semiarid regions of Texas and the United States. Salinization results from both natural and anthropogenic processes, which can occur together or separately. To recognize regional salt-water sources and understand salinization mechanisms in the Concho River valley, we investigated chemical and physical characteristics associated with saline ground water. Using more than 1,200 chemical analyses of water samples from previous studies and 76 analyses of samples from this investigation, we differentiated salinization mechanisms by mapping hydrogeologically controlled salinity patterns and hydrochemical facies and by graphically analyzing isotopic compositions and ionic ratios.

In the eastern part of the study area, located in Runnels County, evaporation of irrigation water and ground water from a shallow aquifer accounts for most salinization. In the western part of the study area, located in Irion and Tom Green Counties, much of the saline to brackish ground water is interpreted as being a naturally occurring mixture of subsurface brine flowing eastward from the Midland Basin and shallowly circulating meteoric water recharged in the Concho River watershed. Test drilling to depths below the base of fresh water confirmed the presence of subsurface brine in shallow Permian formations. Aquifers that contain relatively fresh water in outcropping Permian rocks also contain brine and hydrocarbons at depths as shallow as 60 to 275 m (200 to 900 ft), tens of kilometers to the west.

Test drilling also helped document two anthropogenic mechanisms for local mixing of subsurface brine and shallow ground water: (1) upward flowing of brine allowed by abandoned oil and gas exploration holes, where surface casing and borehole plugs are above the base of fresh water, and (2) leaching of accumulated salt from soil beneath former brine-disposal pits, an ongoing process even 20 years after this brine-disposal method was discontinued. A third mechanism, mixing of brine and shallow ground water via abandoned water wells, could not be tested. No records exist on deep water wells that reportedly were drilled into saline portions of aquifers and were abandoned without being plugged.

Chemical compositions of subsurface brines make up a continuous array between two endmember groups in Permian and Pennsylvanian formations. The end-member groups are distinguishable by graphical analysis of the (1) calcium, magnesium, sodium, and sulfate concentrations, (2) Br/Cl ratio plotted against chloride concentration, and (3) Cl/SO₄ ratio plotted against sulfate concentration and Na/Ca ratio. Most saline samples of shallow ground water in the Concho River watershed are chemically similar to the Permian formation brine end member. Coleman Junction Formation brines cannot be chemically distinguished from other Permian formation brines. Information about organic-acid anions, minor and trace constituents other than bromide, and isotopes of hydrogen, oxygen, carbon, and sulfur also can be used to differentiate between Permian and Pennsylvanian brines but may not always be useful measurements to determine sources of salinization in shallow ground waters.

KEYWORDS: Concho River, contamination, hydrogeochemistry, hydrogeology, Permian formations, salinization sources, West Texas

Introduction

Salinization of soil and shallow ground water and the resulting barren areas are major agricultural and water-supply problems in parts of Texas and other semiarid areas. In the Concho River watershed and in its confluence with the Colorado River valley in West Texas (fig. 1), many water wells vield saline to brackish ground water and soil salinization is widespread (Richter and Kreitler, 1987). Hypothesized regional sources of salinization previously identified in the study area and in similar settings include (1) evaporative concentration of ground water from shallow water tables that rose in response to changed agricultural landscaping and increased recharge (Miller and others, 1981), (2) natural discharge of subsurface brines (Dutton and others, 1989), (3) seepage of saline water from rocks beneath former brine-disposal pits (McMillion, 1965; Pettyjohn, 1971, 1982; Rold, 1971), and (4) upward movement of brine across confining beds through oil wells and deep, unplugged water wells (Wait and McCollum, 1963; Rold, 1971). A fifth possible source, infiltration of dissolved salts used for road deicing (Field and others, 1974), is not a concern in the area.

We designed this study to (1) define the regional hydrogeologic setting, which is essential for understanding the distribution of saline water, (2) determine the chemical characteristics of fresh and saline ground waters and subsurface brines, (3) test salinization sources in the field, and (4) develop diagnostic hydrochemical tools to recognize and locate sources of saline ground water in shallow aquifers. We limited the study area to those parts of the Concho and Colorado River watersheds in northern Concho, eastern Irion, southern Runnels, and Tom Green Counties (fig. 1) where salinization reports are available.



Figure 1. Generalized geologic map of the Concho River watershed and its confluence with the Colorado River, west-central Texas. Modified from Brown and others (1972), American Association of Petroleum Geologists (1973), and Eifler (1975).

Hydrogeologic Setting

The study area is located at the eastern side of the Southern Great Plains physiographic province, which slopes gently to the southeast from elevations of 1,800 to 2,400 m (6,000 to 8,000 ft) in eastern New Mexico to elevations of 450 to 600 m (1,500 to 2,000 ft) in Central Texas (fig. 1). Physiographic features of the study area include flat, alluviumfloored valleys, formed by the Concho and Colorado Rivers and their tributaries and separated from the gently rolling, dissected upland of the Edwards Plateau by an escarpment with a maximum height of approximately 30 m (100 ft). The informally named Southern Great Plains regional ground-water-flow system includes diverse hydrostratigraphic units in Cambrian to Neogene rocks, including fresh-water aquifers at shallow depths and deeply buried formations containing brine and hydrocarbons (Jorgensen and others, 1988). In this report, the term "shallow ground water" refers to potable water supplies in aquifers less than about 120 m (400 ft) deep. "Subsurface brine" refers to high-salinity water typically associated with oil fields and commonly greater than 240 m (800 ft) deep. "Shallow water table" refers to a water table less than approximately 1.2 m (4 ft) beneath land surface.

Shallow Ground Water

Cretaceous carbonate rock forms the Edwards Plateau in the study area and unconformably overlies Permian sandstone, carbonate rock, and shale. The Permian formations were deposited on the Eastern Shelf of the Midland Basin and dip to the west at approximately 9.5 m/km (50 ft/mi). Fredericksburg Group limestone and Trinity Group sandstone form an interconnected aquifer in the Cretaceous rock (table 1). Potable ground water is also produced in the river valleys from aquifers in Quaternary alluvium and locally from Permian limestone and gypsum beds, but the quality and quantity of ground water in these units are variable (Willis, 1954; Lee, 1986).

Potentiometric surfaces of shallow aquifer units are inclined toward the Concho and Colorado Rivers and their tributaries (Jones, 1972; Lee, 1986), reflecting topographic control on flow directions of shallow ground water. Lee (1986) reported that the hydraulic head of ground water decreases with depth beneath the Edwards Plateau and increases with depth along stretches of the Concho River. This pattern indicates that Edwards Plateau rocks are local recharge areas and that ground-water discharge is focused in the river bottoms. Flow studies of the lower Concho River and Colorado River showed that the quantity of base flow from ground-water discharge is significant (R. M. Slade, Jr., personal communication, 1988). Similar relationships probably exist in valleys of parallel river systems across the eastern side of the Southern Great Plains.

The base of the fresh water in the area is defined locally by water-well drillers as the first occurrence of thick "blue shale," normally 30 to 60 m (100 to 200 ft) beneath land surface. Saline water generally is encountered within or below the shales. Driller's logs indicate the depth to "blue shale" but seldom record whether salt water was encountered during drilling. Because the deepest water wells in an area are assumed to be above the base of fresh water, the Texas Water Commission uses these wells to determine the minimum depth of required surface casing in oil and gas wells. In the study area, the base of fresh water is estimated to range from about



Figure 2. Surface-casing depths in oil and gas exploration holes required by Texas Water Commission. Modified from official map, Railroad Commission of Texas, District 7C, San Angelo.

150 m (500 ft) below land surface in the southwest beneath the Edwards Plateau to about 30 m (100 ft) in the northeast beneath the Concho River valley (fig. 2). We did not verify the base of fresh water using exploration geophysical logs because most logs begin at depths greater than the base of fresh water.

Subsurface Brine

Regional and local topographic relief has major effects on ground-water flow paths (Tóth, 1962, 1963, 1978); these effects must be understood to distinguish naturally occurring saline waters from salt-water contamination in the Concho and Colorado River watersheds. Regional topographic relief across the Southern Great Plains imposes a hydrodynamic gradient on subsurface brine in Paleozoic rocks (McNeal, 1965; Dutton and Orr, 1986; Jorgensen and others, 1988). Potentiometric surfaces of deep-brine aquifers dip to the east, indicating potential for eastward fluid flow toward formation outcrops (fig. 3). Potentiometric surfaces of hydrostratigraphic units in Paleozoic rocks

 Table 1. Generalized stratigraphic chart for the Concho River watershed. Modified from Brown and others (1972), American Association of Petroleum Geologists (1973), Eifler (1975), and Lee (1986).

SYSTEM	SERIES	GROUP	FORMATION	LITHOLOGY
	HOLOCENE			alluvium
QUALETINATT	PLEISTOCENE		Leona	caliche and gravel
TEDTIADY	PLIOCENE		0	arrayal and and aslight
TENTIANT	MIOCENE		Ogaliala	gravel, sand, and caliche
		Washita	Buda	argillaceous limestone
			Edwards	limestone and dolomite
CRETACEOUS	COMANCHEAN	Fredericksburg	Comanche Peak	limestone
			Walnut	limestone and clay
		Trinity	Antlers	sandstone and shale
TRIASSIC	ASSIC UPPER Dockum			sandstone and shale
	OCHOAN	Quartermaster		sandstone and
		Whitehorse		gypsiferous shale
			San Andres (Blaine)	sandstone
	GUADALUPIAN	Pease River	San Angelo	sandstone, gypsum, and dolomite
			Choza	sandstone and dolomitic
	LEONARDIAN	Clear Fork	Vale	limestone
DEDMIAN			Arroyo	shale and marly limestone
			Lueders	limestone and dolomite
			Talpa	
			Grape Creek	
		Wichita-Albany	Bead Mountain	
			Jagger Bend-Valera	limestone and shale
			Elm Creek	
			Admiral	
	WOLFCAMPIAN		Coleman Junction	
	VIRGILIAN	Cisco		
	MISSOURIAN	Canyon		limestone and shale
PENNSYLVANIAN	DESMOINESIAN	Strawn		
ne – eterne menneteringen besteringen besteringen.	ATOKAN	Bond		sandstone, shale, and
	MORROWAN	Bend		limestone
ORDOVICIAN	CANADIAN	Ellenburger		dolomite
PRECAMBRIAN				granite and gneiss

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Figure 3. Potentiometric surface of the Guadalupian Series based on equivalent fresh-water hydraulic head. Modified from McNeal (1965).

mapped by McNeal (1965) indicate that in parts of West Texas potential exists for subsurface brine to move upward from overpressured formations and across confining layers toward discharge sites. Possible pathways for cross-formational flow include natural fractures and drillholes. Potentiometric surfaces of brine-bearing formations are near or even above land surface in the Concho and Colorado River valleys. For example, the Permian Coleman Junction Formation (table 1) is a regionally extensive, artesian brine-bearing unit at approximate depths of 900 m (3,000 ft) in the western side of the study area to 240 m (800 ft) in the eastern side. Wellhead pressures are as much as 862 kPa (125 psi), enough to lift brine to 75 m (250 ft) above land surface. Subsurface brine also discharges at shallow depths of less than 50 m (150 ft) below land surface in parts of the southern Rolling Plains northeast of the Concho River watershed, as noted by Richter and Kreitler (1986).

During the past several million years, regional flow probably has continually transported subsurface brine to near land surface, where the brine has mixed with locally recharged, shallowly circulating water. Salt water occurring near land surface in the study area is not just a recent



Figure 4. Total dissolved solids in subsurface brine from the Guadalupian Series. Modified from McNeal (1965).

phenomenon; it was reported as early as 1911 (Udden and Phillips, 1911). Upper Permian rocks that form fresh-water aquifers beneath the Concho River valley contain brine and hydrocarbons just tens of kilometers to the west in the subsurface (McNeal, 1965; Core Laboratories, 1972). For example, salinity of subsurface water in the Permian Guadalupian Series (table 1) varies from 50,000 mg/L near its outcrop at the western side of the study area to more than 200,000 mg/L westward in the Midland Basin (fig. 4).

Drilling and production of oil began in the area in the 1890's. Oil and oil shows (fig. 5) were originally encountered at depths as shallow as 13 m (43 ft) (Udden and Phillips, 1911). Oil and gas are now produced at depths ranging from 270 m (900 ft) in Permian formations to greater than 1,800 m (6,000 ft) in Pennsylvanian and Ordovician rocks. Salt water is also produced in varying proportions with the oil and gas. In previous years, field operators discharged salt water into surface drainages and later into injection wells and unlined surface pits. Since 1969, Texas authorities have prohibited surface disposal in unlined pits, and all brines now are reinjected into underground saline formations.



Figure 5. Oil and gas fields, depths of oil shows during the early 1900's, and depths of saline water in the study area as reported by Udden and Phillips (1911).

Methods

Previously Identified Geochemical Indicators

In a study of salt-water sources in North-Central Texas, Richter and Kreitler (1986) showed that stable isotopes of oxygen and hydrogen in water and the ratios Na/Cl, Br/Cl, I/Cl, Mg/Cl, K/Cl, and (Ca+Mg)/SO₄ can be used to distinguish between (1) salt water derived from dissolution of halite by shallowly circulating, meteoric ground water and (2) deep-basin brine moving long distances from the Midland Basin. Novak and Eckstein (1988) also suggested using ionic ratios to distinguish salinity

sources at low concentrations. Differentiation between salt-water sources is clearest when total dissolved solids concentrations are greater than 10,000 mg/L. Whether these ionic ratios can be used to distinguish between salt-water sources where salinity is less than 5,000 mg/L has not been determined (Richter and Kreitler, 1986).

Shallow ground waters in the Runnels County area typically exhibit high concentrations of nitrate because recharge water percolating through the vadose zone dissolves cultivation nitrate (Kreitler, 1975). Dryland farming before the 1950's caused oxidation of organic nitrogen to nitrate in the soil zone. Nitrate leached from the soil zone did not reach the water table until the late 1950's and early 1960's, when terracing raised the water table to within a few meters of land surface (Kreitler, 1975). Elevated nitrate concentrations and other evidence may therefore indicate salinization of shallow ground water by evaporative concentration at shallow water tables. Subsurface brines, in contrast, normally do not contain appreciable amounts of nitrate.

Subsurface brines in the Palo Duro Basin (Dutton and Orr, 1986; Dutton, 1987b; Fisher and Kreitler, 1987) and in the Rolling Plains (Richter and Kreitler, 1986) typically are isotopically enriched in oxygen and deuterium with respect to shallow ground water. Deep-basin brines in the Concho River watershed were expected to show the same isotopic relationship. Evaporation of ground water from a shallow water table also may result in an isotopic shift toward enriched values (Chapman, 1986).

Data and Techniques

We conducted this investigation in two phases. from January through April 1985 and from June 1986 through July 1987. To document hydrogeologic controls on local variations and historic changes in ground-water composition, we compiled more than 1,200 chemical analyses of ground water in Concho, eastern Irion, Runnels, and Tom Green Counties from published reports (Work Projects Administration, 1941; Willis, 1954; Jones, 1972; Pool, 1972; Lee, 1986) and from computerized and open-file records of the Texas Natural Resources Information System. Because data from Concho County were sparse, we confined discussion of water chemistry to the other three counties. The reported chemical analyses vary in completeness and in conditions of sample treatment. For example, charge balance of anions and cations is almost always exact, indicating that sodium and potassium usually were determined together by difference (Hem, 1985, p. 164). Also, temperature, pH, and alkalinity are not always measured onsite and therefore are unreliable measurements of in situ values, and pH commonly is not reported.

We collected new samples to supplement previous data (fig. 6). Fifty-three shallow groundwater samples from water-supply wells were collected in February 1985 and during April and May 1987 (app. A). During 1985, brine samples were collected from (1) an abandoned exploration well completed in the Coleman Junction Formation, (2) 30-m-deep (100-ft) core holes with water flowing at land surface, (3) two leaky injection wells, and





(4) an oil well producing from the San Angelo Formation in western Tom Green County (no. 82, app. B). During 1986, to establish whether chemical composition of subsurface brine varies between formations and whether diagnostic tracers of formationspecific brines can be identified, we collected 17 additional subsurface brine samples (app. B) from oil and gas fields in eastern Irion and Tom Green Counties (figs. 5 and 6). Brines were taken from the same formation at different fields, but only one sample was collected at each field. Lease permits and interviews with field operators helped us recognize and avoid fields where salt water had been injected for disposal or for secondary oil recovery. However, all oil-producing fields in the shallow Permian formations in the study area contain some salt-water-injection wells. To collect subsurface brine that is representative of these formations, we sampled wells that were farthest (at least 1 km) from the injection wells.

Test holes were drilled during 1986 and 1987 to obtain samples from (1) below the base of fresh

water (six wells), (2) shallow water tables at surface seeps (two wells), and (3) beneath abandoned brinedisposal pits (three wells). During this investigation, all test holes were drilled with an air-rotary rig and were backfilled entirely with cement after sample collection, except where landowners desired completion as water wells. Test holes were drilled at sites where landowners had previously encountered salt water during water-well drilling. Fresh-water-bearing zones that were encountered during drilling were cased before drilling continued into salt-water zones. At the first saturated zone encountered, we took water samples and tested the salinity. Soil samples were obtained in 1.5-m (5-ft) and 3-m (10-ft) increments during drilling of test holes in brine-disposal pits. To preserve soil samples for measuring chloride concentration and moisture content, we weighed the samples, stored them in plastic cups with screw caps, and kept them chilled until they reached the laboratory.

Ground-water sampling conducted during this study focused on waters having relatively high salinity. Salinity distribution among samples does not reflect normal quality of potable ground water in the area. In contrast, previous water-resource investigations (for example, Willis, 1954; Lee, 1986) report mainly low-salinity samples.

We followed similar methods for collecting and treating both subsurface brine and shallow ground water; however, removing oil from subsurface brine necessitated additional procedures. The proportion of gas, oil, and water produced from sampled oil wells varied among fields. The water/oil ratio in fluid produced from some fields was high enough to separate an adequate sample volume from oil at the wellhead. At other fields, samples were taken from a separator tank; tanks were not drained before sampling, and elapsed time varied since water had been produced. Sampling generally followed the methods for collecting oil-field waters recommended by Lico and others (1982). Oil and water mixtures were collected in a 1-gal bucket with an inserted drum tap, and after approximately 5 minutes, separated water was drained through glass wool to remove residual oil. Samples were transferred to a filter chamber and forced under nitrogen gas pressure through a 0.45-µm membrane filter to remove pipe scale and other suspended solids.

We measured temperature, pH, and titrated alkalinity at well sites following procedures recommended by Wood (1976). Alkalinity and pH of nine subsurface-brine samples could not be measured at well sites because the field pH meter malfunctioned. Water samples for determining cation concentrations were acidified at well sites and analyzed using an inductively coupled plasmaatomic emission spectrometer. Chloride was determined in unacidified samples by potentiometric titration, sulfate was measured by ion chromatography, and bromide was measured by the oxidation-spectrophotometric method. Aliphatic-acid anions (acetate, propionate, butyrate, and valerate) were measured by gas chromotography in samples to which mercury chloride was added to eliminate algal and bacterial activity. To measure oxygen isotopic composition, water samples were equilibrated with CO2; 818O values are uncorrected for effects of dissolved salts. Dissolved sulfide (found in two samples) was precipitated as cadmium sulfide, and $\delta^{34}S$ values represent isotopic composition of dissolved sulfate. Adding a concentrated ammoniacal strontium chloride solution to the brine precipitated dissolved inorganic carbon for analyzing δ^{13} C (Gleason and others, 1969). Values of $\delta^{18}O$ and δD are reported relative to SMOW, 834S relative to the Canyon Diablo troilite standard, and 813C relative to PDB. General precisions for ionic and isotopic analyses were approximately 0.5 to 3 percent and 2 to 10 percent, respectively.

Shallow Ground Water

Hydrochemical Facies

Hydrochemical facies distribution reflects rock type and position along a ground-water flow path. Hydrochemical facies are named here for the ions that account for at least 50 percent of total equivalent concentration, as depicted in Piper diagrams (Piper, 1944; Back, 1966); mixed-cation and mixedanion hydrochemical facies are defined as waters in which no one cation or anion is dominant. Major hydrochemical facies in Irion, Runnels, and Tom Green Counties include Ca-HCO₃, Na-HCO₃, and mixed-cation-HCO₃ types in Cretaceous limestones and sandstones of the Edwards Plateau; mixedcation-Cl, mixed-cation-SO₄, and mixed-cationmixed-anion types in Quaternary sand and carbonate gravel beneath the Concho River valley; and Na-CI, Ca-SO, mixed-cation-CI, mixedcation-SO₄, and mixed-cation-mixed-anion types in Permian formations beneath Quaternary alluvium in the Concho River valley (figs. 7 and 8). Depicting all samples on one hydrochemical facies map (fig. 8) is possible because ground-water resources in an area generally are developed in only one formation; local exceptions to this possibly account for hydrochemical anomalies. Some samples of Na-Cl, Ca-SO, Ca-mixed-anion, and Na-mixed-anion hydrochemical facies are considered geographically anomalous because they are isolated within large areas dominated by other hydrochemical facies (fig. 8).

The Ca–HCO₃ hydrochemical facies (figs. 7a and 8) most likely originates from recharging water reacting with calcite and dolomite in Cretaceous carbonate rocks of the Edwards Plateau. The Ca²⁺ and Mg²⁺ ionic activities coincide with the phase boundary between calcite and dolomite (fig. 9). Scatter about the calcite-dolomite equilibrium line is partly due to faulty pH measurements taken away from well sites, to nonideal dolomite compositions in Cretaceous formations, and to variations in proportions of calcite and dolomite encountered along flow patterns, as suggested by Langmuir (1971).

The Na-HCO₃ and mixed-cation-HCO₃ hydrochemical facies (figs. 7b and 8) replace Ca-HCO₃ facies as ground water flows through Cretaceous rock toward discharge areas in the Concho River valley. This change is partly due to ionic exchange of dissolved calcium for sodium adsorbed on terrigenous clays in shale partings and disseminated in argillaceous limestone. Although hydrochemical facies have not been distinguished by aquifer unit, ground water in Trinity sandstone (table 1), produced from wells near the escarpment, might be more sodium rich than ground water in the Fredericksburg carbonate rock due to reactions with silicate minerals. Solution of dolomite continues along the flow path and accounts for increased magnesium concentration.

Presence of Ca–SO₄ and Na–Cl hydrochemical facies (figs. 7c, 7d, and 8) and elevated salinity in shallow aquifers in Permian formations beneath the Concho River valley suggest that these formations focus the discharge of the naturally occurring saline ground water that flows eastward from the Midland Basin within the Southern Great Plains regional flow system, as will be discussed. The mixed-ion composition of ground water prevalent in Concho River valley alluvium (figs. 7e, 7f, and 8) may originate where ground water that is discharged from Permian and Cretaceous formations mixes with ground water that is locally recharged to the alluvium by precipitation, irrigation, and seepage from rivers and streams.

Hydrochemical facies in ground water having chloride concentrations less than 250 mg/L (recommended concentration limit for drinking water [Freeze and Cherry, 1979]) are similar in the western and eastern parts of the study area (fig.10). Among samples having chloride concentrations greater than 250 mg/L in Tom Green County, there is a trend of increasing Na+ proportion with increasing CI⁻ proportion. However, samples from Runnels County having chloride concentrations in excess of 250 mg/L are dominated by mixed-cation hydrochemical facies and lack the trend of increasing Na⁺ proportion. This finding and other evidence, to be discussed further, suggest that different salinization mechanisms control the distribution of chemical constituents in the western and eastern parts of the study area.

Salinity Distribution and Ionic Ratios

Lee (1986) and Richter and Kreitler (1987) recognized that patterns of high chlorinity in Tom Green County changed between the 1940's and 1970's. Our study reanalyzed distribution of salinity in Tom Green and eastern Irion Counties to determine if patterns correlate with formation lithology and local physiography. Total dissolved



Figure 7. Piper diagrams of hydrochemical facies in shallow ground water. (a) $Ca-HCO_3$. (b) $Na-HCO_3$, $Mg-HCO_3$, and mixed-cation-HCO_3. (c) $Ca-SO_4$. (d) Na-CI and Ca-CI. (e) Ca-mixed-anion and Na-mixed-anion. (f) Mg-mixed-anion and mixed-cation-mixed-anion, $Mg-SO_4$ and mixed-cation-SO₄, and Mg-CI and mixed-cation-CI.



Figure 8. Hydrochemical facies in shallow ground water. See figure 7 for corresponding Piper diagram.

solids tend to be less than 500 mg/L in Cretaceous limestones of the Edwards Plateau but greater than 1,000 mg/L in Concho River valley alluvium and subcropping Permian formations (figs. 11 through 13). Numerous water samples from wells in the valleys have total dissolved solids greater than 10,000 mg/L. The area of high salinities in Permian outcrops and subcrops in central and eastern Tom Green County extends throughout most of Runnels County (fig. 13). Salinity of ground water sampled before 1942 has a strong stratigraphic association with the outcrop and subcrop of Permian formations, which strike northeastward across the study area (figs. 1 and 11). Salinity distributions mapped from water samples collected between 1942 and 1954 (fig. 12) and between 1955 and 1980 (fig. 13) appear to be less strongly correlated with Permian strata than with proximity to the Concho River. Overall salinity in the Concho River valley increased from pre-1942 to the early 1950's; a small 1980's data set suggests a subsequent salinity decrease. Lee (1986)



Figure 9. Chemical composition of shallow ground waters, relative to stability fields of calcite and dolomite at 25°C, based on data from Helgeson (1969, 1978). Axes are ratios of ionic activities (act.).



Figure 10. Piper diagrams of shallow ground water with chloride concentrations less than and greater than 250 mg/L in Tom Green County (a and b) and Runnels County (c and d).

Figure 11. Total dissolved solids in shallow ground water collected before 1942 in eastern Irion and Tom Green Counties. Variable contour interval (500–1,000–2,000–3,000–10,000–50,000 mg/L).

hypothesized that in the 1950's recharge from evaporatively concentrated irrigation water increased salinity in the alluvial aquifer. Data availability affected the determination of exact salinity patterns, because different wells were sampled for each map. Changes in countywide salinity patterns, therefore, may not reflect changes in water quality at any one well.

Water samples from wells and test holes belong to two categories, groups 1 and 2, defined by variation in ratios of major chemical constituents (fig. 14). Among group 1 samples, slopes of Mg²⁺ and SO₄²⁻ plotted against Cl⁻ on logarithmic scales are not significantly different from 1.0 ($\alpha = 0.05$), whereas among group 2 samples, slopes of Ca²⁺, Mg²⁺, and SO₄²⁻ plotted against Cl⁻ are significantly different from 1.0 ($\alpha = 0.05$). The differences are interesting because ground-water evaporation without mineral precipitation gives rise to ionic relationships with unit slope because ionic concentrations increase without changing molar ratios of chemical constituents. Therefore, it is

Figure 12. Total dissolved solids in ground water collected from 1942 through 1954 in eastern Irion and Tom Green Counties. Variable contour interval is same as shown in figure 11.

reasonable to suspect that group 1 data are influenced by evaporation. Group 2 data and subsurface brines have similar ionic relationships (fig. 14). Group 1 samples are made up of data from Runnels and eastern Tom Green Counties, whereas group 2 samples are made up of data from western Tom Green County. Although most samples from the eastern area belong to group 1, samples 4 and 6 (fig. 14) are chloride-rich groundwater samples from central Runnels County that resemble group 2 data from the western area. These two samples were collected from abandoned water wells near producing oil wells.

Seep samples, obtained from shallow wells in topographically low areas where the water table is within a few meters of land surface, are associated with group 1 but overlap with group 2 (fig. 14). The seep samples are not as saline as expected. The low salinity and consequent lack of distinctiveness result from the samples being collected during early February, when evaporation rate is low. Seep samples collected in the summer should plot along

Figure 13. Total dissolved solids in ground water collected after 1954 in eastern Irion, Runnels, and Tom Green Counties. Variable contour interval is same as shown in figure 11.

the trend defined by group 1 if evaporation is the cause of high salinity.

Nitrate concentrations in shallow ground water range from less than 1 to more than 200 mg/L (fig. 15). Low concentrations of nitrate were measured in ground water in western Tom Green County and central Runnels County as well as in all subsurface brines, discussed later. Concentrations exceed 100 mg/L in ground water from farmland in the Concho River valley and similar areas in southern Runnels and northern Concho Counties (Kreitler, 1975). Four of five seep samples from shallow water tables have nitrate concentrations ranging between 121 and 158 mg/L because of dissolution of nitrate in the soil zone. The fifth sample (no. 15) has a low nitrate concentration and was obtained from a flowing well used to drain and reclaim the waterlogged seep area. According to the landowner,

Figure 14. Variations in calcium (a), magnesium (b), and sulfate (c) concentrations with chloride concentration in shallow ground water and in subsurface brine. Trend of group 1 data (solid dots; solid line) is similar to theoretical evaporation line (unit slope). Trend of group 2 data (pluses; dashed line) points toward subsurface brine composition (squares).

Figure 15. Nitrate concentrations in shallow ground water in western (a) and eastern (b) parts of study area. No samples from western area are in the 126–175 mg/L class intervals, whereas approximately 30 percent of samples from eastern area fall within these class intervals.

this well stops flowing whenever nearby wells are pumped for irrigation. Ground-water flow at this well is active because of local topographic relief, in contrast to a sluggish or stagnant ground water at the other seeps. Flushing along this particular flow path may explain the low nitrate concentration of sample 15 in contrast to other seep samples.

Subsurface Brine

In the study area, two major subsurface brine end members are defined on the basis of ionic and isotopic composition: (1) Permian formation brines from the Clear Fork Group and Coleman Junction, San Angelo, and San Andres Formations (table 1), and (2) Pennsylvanian formation brines. One end member, represented by Permian formation brine, plots close to the meteoric water line (Craig, 1961) and is isotopically similar to shallow ground waters (fig. 16). Brine samples from Pennsylvanian formations, plotted to the right of the meteoric water line, define the other end member. Subsurface brine analyses grade in isotopic and ionic composition between the end members rather than form distinct groups or associations (fig. 16). The end members are not defined by individual samples but by clusters at the end of the trends. Differences between Permian and Pennsylvanian end members do not simply reflect differences between shallow and deep waters. Two deep Pennsylvanian samples (Eliza Baker North and H-J fields, samples 30 and 84

Figure 16. Variation in δD and $\delta^{18}O$ in shallow ground water (pluses) and in subsurface brine (squares). Meteoric water line: $\delta D = 10 + 8 \ \delta^{18}O$ (Craig, 1961). Brine end members marked as Pr = Permian, Pn = Pennsylvanian, and W = Wolfcampian.

[app. B]) are similar to the Permian end member, and two shallow Permian samples are similar to the Pennsylvanian end member. One brine sample, from an oil field identified as Wolfcampian (W), plots far from other Permian samples and is more enriched in δ^{18} O and δ D than are the Pennsylvanian samples.

The Br/Cl ratio in subsurface brines increases with increasing chloride concentration and shows the same end members (fig. 17). The Br/Cl ratio of the Pennsylvanian end member is similar to that of most deep-basin brines (Whittemore and Pollock, 1979; Whittemore, 1984; Richter and Kreitler, 1986). The Permian subsurface brine end member has a Br/Cl ratio similar to that derived from halite dissolution (Dutton, 1987a). The Br/Cl ratio of shallow ground water from the Concho River watershed shows an opposite trend of decreasing Br/Cl ratio with increasing chloride concentration. Ground-water samples with the highest chlorinities and lowest Br/Cl ratios plot near the subsurface brine end member from Permian formations and ionically are distinct from deeper Pennsylvanian formation brines (fig. 17). Weight ratios of Br/Cl greater than 0.003 are typical of the shallow ground water, and ratios less than 0.002 are typical of the Permian formation brine end member. Ratios of Sr/Br. Li/Br. and Ba/Br show similar relationships

Figure 17. Variation in Br/Cl ratios with chloride concentration in shallow ground water (pluses) and in subsurface brine (squares). Brine end members defined in figure 16. Samples 4 and 6 from Runnels County are associated with group 2 data.

Figure 18. Variation in calcium (a), magnesium (b), sodium (c), and sulfate (d) concentrations with chloride concentration in subsurface brine: (1) San Andres, San Angelo, and Clear Fork (open dots), (2) Coleman Junction (solid dots), (3) brines from surface leaks and of unknown origin (pluses), and (4) Pennsylvanian and the Wolfcampian sample (squares). (Analyses from Willis, 1954; Laxson, 1960; Core Laboratories Inc., 1972; Price, 1978; open-file information, Aqua Science Laboratory, San Angelo; and open-file information, Railroad Commission of Texas, District 7C, San Angelo, Texas.)

between brine end members, but such data are not usually reported for shallow ground water.

Brines in Pennsylvanian formations generally have higher calcium, magnesium, sodium, and chloride concentrations but lower sulfate concentrations than most brines sampled from Permian units (fig. 18). Chemical compositions of brines from the San Andres, San Angelo, Clear Fork, and Coleman Junction Formations are similar, but brine composition in the Coleman Junction Formation is remarkably uniform in the study area and adjacent counties from which samples were taken. Coleman Junction brine, therefore, cannot be readily distinguished from San Angelo, San Andres, and Clear Fork brines. Miscellaneous subsurface brines collected by the Railroad Commission of Texas (RRC) from leaky injection wells, leaky tank batteries, flowing core holes, and abandoned exploration holes overlap with Coleman Junction and shallow Permian brines (fig. 18) but generally have lower ionic concentrations than do brines in Pennsylvanian units.

Figure 19. Variation in acetate concentration with δ^{18} O in subsurface brine. Brine end members marked as Pr = Permian, Pn = Pennsylvanian, and W = Wolf-campian.

Alkalinity composition varies between brines from shallow and deep oil fields. Alkalinity of subsurface brine at depths of 300 to 550 m (1,000 to 1,800 ft) in shallow Permian oil fields results from dissolved bicarbonate ions; the source of alkalinity in deeper Wolfcampian and Pennsylvanian fields is mainly short-chain aliphatic-acid anions (app. B). Acetate and propionate account for 61 to 98 percent of total organic carbon. Analytic error and presence of organic ions other than these aliphatic-acid anions account for the discrepancy; mass balance error seems to be independent of total organic content. Acetate concentration is significantly correlated with $\delta^{18}O$ (fig. 19) and $\delta^{13}C$ values. The Permian formation brine end member has low acetate concentration, high bicarbonate alkalinity, and the most negative $\delta^{18}O$ and $\delta^{13}C$ values (figs. 19 and 20). The Pennsylvanian end member has greater acetate concentrations and more positive $\delta^{18}O$ and $\delta^{13}C$ values; the sample from the Wolfcampian rocks has the highest acetate concentration and highly enriched $\delta^{18}O$ and $\delta^{13}C$ compositions (figs. 19 and 20).

There is no significant relationship between δ^{34} S and dissolved sulfate concentrations, although the previously defined end members are recognizable in the plot (fig. 21). Sulfate concentration is controlled by salinity, formation temperature, equilibrium with anhydrite and gypsum, and activity of sulfate-

Figure 20. Variation in δ^{13} C with δ^{16} O in subsurface brine. Brine end members marked as Pr = Permian, Pn = Pennsylvanian, and W = Wolfcampian.

Figure 21. Variation in δ^{34} S with sulfate concentration in subsurface brine. Brine end members marked as Pr = Permian, Pn = Pennsylvanian, and W = Wolf-campian.

reducing bacteria. Sulfate concentration tends to decrease with depth. High sulfate concentrations in shallow Permian formations might reflect (1) dissolution of bedded anhydrite, (2) low activity of sulfate-reducing bacteria, or (3) oxidation of sulfides as subsurface brines move to shallow depths along inferred regional flow paths across the Eastern Shelf of the Midland Basin. Some of the subsurface brines have δ^{34} S values similar to values typical of Permian sulfate-bearing rocks (Holser, 1979), possibly reflecting dissolution of anhydrite. The δ^{34} S compositions of other brines throughout the stratigraphic section are enriched relative to Permian and Cretaceous anhydrite. Sulfate reduction by bacteria preferentially acts on isotopically light sulfate and leaves remaining dissolved sulfate enriched in δ^{34} S.

Salinization Sources

In the study area, sources of salinization hypothesized by Richter and Kreitler (1987) include (1) evaporative concentration of ground water from shallow water tables and (2) mixing of shallow ground water with subsurface brine (fig. 22). Most shallow ground waters have certainly been influenced by some amount of salt water from at least one of these sources. Among all samples, irrespective of hydrochemical facies, chloride concentration is closely correlated with sodium concentration (fig. 23). Subsurface brines collected during this study form an end member of the Na–Cl trend. The geographically anomalous samples of Na–Cl, Ca–SO₄, and mixed-anion hydrochemical facies that were previously mentioned and the saline samples of shallow ground water collected for this investigation are intermediate in salinity between shallow fresh ground-water samples and subsurface brines.

Figure 22. Conceptual model of salinity sources in the Concho River watershed: (1) upward flow of brine through inadequately plugged and leaky boreholes, (2) leaching of salt beneath abandoned brine-disposal pits, (3) evaporation of ground water from a shallow water table, and (4) discharge of subsurface brine from regional flow system.

Figure 23. Variation in sodium and chloride ionic concentrations in shallow ground water (pluses) and in subsurface brine (squares). Geographically anomalous samples of Na–Cl and Ca–SO₄ hydrochemical facies (dots) and saline water collected from test wells during this study plot between subsurface brines and shallow ground water.

Evaporative Concentration

Farmland in many localities in the eastern part of the study area was terraced during the 1950's to reduce surface-water runoff and erosion. Landscape terracing and return to normal precipitation rates increased ground-water recharge rates, resulting in a gradual rise of the water table to within a few meters of the land surface. Conditions favor evaporation of ground water in the eastern part, where water-table elevation is within a meter of land surface in many topographically low areas used as farmland, whereas throughout the western part, water-table elevation is tens of meters below land surface. Soil salinization is associated with shallow water-table areas. Irrigation water as well as naturally occurring ground water may be evaporatively concentrated (fig. 22). Precipitated salts are dissolved in ground water after rainfall; ground-water flow toward stream valleys spreads the dissolved salts. Salinization due to terracing is a problem not confined to Texas; it occurs throughout the Great Plains from Texas to Montana (Miller and others, 1981).

As previously mentioned, shallow ground-water samples from the eastern part of the study area (group 1) form a trend with a slope close to unity in bivariate plots of ionic concentrations (fig. 14). The similarity of group 1 data trends to an evaporation trend (unit slope) and the similarity of chemical compositions between group 2 data and subsurface brines suggest that evaporation is a salinization mechanism in the eastern part of the study area, whereas mixing of shallow ground water and subsurface brine affects saline samples in the western part. Both salinity sources possibly exist in the eastern part of the area, as suggested by samples 4 and 6 from the east, which plot along the trend of group 2 data. The evaporation trend, in comparison with the brine-mixing trend, has (1) higher Ca/Cl, Mg/Cl, and SO,/Cl ratios, and (2) lower chloride concentrations (fig. 14). Differentiation of salt-water sources is not feasible at low salinities. As chloride concentration increases, the differences between the two trends increase, making it possible to distinguish salt-water sources.

Figure 24. Variation in CI/SO_4 ratio with SO_4 concentration in shallow ground water (pluses and dots) and in subsurface brine (squares).

Mixing Mechanisms

Widespread mixing between subsurface brine and group 2-type shallow water is indicated by similarity of chemical composition (fig. 14). Among subsurface brine samples, concentrations of dissolved sulfate and chloride ions are inversely related (fig. 24); as is commonly observed, sulfate concentrations are low in brines containing the highest chlorinity. The decrease in sulfate (increase in Cl/SO, ratio) with a corresponding increase in salinity in waters associated with oil fields probably reflects the action of sulfate-reducing bacteria or anhydrite precipitation. A similar inverse trend exists among shallow ground waters in the study area. Although there is considerable scatter, the negative slope of the data is statistically significant. The Permian brine end member is similar in chemical composition to shallow ground-water samples with high sulfate concentration and low CI/SO, ratio. The more saline shallow ground waters collected during this study from water wells and test holes and some of the anomalous samples of Na-Cl, Ca-SO, and mixedanion hydrochemical types plot closest to the Permian brine end member. The end-member association between saline shallow ground water and Permian subsurface brine suggests that the poor quality of ground water partly results from shallow ground water mixing with subsurface brines from Permian formations.

Figure 25. Variation in CI/SO_4 with Na/Ca ratios in shallow ground water (pluses and dots) and in subsurface brine (squares).

A plot of Cl/SO₄ versus Na/Ca ratios of ions in shallow ground waters (fig. 25) shows a positive slope that reflects the dominance of Na-CI facies. The low Na/Ca ratio and enriched, nonmeteoric δ18O value of the Wolfcampian sample is unique in the data set from this study but is typical of brine composition that developed by modification of connate water in the Midland Basin (Dutton, 1987b). Samples of saline shallow ground water and anomalous Na-Cl and Ca-SO, facies from shallow aquifers again are more similar to the Permian end member of subsurface brines than to the Pennsylvanian end member (fig. 25). Variation of Na/Ca ratio in shallow ground waters and some subsurface brines having "meteoric" values of δD and $\delta^{18}O$ may be due to ionic exchange. Another source of variation in Na/Ca ratio is mixing of shallow calciumrich ground water with Na-CI-dominated subsurface brine.

The same association of shallow ground water and the Permian end member is shown in the plot of Br/Cl ratio versus Cl (fig. 17). The gradation in Br/Cl ratios suggests that low-salinity water having high Br/Cl ratios mixes with high-salinity water having low Br/Cl ratios. Low Br/Cl ratios in chloride-rich ground water eliminates Pennsylvanian brines as possible salt-water sources for most poor-quality ground waters. The fivefold difference in ratios between shallow ground waters in the eastern and western parts of the study area is smaller, however, than the tenfold difference in Br/Cl ratios used by Whittemore and Pollock (1979) and Richter and Kreitler (1986) to distinguish brine sources. More important, at low concentrations, analytical errors in bromide measurement affect Br/Cl ratios. For example, with bromide and chloride concentrations of 1.5 and 639 mg/L, respectively, and Br/Cl equal to 0.0023. sample 43 (app. A) plots within the interpreted mixing trend between brine and fresh water (fig. 17). A 33-percent error in bromide measurement, giving a bromide concentration of 2 mg/L and Br/CI equal to 0.0031, would make this sample fall within the range of fresh water, with little indication of mixing with subsurface brine. Accuracy and precision of bromide determinations were generally high during this investigation; standard deviations of repeated bromide analyses ranged from 0.2 mg/L for bromide concentrations less than 20 mg/L to 0.4 mg/L for bromide concentrations greater than 20 mg/L. Routine use of the Br/Cl ratio by commercial laboratories to evaluate possible salinity sources would require comparable accuracy and precision.

High nitrate and chloride concentrations may reflect contamination from animal wastes in feedlots or mixing between chloride-rich subsurface brine and nitrate-rich shallow ground water. Other constituents have to be considered to distinguish between these sources. Samples with low nitrate and high chloride concentrations could reflect mixing between shallow ground water and subsurface brine. Nitrate is a more suitable tracer of salinization sources in Runnels County and the Concho River valley than of sources beneath the Edwards Plateau, where nitrate concentrations in shallow ground water are low.

Samples 4 and 6 from Runnels County, previously interpreted as more similar in Ca/Cl, Mg/Cl, and SO_4/Cl ratios to western (group 2) samples than to eastern (group 1) samples (fig. 14), also are distinct from other eastern samples in nitrate concentrations and Br/Cl ratio (figs. 15 and 17, respectively). Both nitrate concentrations and Br/Cl ratio are lower in samples 4 and 6 than in other eastern samples and are similar to values determined for brines. Proximity of these wells to producing oil wells suggests that brines derived from the oil fields along some flow path have influenced water quality.

Possible mechanisms or pathways for mixing Permian formation brine and fresh ground water are (1) natural discharge of salt water across formation boundaries or in outcrop areas, (2) deep water wells, (3) abandoned oil and gas exploration holes, (4) unlined brine-disposal pits, and (5) faulty fluid-injection systems. Pennsylvanian brines can enter shallow aquifers in the Concho River watershed (1) through abandoned oil and gas exploration holes, (2) along faulty fluid-injection systems, and (3) from former brine-disposal pits.

Natural Discharge from Permian Formations

Early documentation that salt water is encountered at shallow depths in Permian Formations (Udden and Phillips, 1911) indicates that poor-quality ground water occurs naturally in the San Angelo Formation. Udden and Phillips (1911) reported a salt-water zone at a depth of 90 m (300 ft) in a 330m-deep (1,000-ft) well near Red Arroyo, a tributary of the Concho River within the City of San Angelo, and an oil-bearing brine at a depth of 68 m (228 ft) in a well 90 m (300 ft) deep. Willis (1954) reported saline water analyzed in 1948 to have a chloride concentration of 29,500 mg/L from a 37-m-deep (122-ft) well also near Red Arroyo. That sample predated most oil-exploration drilling in the area.

Water samples from the San Angelo Formation obtained at two test holes drilled in this study (nos. 60 and 61 [fig. 6]) had high chloride concentrations, whereby sample 60b resembled the analysis made in 1948 (app. B). Dissolved chloride concentrations in test hole 60, drilled next to a tributary of Red Arroyo in San Angelo, increased from 6,430 mg/L at a 2-m (7-ft) depth to 33,140 mg/L at a 20-m (68-ft) depth below land surface (nos. 60a and 60b [app. B]). Twelve hours after this well was drilled, hydrogen sulfide brine started flowing at land surface from 20 m (68 ft) below land surface. In test hole 61, water with a chloride content of 5,280 mg/L (app. B) was encountered at 17 m (58 ft) below land surface. These analyses further suggest the natural presence of subsurface brine in the San Angelo area but do not preclude other local sources of salt water, such as discharge from abandoned oil and gas wells.

The elevated salinity (figs. 11 through 13) and Na–Cl and Ca–SO₄ hydrochemical facies (fig. 8) in shallow ground water in Permian formations beneath the Concho River valley and the similarity of ionic ratios between Permian formation brine and saline end members of shallow ground water (figs. 16, 17, 24, and 25) suggest that discharge of naturally occurring saline ground water moving eastward from the Midland Basin in the Southern Great Plains regional flow system is focused within certain Permian formations (fig. 22) (Dutton and others, 1989). This finding assumes that (1) mixing between subsurface brine and shallow ground water accounts for the observed chemical-composition gradation and

(2) point-source pollution does not pervasively affect ground-water guality across the region. Lee (1986) hypothesized that the 1950's salinity increase in the alluvial aquifer was caused by partial evaporation of irrigation water applied during a drought and by leaching of accumulated salt from soil. Precipitation as much as 50 percent below normal from 1950 to 1956 and from 1962 to 1966 resulted in increased ground-water production for irrigation and a 6- to 18-m (20- to 60-ft) drop in ground-water levels. Marked decrease in hydraulic head in the shallow aguifers would have increased the amount of subsurface brine that discharged from the regional flow system and mixed with shallow ground water. This explanation is an alternative to the possibility that recharge from evaporatively concentrated irrigation water caused the salinity increase observed during the 1950's and 1960's (Lee, 1986).

Abandoned Deep Water Wells

Pathways for upward movement of salt water into fresh-water aquifers can occur in deep. abandoned wells that were not plugged or were inadequately plugged by present standards, including water wells and oil and gas wells (fig. 22). When ground-water levels dropped below the base of existing water wells during the drought, many dry wells were deepened and new water wells were drilled to depths as great as 150 m (500 ft) in the area west of the City of San Angelo. Marshall (written communication to T. L. Koederitz, 1976) reported that many of these deep water wells encountered saline water and were abandoned without being plugged. This finding is difficult to confirm because Marshall did not report the well locations. No supporting evidence exists among hundreds of water-well driller's logs from western Tom Green County on file at the Texas Water Commission Central Records in Austin, Texas. Furthermore, local water-well drillers and a wellservice company representative, who have decades of experience in the study area, recalled that only a few such deep water wells have ever been drilled. Therefore, saline water leakage via deep water wells is assumed to play a less-significant role than regional discharge of subsurface brine, evaporation, or contamination from oil and gas development activities.

Abandoned Oil and Gas Wells

Abandoned oil and gas wells and unplugged core holes and shot holes provide pathways for upward movement of subsurface brine where surface-casing depth and location of plugs beneath

Figure 26. Location of abandoned oil and gas exploration boreholes, Tom Green County.

the fresh-water section are inadequate (Wait and McCollum, 1963; Payne, 1966) (fig. 22). For example, ground water beneath an estimated 1.6 to 2.4 km² (400 to 600 acres) of land in southern Scurry County was affected by salt water from an unplugged, abandoned exploration hole that leaked brine into shallow ground water for 22 yr (Reed, 1961). The RRC, investigating reports of brine flow from abandoned boreholes and contamination of shallow ground water, reentered and plugged 11 wells in Tom Green County from 1984 to 1987 (A. J. Raschke, personal communication, 1987). Some of the 11 exploration holes had never been plugged and others had inadequate plugs. Leakage of brine from artesian brine-bearing formations upward through unplugged and uncased abandoned wells is suspected of often causing salinization in the study area.

We confined inventory and study of exploration holes to Tom Green County because of the vast number of exploration holes drilled in the study area. In this county alone, more than 1,000 evenly distributed deep oil-exploration wells were abandoned because no oil or gas was found (fig. 26). Many of these wells were drilled and abandoned before drilling and plugging regulations existed or were strengthened to protect water

Figure 27. Schematic diagram of abandoned borehole 47 and test well 48, Washington County School Land lease. (a) Condition according to plugging report. (b) Actual condition of abandoned hole. (c) Testing of abandoned hole. (d) Shallow test hole 48 offset from abandoned well 47.

resources. Local residents who performed or observed plugging procedures recall that wells were rarely plugged before 1960 and recount incidents of trash, rocks, or tree trunks being used to plug abandoned boreholes. Sometimes the hole was merely covered with a steel plate, rock, or cement cap. As documented by Reed (1961), brine contamination from such inadequately abandoned or plugged holes can become extensive where it remains undetected. Cement plugs are required because even properly cased wells can develop leaks. Highly corrosive Coleman Junction brine is known to cause fist-sized holes in steel production pipe within 4 or 5 yr of well construction if remedial action is not taken (Indian Wells Oil Company, San Angelo, personal communication, 1987).

Excluding areas where Cretaceous rocks overlie Permian strata (fig. 1), required surface-casing depths vary from 30 to 120 m (100 to 400 ft) below land surface (fig. 2). Where there is a pathway, brine will flow to land surface or into shallow aquifers from the overpressured Coleman Junction Formation and from other artesian brine-bearing units. Therefore, using the correct depth of surface casing and putting cement plugs in abandoned holes are important for protecting ground-water resources.

To check the accuracy of plugging reports and the past effectiveness of a plug, we selected one abandoned dry hole for test drilling. After obtaining a permit from the RRC to reenter and replug the selected well, we had the surface plug drilled out. We then compared the plug thickness and position with those mentioned in the original plugging report.

According to the plugging report, the abandoned borehole had a short surface casing but lacked a plug between the Coleman Junction Formation and the base of the casing (fig. 27a). The hole had been drilled to a depth of 1,893 m (6,212 ft) in 1955 and plugged within 30 days after drilling was completed. Reportedly, plugs made of 5 sacks of cement were placed at the top of the well and at the base of surface casing at a depth of 30 m (100 ft), and plugs made of 20 sacks of cement were placed at depths of 1,487 m (4,880 ft) and 1,582 m (5,190 ft) (fig. 27a). However, the uppermost plug was absent, and drilling mud stood in the hole from 0.3 m (1 ft) below the capped wellhead to a depth of 27 m (90 ft) (fig. 27b), where a 9.1-m-thick (30-ft) plug was found.

The potential for brine flow was tested by drilling out the plug and bailing drilling mud and water from the borehole until the fluid level in the well was drawn down 41 m (134 ft). Within 30 minutes, fluid level recovered and hydrogen sulfide-rich brine began flowing at land surface at a rate of 0.5 L/sec (8 gal/min) and a wellhead pressure greater than 414 kPa (60 psi) (fig. 27c). Chloride concentration was 29,610 mg/L in a sample obtained after drilling mud was bailed from the well and after the flowing water had become clear (no. 47, app. B). A 48-mdeep (160-ft) test hole was drilled approximately 45 m (150 ft) north of the well (fig. 27d), downgradient along shallow ground-water flow paths (Lee, 1986). No major water-bearing units were encountered during drilling, but a seep was detected at approximately 38 m (127 ft) below land surface. After 24 hours, 10 m (35 ft) of water had collected in the borehole from this seep. The water sample (no. 48, app. B) was a hydrogen sulfide brine with a chloride concentration of 19,380 mg/L, lower than that in the adjacent abandoned borehole. The Na-Cl samples from the abandoned borehole and the test hole have identical proportions of major cation and anion concentrations, indicating the same water type. Concentrations of bicarbonate and bromide, however, have different dilution ratios, perhaps due to mineralogic reactions, degassing, and measurement errors. Ionic ratios indicate that sample 48 from the test hole could result from dilution of 1 part of sample 47 from the abandoned well by approximately 0.6 part of local shallow ground water.

Underground seepage of brine may occur from other deep-exploration boreholes that were abandoned more than 25 yr ago. Abandoned boreholes that possibly allow Coleman Junction brine to flow upward into permeable units at shallow depths appear to be most numerous in east-central Tom Green County. Current regulations specify that surface casings in that area should extend to depths ranging from 45 to 105 m (150 to 350 ft) below land surface, reflecting the approximate depth to the base of fresh water (fig. 2). In 1985, the RRC studied local abandoned exploration holes after drillers of a water well encountered saline water (chloride = 4,676 mg/L) at a depth of 23 m (75 ft). An abandoned exploration hole 1.6 km (1 mi) south of the contaminated well, with surface casing extending to a depth of 72 m (240 ft) and a reported cement plug from depths of 61 to 75 m (204 to 248 ft), was suspected as being the source of salt water. The abandoned hole was reentered and replugged by the RRC. During the present study, test drilling recovered an identical saline water (chloride = 4,450 mg/L) at a depth of 23 m (75 ft) from a test hole located at the site of the previously drilled and plugged water well (no. 45 [app. B]). This finding indicates that brine still exists in the shallow subsurface in this area, either as a residual plume or because of another unplugged exploration well. Among several abandoned wells that could allow continued brine leakage from the Coleman Junction Formation in this area, one borehole seems to be the most likely source. The borehole is suspected because of its proximity to test hole 45, its short casing (51 m [170 ft]), and the reported position of its plug (25 sacks of cement at a depth of 60 m [195 ft]), which is too shallow relative to the base of fresh water (depth of 75 to 106 m [250 to 325 ft]).

Brine-Disposal Pits

Seepage from abandoned brine-disposal pits has caused several occurrences of oil-field-related water and soil pollution in West Texas and other oilproducing states (Burnitt and Crouch, 1964; Crouch and Burnitt, 1965; McMillion, 1965; Pettyjohn, 1971, 1982; Rold, 1971; Fryberger, 1975). The amount of salt-water contamination from unlined brine-disposal pits in the study area has not been quantified. Brine disposal into unlined surface pits was gradually discontinued in the late 1960's after several occurrences of brine contamination of shallow ground water were traced to such disposal pits. Unlined pits were banned in Texas in 1969 after documentation showed that most of the brine pumped into the pits did not evaporate but instead percolated downward and recharged shallow ground water (fig. 22). Salt water and precipitated salts probably remain beneath most pits and continue to be flushed along ground-water flow paths toward wells and streams (Reed, 1961; Fryberger, 1975; Pettyjohn, 1982).

Aerial photographs of Tom Green County, archived at the U.S. Soil Conservation Service District Office, San Angelo, clearly show brinedisposal pits operating in 1964 when the pictures were taken. A total of 111 brine-filled pits are visible

Figure 28. Active brine-disposal areas identified in 1964 aerial photographs, Tom Green County.

in 22 general areas (fig. 28). No field check of all these areas was performed, and they were not the only disposal sites being used in this county. To determine whether salt water is still being flushed from beneath pits and whether the remaining salt still poses a pollution hazard, we had test holes drilled at three of the abandoned brinedisposal pits to evaluate soil chlorinity and chemical characteristics of shallow ground water.

In one area, 3.2 km (2 mi) east of Tankersley (fig. 28), approximately 100,000 bbl of brine was discharged into as many as five ponds between 1952 and 1967 (RRC files, District 7C, San Angelo). The abandoned pits are now revegetated. During test drilling, the odor of hydrocarbons was detected in the upper 1 m (3 ft) beneath land surface, and ground water at the 14-m-deep (46-ft) water table was found to be saline with a chloride concentration of 20,750 mg/L (no. 76, app. B). Chloride concentrations in soil samples were highest at shallow depths (fig. 29).

Lower chloride concentrations were measured in soils beneath abandoned brine-disposal pits at the Susan Peak field in southeastern Tom Green County. Maximum concentrations of 0.7 and 1.3 mg/cm³ occur in soil samples from two disposal pits (fig. 30). However, chloride concentration in

Figure 29. Relationship between chloride concentration and depth in soil at site of abandoned brinedisposal pit near Tankersley (see figs. 6 and 28). Samples from borehole 76 were obtained from soil underlying the pit, whereas samples from borehole 75 were obtained from outside the pit area.

subsurface water collected at one of the test holes was 13,070 mg/L (no. 46, app. B). Brine-disposal pits in the Susan Peak field appear inactive in the 1964 aerial photographs. Many brine-disposal ponds had existed in the Susan Peak field, but duration of their use and the amount of brine they received are unknown. The lower soil salinity may be explained by either brine having been discharged in smaller quantities in the Susan Peak pits than in the Tankersley pits, or flushing having been less effective at Tankersley.

A minimum estimate of chloride still stored beneath the sampled Tankersley pits can be made from average soil chlorinity and average pit size, assuming a uniform concentration beneath the pit. First, the original chloride load was estimated as follows. Average chloride concentration in subsurface brine was assumed to be 80,000 mg/L on the basis of samples collected in this study (salinity varies in the region from 50,000 to more than 150,000 mg/L [McNeal, 1965; Core Laboratories, 1972]). Given the estimate that 100,000 bbl (about 16 million liters) of salt water went into the ponds between 1952 and 1967 (RRC records, District 7C, San Angelo), roughly 1,270 metric tons of dissolved chloride was pumped into the pits. Second, present chloride content in soil from test hole 76 varies from 0.6 to 5.8 mg/cm3 and averages 2.4 mg/cm³. In contrast, the background chloride content of soil outside the pit area, based

Figure 30. Relationship between chloride concentration and depth in soil underlying abandoned brinedisposal pits 46a and 46b in the Susan Peak field (figs. 6 and 28).

on the upper 6 m (20 ft) of test hole 75, is only 0.007 mg/cm3, which is 0.3 percent of the average concentration beneath the abandoned pit. Therefore, an estimated 66 metric tons of chloride in the soil exists beneath the five abandoned pits and above water table at a depth of 14 m (45 ft). This calculation assumes that (1) the soil-chloride profile of the test hole is representative of the entire pit area, (2) average chloride content of the soil is 2.4 mg/cm3, and (3) the size of the five pits is approximately 36 by 55 m (120 by 180 ft). The 66 metric tons, approximately 5 percent of the total amount of dissolved chloride that was originally pumped into the disposal ponds, represents a significant, longterm salinization potential when compared with the background amount of 0.2 metric ton of chloride estimated in the same volume of soil outside the pit area. Chloride concentrations in the disposal pit area would take more than 500 yr to return to natural levels in soil measured away from the abandoned disposal pits. This conclusion assumes that the ground-water recharge rate is 0.3 cm (0.12 inch) per year (based on estimates for the southern part of the Southern High Plains located about 180 km [110 mi] to the northwest of the study area [Knowles and others, 1984; Luckey and others, 1986; Ostercamp and Wood, 1987]) and that chloride is leached from the soil to produce salt water with a constant chloride concentration of 20.000 mg/L (as in sample 76). Locally higher recharge rates would proportionally reduce residence time of saline water in the flow system.

In the Tankersley area, salt water that leaked into shallow ground water may have spread a considerable distance, mainly downstream along the regional hydraulic-head gradient. The salt water may have also spread upgradient as a result of the impression on the water table, or mounding, caused by local recharge from the brine pond. Test hole 75 was drilled approximately 90 m (300 ft) west and test hole 77 was drilled 0.8 km (0.5 mi) east of the pit. Drill locations were selected upgradient and downgradient from the pit on the basis of groundwater potentiometric surface maps (Lee, 1986). Sample 76, obtained from a conglomerate bed 14m (46 ft) directly below the pit floor, had a chloride concentration of 20,750 mg/L. The downgradient water sample, taken from a conglomerate bed at a depth of 7 m (24 ft), had a chloride concentration of 12,190 mg/L (no. 77, app. B). In plots of calcium, magnesium, sodium, and sulfate versus chloride (fig. 31), sample 77 lies between sample 76 and samples obtained from the upgradient test hole (no. 75). Salinity of the contaminant plume appears to decrease along the flow path as the salt water spreads out and becomes diluted. Athough test hole 75 is located upgradient (Lee, 1986) from the abandoned pits, its samples are also affected by the salt-water plume, partly because the impression of the recharge on the shape of the water table beneath the pit changed local flow directions.

In 1978, during an investigation of poor-quality ground water, the San Angelo district office of the RRC analyzed water samples from 21 water wells located between Tankersley and a point approximately 10 km (6 mi) east of Tankersley. In plots of calcium, magnesium, sodium, and sulfate versus chloride, the trend of these samples consistently differs from the trend defined by samples 75, 76, and 77 (fig. 31). Therefore, samples 75, 76, and 77 are anomalous for this area. Leaching of salt from beneath abandoned disposal pits accounts for this anomalous water composition.

To assess the potential for salt-water pollution from former brine-disposal pits, we estimated the amount of subsurface brine disposed in unlined pits in Tom Green and Irion Counties from 1950 to 1969, the year unlined disposal pits were banned, by multiplying reported volume of oil production by water/oil ratios estimated from leases in the study area. Page (1967) estimated water/oil ratios statewide to be about 2.5 to 3 bbl of water for each barrel of oil produced during 1966, with an average statewide daily production of 7.5 MMbbl of brine. Approximately 20 percent of brine produced from

Figure 31. Variation in calcium (a), magnesium (b), sodium (c), and sulfate (d) concentrations with chloride concentration in shallow ground water in the Tankersley area. Samples (represented by solid dots) from wells along a transect through the brine-disposal pit are anomalous for this area.

Texas oil and gas fields was discharged into surface pits in 1966 (Petroleum Engineer, 1967). Our study made two independent estimates of water/oil ratios on the basis of 4 years of representative data reported on form W-10 (Oil Well Status Report of the RRC) and brine-production data in three operator surveys conducted by the RRC (table 2). Response to the salt-water surveys was voluntary and appeared less complete than Form W-10 data. Because all reported estimates of brine production are unconfirmed, salt-water quantities are presumably underestimated (Burnitt and Adams, 1963). Water/oil ratios were calculated for individual leases from W-10 data and then averaged; ratios from saltwater surveys are averages of total water and oil produced (table 2). Most brine produced in Tom

	Wat	er/oil ratios fro	om W-10 forn	ns (bbl/bbl)
	1953	1958	1964 1	969
Arithmetic average	0.94	0.56	0.68	1.37
Geometric mean (µ)	0.05	0.02	0.17	0.18
Mean +1 standard deviation	1.45	0.77	1.62	2.18
Mean -1 standard deviation	0.002	0.001	0.017	0.014
Sample size	15	15	22 2	9
	Wa	ter/oil ratios f	rom salt-wate	er surveys
	1957	1961	196	7
Brine production (bbl)	938,050	2,285,129	2,397,4	17
Oil production (bbl) ¹	2,576,564	2,208,644	2,908,6	02
Water/oil ratio (bbl/bbl)	0.36	1.04	0	.82
	Est	imate of brine	production (1,000 bbl)
	pre-1953	1954-1958	1959-1964	1965-1969
Water/oil ratio (bbl/bbl)2	0.92	0.68	1.08	1.46
Oil production ¹	6,428	11,030	13,268	11,494
Brine volume ²	5,914	13,414	21,743	44,524

Table 2. Data used to estimate amount of salt water produced from oil and gas fields in Tom Green and Irion Counties, 1950–1969.

¹From annual reports of the Oil and Gas Division, Railroad Commission of Texas ²Best estimate

Green and Irion Counties is assumed to have been discharged into surface pits; however, information is sparse concerning the ratios of brine quantities disposed into pits versus quantities disposed into injection wells.

Geometric mean (μ) and standard deviation (σ) of the logarithm of water/oil ratios were calculated because the data distribution was skewed toward small values. The water/oil ratios range from 0.36 in 1953 to 2.18 in 1969, slightly increasing during the life of the oil fields (table 2, fig. 32). Table 2 gives our best estimates of local average water/oil ratios during 1950 to 1969. Using these ratios, we calculate cumulative brine production from oil fields to be about 45 MMbbl. If spread uniformly across the two counties, the average annual discharge of salt water to the pits during this period would form a 0.106-cm-thick (0.002-inch) layer. In comparison, natural specific discharge of ground water from the Midland Basin has been estimated at 1.08 cm/yr (0.43 inch/yr) (Senger and others, 1987). Therefore, the cumulative volume of salt water discharged into brine-disposal pits is within an order of magnitude of the volume of natural discharge. This amount of discharge could be a significant component of regional salinization, depending on the validity of

Figure 32. Estimates of water/oil ratios produced from oil and gas wells in Tom Green and Irion Counties, 1950–1969, based on Railroad Commission of Texas data. Solid dots and bars represent geometric mean ratios ± 1 standard deviation, as calculated from W-10 reporting forms data; triangles represent mean ratios derived from salt-water surveys (see table 2).

Field	Pressure (psi)	Depth (ft)	Gradient (psi/ft)
Atkinson ¹	700	869	0.81
Dove Creek ¹	569	1,070	0.53
Dove Creek, E. ¹	1,280	1,120	1.14
Kenker ²	400	600 to 900	0.44 to 0.57
Water Valley ²	700	1,235	0.57

Table 3. Injection pressures for salt-water disposal in Tom Green County.

¹ Data on permitted pressures from files of Railroad Commission of Texas, District 7C, San Angelo

² Data on recorded pressures from disposal-survey questionnaire, 1967–1968, on file at Railroad Commission of Texas, Austin

numerous assumptions, especially the assumption that all produced water was discharged into pits and not reinjected. Locally, brine-disposal pits have major impacts on ground-water quality.

Production and Injection System Leaks

Contamination due to leaks in fluid production and injection systems may be important but was not investigated during this study. Leaks in production pipes at land surface can cause significant salt-water spills that later percolate downward to the water table. Salt-water injection to enhance recovery of oil and gas or brine disposal in saline formations can cause subsurface brine to mix with shallow ground water where well tubing and casing are leaky or where injection pressures into shallow horizons greatly exceed hydrostatic pressure (Rold, 1971). Some injection pressures are much higher than hydrostatic pressure (table 3) and can drive injected salt water upward across confining beds into shallow aquifers (fig. 22). Some operators reportedly exceed permitted injection pressures by accident or to maximize injection volume, suggesting that injection pressures need to be more closely monitored. Until recently, reinjection of salt water for disposal into shallow saline-waterbearing formations and into the Coleman Junction was practiced in the area. Because pressures in these formations are naturally high, the RRC recently amended regulations for salt-water disposal permits and established guidelines for injection below the Coleman Junction. However, salt-water injection for secondary oil and gas recovery is common in the Concho River watershed in both shallow (335 m [1,100 ft]) and deep (2,018 m [6,600 ft]) fields.

Conclusions

Occurrence of poor-quality ground water in the Concho River watershed of West Texas is not a recent phenomenon; it can be traced to the earliest records of water quality in the area. At chloride concentrations less than 250 mg/L, effects of different salinization mechanisms cannot be distinguished. At chloride concentrations in excess of 250 mg/L, however, two major salinization mechanisms, evaporation and brine mixing, can be distinguished by hydrochemical facies and graphical analysis of ionic ratios such as Ca/Cl, Mg/Cl, SO,/ Cl, and Br/Cl. Evaporation of shallow ground water in the eastern part of the study area is evidenced by (1) the increase in number and size of seep areas with time, (2) greater ground-water salinity in summer than in winter, and (3) chemical similarity between shallow ground water and theoretical composition of evaporated water. Mixed-cationmixed-anion hydrochemical facies and ionic ratios that are similar to ratios produced by evaporation characterize ground-water samples in the eastern part of the study area. Nitrate concentrations are high owing to dissolution of soil nitrate by shallow ground water or owing to contamination from feedlots. The water table is within approximately 1 m (3 ft) of land surface, creating seepage in topographically low areas. Evaporation at these seepage areas is greatest during the summer, resulting in high concentrations of chemical constituents harmful to plant growth. This salinization mechanism started with terracing of farmland, which destroyed natural surface drainages and increased infiltration of surface water. Irrigation may contribute to this salinization mechanism.

Ground-water evaporation is not a major salinization mechanism in the western part of the study, where the water table is generally too deep for evaporation and where irrigation is less common. lonic ratios in saline shallow ground water from the western part are similar to those of subsurface brines and differ from ratios due to evaporation. Three major brine-bearing sections underlie the area: (1) the Permian Clear Fork Group and San Angelo and San Andres Formations, which compose aguifers in their outcrop but which bear brine and oil downdip to the west; (2) the Permian Coleman Junction Formation; and (3) the Pennsylvanian formations. Permian brine appears to be the dominant source of brine contamination in the area. However, because San Angelo, San Andres, and Clear Fork brines are similar to overpressured Coleman Junction brines, the mixing mechanisms associated with shallow Permian brines cannot be chemically differentiated from those associated with deep Permian brines. Pennsylvanian and Permian brines can be distinguished by graphical analysis of ionic ratios, by differences in concentrations of organic-acid anions, and by hydrogen, oxygen, and carbon isotopic ratios.

Subsurface brines in shallow Permian formations flow eastward along regional flow paths and discharge into shallow aquifers beneath the study area. Evidence of natural discharge of brine from regional flow systems beneath the Southern Great Plains includes (1) hydraulic-head gradients indicating a potential for eastward flow of brine from the Midland Basin toward formation outcrops, (2) prevalence of subsurface brine within tens of kilometers of formation outcrops and at depths of less than 335 m (1,100 ft) beneath the study area, (3) high salinity and Na-Cl and Ca-SO, hydrochemical facies closely associated with outcrop and subcrops of Permian formations, and (4) chemical similarity between ionic and isotopic ratios in Permian formation brine and shallow ground water.

Water wells drilled into shallow Permian formations and abandoned without appropriate plugs created artificial pathways for salt-water contamination. Existence, location, and number of such wells could not be confirmed; no records of such wells exist. Brine from the Coleman Junction Formation and other artesian brine-bearing formations is expected to be discharged into shallow aquifers through inadequately plugged boreholes. This discharge is anticipated because (1) artesian fluid potentials in the Coleman Junction are higher than those in overlying formations and are close to or above land surface, (2) brine discharge from an abandoned hole was detected during this study and has been detected in other abandoned holes during past decades, (3) Coleman Junction brine can corrode steel tubing and casing in a few years, and (4) accuracy of plugging reports of wells that were abandoned more than 25 years ago is questionable.

Before 1969, millions of barrels of Permian and Pennsylvanian oil-field brines were discharged into unlined surface pits that allowed downward percolation and contamination of soils and shallow ground water. Leaching of residual salts is an ongoing process, and abandoned brine-disposal pits remain sources of local ground-water salinization. Not all disposal pits have the same potential for future salt-water pollution. Salinities of soil and ground water beneath abandoned disposal pits vary, depending on the history of brine disposal, formation permeability, water-table depth, and rate of flushing by rainwater at each site.

Oil-field brines are now disposed of by injection into saline formations at various depths beneath the Coleman Junction Formation. Operators discontinued injecting into the first saline formation encountered beneath land surface, above the Coleman Junction, because shallow ground water may become contaminated. However, injection at high pressures and at shallow depths continues for secondary recovery in Permian oil fields in the western part of the study area. Potential for contamination exists where injection pressures are too high or where injection tubing is leaky. Abandoned oil and gas wells that lack adequate cement plugs between shallow ground water and artesian brine-bearing formations, such as the Coleman Junction, also are contamination hazards. Leaky production tubing between surface facilities and in the wellbore poses ground-water salinization risks.

Useful diagnostic constituents to distinguish salinity sources include Ca/Cl, Mg/Cl, SO,/Cl, Br/Cl, Ca/Na, and Cl/SO4 ratios and, to a lesser degree, nitrate concentration. Differentiating saltwater sources is most successful where concentrations of dissolved solids are high. These constituents should be considered together because evaporation and brine mixing can yield similar chemical characteristics. The degree of overlap is most pronounced at low ionic concentrations because fresh water dilutes and masks chemical characteristics of salt-water sources. In addition to the ionic ratios mentioned earlier, $\delta^{18}O$, δD , and δ^{13} C isotopic ratios and the organic-acid anions acetate and propionate can be used to differentiate between Pennsylvanian and Permian brines. Isotopic and ionic data equally differentiate salinity sources; therefore, routinely measuring isotopes in salinity investigations probably is not justified. Because aliphatic-acid anions are dilute in the subsurface brines at shallow depths and might be destroyed by bacteria in shallow aquifers, these constituents probably will not help detect sources of salinization.

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Sample no.	Lat. (°N)	Long. (°W)	Landowner	Depth (ft)	Temp. (°C)	pН	Ca	Mg	Na	к	Sr	Li	
				RU	NNELS C	OUNT	(
3	31.878	100.051	Belk	47	19	8.1	113	35	173	3	1.2	0.03	
4	31.778	99.856	M. Werner	145	20	7.8	255	216	1140	9	52.2	0.21	
5	31.750	99.978	Halfman	70	19	8.1	335	138	269	3	11.9	0.05	
8	31.689	100.039	Matschek	80	20	8.1	731	198	249	5	14.7	0.13	
10	31.583	100.028	Hoelscher	20	18	7.8	350	115	295	2	10.1	<0.03	
11	31.583	100.027	Hoelscher	5	14	8.0	319	154	305	3	16.9	0.09	
12	31.583	100.027	Hoelscher	20	14	8.2	299	137	289	3	17.8	0.05	
13	31.577	100.027	Lisso	110	15	7.7	414	339	512	2	17.6	0.21	
14	31.573	100.015	Lange	20	16	8.0	202	82	245	2	10.0	0.05	
15	31.572	100.011	Fischer	_	16	7.8	585	192	633	5	12.7	0.12	
16	31.579	99.979	Hoffman	_	15	8.3	129	108	218	2	10.0	0.03	
CONCHO COUNTY													
17	31.500	100.033	Dirschke	120	16	8.1	369	50	271	3	2.2	<0.03	
18	31.455	100.011	K. Werner	200	21	7.7	273	764	952	13	12.5	0.2	
			тс	M GREE		TY (cont	. on p. 38)					
19	31.408	100.155	Schriever		20	8.1	185	118	91	2	3.7	0.04	
20	31.393	100.166	Schriever	100	20	8.1	188	115	192	2	12.8	0.07	
21	31.344	100.175	Sefcik	80	18	7.8	212	111	233	2	2.7	< 0.03	
22	31.374	100.225	Beatty	180	18	8.0	157	64	156	3	2.6	<0.03	
24	31.471	100.185	Friend	200	18	8.0	229	96	143	3	2.4	<0.03	
25	31.514	100.184	Hoelscher	85	18	7.6	359	128	334	2	3.4	0.03	
26	31.516	100.215	Hoelscher	140	19	8.1	252	82	169	3	3.5	<0.03	
27	31.472	100.326	Music	85	21	8.3	189	62	114	1	1.9	<0.03	
28	31.535	100.25	Scott	50	21	7.9	525	123	178	4	18.3	0.03	
33	31.581	100.590	Taylor	60	21	8.1	280	192	284	2	3.4	<0.03	
34	33.518	100.473	Sollars	85	19	6.9	133	59	79	2	3.6	0.03	
35	31.514	100.453	Hardy	95	20	6.9	230	112	691	6	4.5	<0.03	
36	31.523	100.413	Book		20	8.0	560	263	978	13	6.7	0.18	
37	31.526	100.41	Rose	240	19	8.0	519	223	220	7	6.5	0.12	
38	31.393	100.383	Stanford	90		7.2	268	97	243	4	2.9	0.04	
39	31.390	100.402	Fairview S.	10 1 0	_	7.6	452	152	363	4	6.4	0.05	
40	31.407	100.396	Lawnhaven	120	20	7.2	413	144	346	5	14.4	<0.03	
41	31.407	100.395	Lawnhaven	100	20	7.0	286	118	340	4	5.3	<0.03	
42	31.406	100.390	McClure	76	19	6.8	492	185	623	20	7.8	<0.03	
43	31.333	100.267	Jost	150	21	7.8	669	242	369	12	10.9	0.15	
49	31.346	100.426	Wash. Co.	105	14	7.7	188	69	232	3	1.7	<0.03	

Appendix A. Chemical analyses of shallow ground water collected for this study (concentrations in mg/L, ratios from mmol).

- Not analyzed

Appendix A (cont.)

Ва	нсоз	SO4	CI	Br	1	NO3	Ca/Cl	Mg/Cl	SO4/CI	D (‰)	18 ₀ (‰)	Group
					RUNNE	LS COUNT	Y					
0.07	294	108	166	0.88	<0.6	155.	0.60	0.31	0.24	-26	-4.5	1
0.02	211	378	2330	5.54	<0.6	<0.5	0.10	0.14	0.06	-34	-4.4	2
<0.01	414	940	452	1.82	<0.6	4.9	0.66	0.45	0.77	-31	-4.2	1
<0.01	327	1815	595	2.38	<0.6	32.5	1.09	0.49	1.13	-29	-3.7	1
0.01	200	591	699	2.48	<0.6	149	0.50	0.24	0.31	-28	-3.8	1
0.06	261	567	723	2.54	<0.6	128	0.39	0.31	0.28	-29	-3.9	1
0.04	211	501	685	2.42	<0.6	158	0.39	0.29	0.27	-29	-3.7	1
0.05	291	1485	983	3.17	<0.6	57.2	0.37	0.50	0.56	-34	-4.3	1
0.04	257	249	454	1.56	<0.6	169	0.40	0.27	0.20	-30	-3.5	1
<0.01	276	2115	735	3.12	<0.6	<0.5	0.71	0.38	1.05	-36	-4.8	1
0.04	387	251	343	1.63	<0.6	121	0.33	0.46	0.27	-29	-4.7	1
					CONCH	O COUNT	Y					
0.05	200	223	720	2.46	<0.6	165	0.45	0.10	0.11	-35	-4.2	2
<0.01	264	2415	1460	8.49	<0.6	30	0.17	0.76	0.61	-34	-5.2	1
				TOM	BREEN CC	UNTY (cor	nt. on p. 39)				
<0.01	288	474	205	0.81	<0.6	34.7	0.80	0.84	0.85	-35	-5.0	1
0.03	304	465	367	1.45	<0.6	27.6	0.45	0.46	0.47	-30	-4.5	1
0.04	363	258	482	1.97	<0.6	131	0.39	0.34	0.20	-35	-5.0	1
0.05	321	261	184	0.82	<0.6	20	0.75	0.51	0.52	-32	-4.4	1
0.04	258	167	454	1.95	<0.6	115	0.45	0.31	0.14	-25	-4.1	1
0.06	228	174	980	3.33	<0.6	229	0.32	0.19	0.07	-34	-4.3	2
0.06	218	270	461	1.86	<0.6	115	0.48	0.26	0.22	-32	-4.3	1
0.06	362	156	236	1.03	<0.6	97.6	0.71	0.38	0.24	-25	-3.8	1
0.03	243	1008	516	0.20	<0.6	147	0.90	0.35	0.72	-33	-5.2	1
0.13	293	225	976	3.23	<0.6	12.9	0.25	0.29	0.09	-37	-4.6	2
0.12	490	65	200	1.9	<1	24	0.59	0.43	0.12	-35	-4.7	2
0.08	385	183	1425	4.7	<1	59	0.14	0.11	0.05	-30	-3.7	2
0.05	206	462	2650	6.22	<0.6	40.8	0.19	0.14	0.06	-34	-4.4	2
0.09	232	753	1060	4.51	<0.6	45.6	0.43	0.31	0.26	-33	-4.8	1
0.11	214	161	735	2.73	<0.6	125	0.32	0.19	0.08	-31	-4.1	2
0.08	202	192	1310	4.44	<0.6	87	0.31	0.17	0.05	-36	-3.9	2
0.08	270	487	1060	4.8	<1	71	0.34	0.20	0.17	-35	-4.3	2
0.08	210	298	920	4.7	<1	138	0.27	0.19	0.12	-33	-4.0	2
0.10	275	350	1880	6.2	<1	85	0.23	0.14	0.07	-32	-3.8	2
<0.01	438	2040	639	1.53	<0.6	<0.5	0.93	0.55	1.18	-30	-4.3	1
0.05	461	113	479	1.35	<0.6	7.8	0.35	0.21	0.09	-29	-3.5	2

Appendix A (cont.)

Sample no.	Lat. (°N)	Long. (°W)	Landowner	Depth (ft)	Temp. (°C)	pН	Ca	Mg	Na	к	Sr	Li
			TO	M GREEN	I COUNT	Y (cont.	from p. 3	6)				
50	31.371	100.432	Gully	90	20	6.8	414	121	314	4	5.2	<0.03
51	31.374	100.433	Block	90	21	7.8	385	124	386	5	4.3	0.05
52	31.384	100.432	Schwartz	100	20	6.7	476	151	662	З	5.9	<0.03
53a	31.384	100.433	Baxter	100	<u> </u>	7.5	536	177	744	3	6.1	0.09
53b	31.384	100.433	Baxter	100	20	6.7	472	150	659	4	5.4	<0.03
54	31.378	100.442	Hoelscher	105	20	6.8	516	180	687	3	6.4	<0.03
55	31.379	100.450	Hoelscher	-		7.8	181	50	391	1	1.9	<0.03
56	31.376	100.447	McCoulskey	90	16	7.6	448	139	732	2	4.8	0.05
57	31.375	100.464	Latham	52	19	6.8	228	80	353	1	3.1	<0.03
58	31.375	100.473	Chandler	30		6.9	455	130	880	7	4.2	0.08
65	31.586	100.646	Corbell	65	20	6.9	169	132	149	1	2.8	<0.03
71	31.375	100.618	King	50	18	6.7	254	319	1020	7	9.0	<0.03
72	31.352	100.610	Johnson	100	21	8.1	212	89	422	4	2.9	0.07
73	31.358	100.609	Mair	85	21	7.5	498	185	1770	12	7.8	0.33
74	31.356	100.609	Williams	95		7.0	530	165	695	11	7.2	0.50
78	31.328	100.638	Bates	60	16	8.4	90	41	113	3	2.0	<0.03
83	31.164	100.546	Richter		20	8.3	73	30	259	8	0.5	0.06

Appendix A (cont.)

Ва	нсоз	SO4	CI	Br	ĩ	NO3	Ca/CI	Mg/Cl	SO4/CI	D (‰)	¹⁸ 0 (‰)	Group
				TOM	REEN CO	UNTY (cor	nt. from p. 3	37)				
0.28	240	106	1300	6.9	<1	69	0.28	0.14	0.03	-32	-3.5	2
0.14	192	131	1230	4.3	<0.6	62.9	0.28	0.15	0.04	-28	-4.1	2
0.09	340	353	1810	4.6	3	66	0.23	0.12	0.07	-23	-1.9	2
0.05	292	386	1970	5.6	<0.6	42.6	0.24	0.13	0.07	-28	-2.4	2
0.06	350	357	1780	6.6	1	62	0.23	0.12	0.07	-23	-1.9	2
0.11	320	310	2040	7.8	<1	75	0.22	0.13	0.06	-23	-2.0	2
0.03	313	284	573	1.9	<0.6	29	0.28	0.13	0.18	-8	-0.5	2
0.05	310	402	1622	4.7	<0.6	17.3	0.24	0.12	0.09	-16	-2.2	2
0.13	400	138	840	2.3	4	8	0.24	0.14	0.06	0.2	1.8	2
<0.10	530	820	1650	4.9	1.6	<2	0.24	0.11	0.18	-9.7	-0.4	2
0.32	500	121	520	2.6	1	13	0.29	0.37	0.09	-37.0	-5.1	2
0.07	860	1430	1430	5.6	2	18	0.16	0.33	0.37	-34.2	-4.7	1
0.02	399	318	712	2.2	<0.6	29.5	0.26	0.18	0.16	-28	-3.6	2
0.11	333	432	3380	6.9	<0.6	43.3	0.13	0.08	0.05	-35	-4.3	2
0.20	330	224	2100	3.0	<1.0	65	0.22	0.11	0.04	-32.7	-4.1	2
0.05	297	128	161	0.6	<0.6	2.3	0.49	0.37	0.29	-31	-3.4	1
0.20	379	180	211	0.7	<0.6	1.6	0.31	0.21	0.31	-38	-5.0	1

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	boreholes, abandoned core holes, and test holes (concentrations in mg/L, ratios from mmol).*																
Sample no.	Lat. (°N)	Long. (°W)	<i>Landowner/</i> field	Formation	Depth (ft)	Temp. (°C)	pН	Ca	Mg	Na	к	Sr	Li	Ва	нсоз	so4	СІ
						IB		DUNTY									
70	31.456	100.706	Arden	Canyon	6500	33.0	6.3	11350	1610	54790	534	819	11.5	56.7	196	10	105300
79	31.233	100.714	Brooks	San Angelo	1300	26.0	7.4	831	599	15840	206	39	3.4	0.4	198	20	26360
80	31.216	100.752	Mim, NW	San Angelo	1100	27.5	6.3	1290	701	27100	216	74	5.7	0.3	294	10	42790
81	31.177	100.716	Dove Creek	Canyon	6700	33.5	6.3	12740	1830	61420	431	769	8.4	131.0	72	11	123600
85	31.109	100.76	Tankersley	Wolfcamp	5500	40.0	6.5	50960	2780	47460	2560	547	4.9	17.4	94	350	176320
						RUN	INELS	COUNTY									
1	?	?	Wingate, NW	Coleman J.		_	6.9	2310	1120	25700	75	49	8.8	<0.2	136	4080	41900
2a	31.883	99.833	Wildcat	Coleman J.	700	22.0	5.0	1940	1059	22500	111	67	8.0	<0.2	1	2310	38000
2b	31.883	100.0	Wildcat	Coleman J.	700	22.0	7.1	2500	1122	22900	80	64	8.6	<0.2	164	4170	38300
6	31.717	100.033	Black	?	35	20.0	7.4	1172	524	1790	3	22	0.4	0.04	279	1092	5130
7	31.7	100.0	Big Ed	Coleman J.		23.0	11.1	4530	5	31600	260	63	7.5	<0.2	985	3750	51600
9	31.667	99.833	Wildcat	?	100	21.5	7.5	1605	1110	7440	18	47	1.3	<0.2	141	3390	15500
					TO	M GREEN	COUN	TY (cont. or	n p. 42)								
23	31.468	100.234	Veribest	Strawn	4700	25.5	6.3	13110	1830	43820	250	598	11.4	5.2	20	53	90740
29	31.583	100.233	SSR	Canyon	4300	29.5	6.9	9560	1530	40840	450	375	12.9	1.8	81	660	78960
30	31.654	100.399	Eliza B., N.	Canyon	6500	22.0	6.5	9970	1970	40560	1050	357	16.9	0.9	145	760	81470
31	31.638	100.625	Carlsbad	Strawn	5860	23.5	5.8	13970	2960	62400	545	1020	13.2	30.4	73	19	119850
32	31.588	100.595	Glass	Leo-Blaine	200	20.0	7.9	921	491	7185	86	20	1.6	0.08	250	2070	11630
44	31.302	100.25	Halfman	Strawn	4700	32.0	6.2	8230	1510	38180	593	269	16.1	0.6	204	950	74250
45	31.329	100.274	Jost	Bullwagon	75	New J	7.3	730	310	2710	50	13	2.5	0.4	430	2500	4450
46	31.417	100.283	Keyes	Com. Peak	42		6.9	1730	1050	4910	57	36	3.4	0.4	265	905	13070
47	31.336	100.426	Wash. Co.	Coleman J.	6212	·	7.6	1720	950	16960	320	343	3.3	0.6	250	4310	29610
48	31.336	100.426	Wash. Co.	Coleman J.	160		7.5	1290	540	11240	155	27	5.0	0.3	435	3130	19380
59	31.375	100.474	Chandler	?	38	5 5	7.2	990	350	1540	32	7.3	1.1	0.3	400	2080	3630

Appendix B. Chemical and isotopic composition of subsurface brines. Samples collected from oil wells, injection wells, wildcat boreholes, abandoned core holes, and test holes (concentrations in mg/L, ratios from mmol).*

*More chemical and isotopic analyses of these sample numbers are shown on page 41.

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Appendix B (cont.)

Sample no.	<i>Landowner/</i> field	Br	1	тос	Acet.	Prop.	Ca/Cl	Mg/Cl	SO ₄ /CI	D (‰)	18 ₀ (‰)	13 _C (‰)	34 _S (‰)
						IR	ION COUNT	Y					
70	Arden	430	27	130	136	14	0.10	0.02	0.00	-8, -9	-0.2	-4.40	22.86
79	Brooks	360	1	<8	2	<1	0.03	0.03	0.00	-35	-4.8	-19.92	40.26
80	Mim, NW	60	3	<2	<1	<1	0.03	0.02	0.00	-27	-4.0	-25.42	
81	Dove Creek	480	51	102	140	11	0.09	0.02	0.00	-12,-15	0.4, 0.7	-7.65	10.31
85	Tankersley	320	75	510	725	6	0.26	0.02	0.01	8	6.2, 6.2	-0.90	14.15
						RUN	INELS COUI	NTY					
1	Wingate, NW	71	2	_	-	_	0.05	0.04	0.04	-30	-3.0	_	_
2a	Wildcat	70	4	<u> </u>			0.05	0.04	0.02	-28	-2.5		
2b	Wildcat	71	2		5		0.06	0.04	0.04	-28	-2.5	20 	
6	Black	3.8	<0.6			-	0.20	0.15	0.08	-29	-4.1	2 <u>000</u>	1000
7	Big Ed	93	3		1000		0.08	0.00	0.03	-32	-4.0	-	
9	Wildcat	37	1	-	_	—	0.09	0.10	0.08	-38	-4.1	-	
						ТОМ	GREEN COU	JNTY					
23	Veribest	360	14	70	137	22	0.13	0.03	0.00	- 9	-1.1	-6.45	19.45, 19.36
29	SSR	280	12	82	130	12	0.11	0.03	0.00	-16	-3.0	-4.26	22.45
30	Eliza B., N.	200	8	52	107	11	0.11	0.04	0.00	-32	-4.0	-3.05	19.07
31	Carlsbad	460	39	80	128	14	0.10	0.04	0.00	- 8	-0.1	-8.76	21.22
32	Glass	9.9	<0.6				0.07	0.06	0.07	-38	-5.3	_	
44	Halfman	230	9	38	79	1	0.10	0.03	0.00	-22, -27	-3.1	0.55	18.97
45	Jost	6.6	<0.2	-		_	0.15	0.10	0.21		10000	10-00	100000
46	Keyes	22.0	0.7	—			0.12	0.12	0.03	-	-	-	—
47	Wash. Co.	33.0	2.1		<u></u>		0.05	0.05	0.05			_	
48	Wash. Co.	40.0	1.6	-			0.06	0.04	0.06				
59	Chandler	8.4	3.0	_		_	0.24	0.14	0.21	-19	-1.9	1 <u>0</u>	—

Appendix B (cont.)*

Sample no.	Lat. (°N)	Long. (°W)	<i>Landowner/</i> field	Formation	Depth (ft)	Temp. (°C)	pН	Ca	Mg	Na	к	Sr	Li	Ba	нсоз	so4	CI
						TOM GRI	EEN CO	OUNTY (cor	nt.)								
60a	31.429	100.484	City of SA	San Angelo	7		7.3	820	920	3960	47	13	2.1	0.4	725	4100	6430
60b	31.429	100.484	City of SA	San Angelo	68	22.0	7.1	1890	760	19730	270	46	8.1	<0.1	500	3695	33140
61	31.460	100.472	Bailey	San Angelo	58	—	7.5	580	200	2670	59	9.8	2.2	0.3	340	590	5280
62	31.465	100.554	Pulliam	Canyon	5200	42.0	6.8	9530	1610	43940	445	378	12.9	1.4	116	540	86150
63	31.491	100.508	Fisher Lake	?	100	20.5	7.7	2400	881	25100	349	55	4.0	<0.2	412	3920	41200
64	31.566	100.649	KWB	Strawn	7500	26.0	6.5	13040	1640	55590	320	1320	15.8	450.0	132	24	113140
66	31.597	100.712	T.D.	Strawn	6900	30.0	6.6	10150	1680	53660	397	587	6.6	178.0	212	10	102840
67	31.599	100.728	Hall	San Andres	1800	31.0	6.8	2410	1330	28930	488	52	3.8	0.6	612	3220	48510
68	31.633	100.856	Water V.	Clear Fork	1500	25.5	6.6	2240	822	29750	445	52	3.0	0.1	797	3490	47680
69	31.645	100.857	Water V.	San Andres	1000	25.0	7.6	1980	867	32620	399	59	3.6	0.2	297	1860	52620
75a	31.361	100.609	Stovall	Leona	32		7.7	130	43	320	10	1.3	0.6	0.2	330	232	335
75b	31.361	100.609	Stovall	Leona	68		7.5	465	195	2790	53	8.1	1.2	0.4	340	515	5030
75c	31.361	100.609	Stovall	Leona	75		7.6	610	240	4640	80	11	1.4	0.4	335	810	8070
76	31.361	100.608	Ducote	Leona	46		6.7	1465	430	11540	165	47	4.6	0.7	555	645	20750
77	31.360	100.600	Bunyard	Leona	24	—	7.2	750	270	6920	175	19	5.0	0.5	365	520	12190
82	31.211	100.683	Atkinson W.	San Angelo	885		7.3	931	696	15600	213	64	4.2	1.1	548	9	27200
84	31.114	100.504	H-J	Strawn	5500	34.5	7.1	2980	682	29180	741	120	10.3	0.4	362	1240	49520

*More chemical and isotopic analyses of these sample numbers are shown on page 43.

Appendix B (cont.)

Sample	Landowner/	Br	12	TOC	Acet	Prop		Ma/Cl	50./01	D (%.)	180 (%)	13 _C	34s
110.	neid	ы.).	100	AUCU	riop.		Mg/OI	304/01	(/00)	(/00)	(700)	(700)
						TOM GRI	EEN COUNT	Y (cont.)					
60a	City of San Angelo	14	2.0		-		0.11	0.21	0.24	-23.7	-2.5		
60b	City of San Angelo	61	2.4		·		0.05	0.03	0.04	-35.3	-5.4	_	
61	Bailey	8.5	0.3	-	1		0.10	0.06	0.04		<u></u>	10000	
62	Pulliam	350	12	52	89	7	0.10	0.03	0.00	-19	-0.8	-3.16	20.55
63	Fisher Lake	83	2	-	3 		0.05	0.03	0.04	-31	-4.2	-	
64	KWB	450	28	128	228	13	0.10	0.02	0.00	-11	0.6	-3.82	13.00
66	T.D.	410	34	88	187	15	0.09	0.02	0.00	-12	0.3	-2.37	
67	Hall	61	3	82	85	2	0.04	0.04	0.02	-33,-35	-2.0	-11.79	27.84,28.30
68	Water V.	73	1	80	<1	<1	0.04	0.03	0.03	-37	-5.2	-19.42	
69	Water V.	67	2	<21	<1	<1	0.03	0.02	0.01	-34,-35	-5.2	-23.91	35.00,35.68
75a	Stovall	1.8	1.0		83-7	(<u></u>).	0.34	0.19	0.26	-31.0	-4.0		-
75b	Stovall	9.6	1.0		3 	-	0.08	0.06	0.04	-31.0	-4.2		—
75c	Stovall	16	2.0				0.07	0.04	0.04	-34.6	-4.1	-	
76	Ducote	35	4.0		i:		0.06	0.03	0.01	-28.4	-3.2		
77	Bunyard	15	0.5	<u></u>	(<u>and a</u>	2 <u>000</u> 0	0.05	0.03	0.02	<u></u> 2		100.00	
82	Atkinson W.	57	2	1.000			0.03	0.04	0.01	-36	-5.3	5	
84	H-J	50	1	38	27	4	0.05	0.02	0.00	-44	-5.5	1.58	22.28

Not analyzed
 TOC Total organic carbon
 Acet. Acetate

Prop. Propionate

