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Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA

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Abstract

An extensive saline plume (>250 km²) within the regionally important unconfined aquifer in the Neogene Ogallala Formation overlies the Panhandle oil and gas field in the Southern High Plains, Texas, USA. Relative to upgradient Ogallala water, the plume waters have $\delta^{18}O$ (-6.7 to -8.8‰) and δD (-42 to -88‰) values that tend to be depleted and have higher Cl (>150 mg/l) and SO₄ (>75 mg/l) concentrations. Various end-member-mixing models suggest that the plume composition reflects the presence of paleowaters recharged during Middle to Late Wisconsinan time rather than salinization associated with petroleum production. Paleowaters probably mixed with salt-dissolution zone waters from the underlying Upper Permian formations before discharging upward into the Ogallala Formation. Cross-formational discharge is controlled primarily by the geometry of the underlying units, as influenced by the Amarillo uplift, pinch-out of the laterally adjoining confined aquifer in the Triassic Dockum Group, variations in the saturated thickness of the Ogallala aquifer and the presence of potential pathways related to salt dissolution. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Salinization of aquifers located in arid and semi-arid regions of the world is a major concern. Where active oil and gas production also occurs, it is critical to determine whether the salinization is due to anthropogenic or natural reasons for the purposes of remediation and management of limited water resources. Various geochemical studies have been conducted to characterize the source and the mechanism of salinization in such settings (e.g., Whittemore, 1995; Spangler et al., 1996).

In the Southern High Plains of Texas, USA, several regions of saline water are present in the regionally important Ogallala (High Plains) aquifer (Knowles et al., 1984). In the southern half of the Southern High Plains, extensive salinization (total dissolved solids [TDS] ranging from 400 to > 3000 mg/l) is associated with evaporation of ground water and deflation of salts from playas above Cretaceous bedrock highs (Wood and Sanford, 1995). In contrast, the Ogallala aquifer north of the Cretaceous subcrop and south of the Canadian River typically has TDS <400 mg/l. However, a saline plume with areal extent $> 250 \text{ km}^2$ exists along the northeastern margin of the Southern High Plains. It lies above the Panhandle oil and gas field in Carson, Gray and Roberts Counties, overlapping the Palo Duro and Anadarko Basins (Fig. 1).

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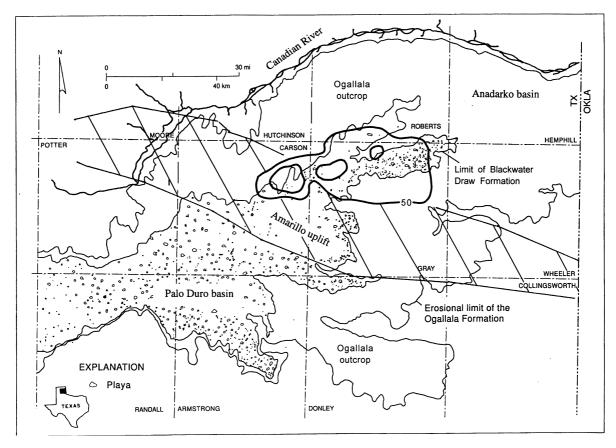


Fig. 1. Location of saline plume in the study area. The Cl concentration contours are 50 and 150 mg/l. The Amarillo uplift is hachured. The geologic map is modified from Eifler and Barnes (1969); Mullican et al. (1997).

Chloride concentrations range from 50 to > 500 mg/l and TDS from 400 to > 2000 mg/l. No significant information is currently available regarding the mechanism or the source of observed salinization, even though it was first reported by local residents prior to 1926 (Long, 1961) and mapped by McAdoo et al. (1964) and Knowles et al. (1984). Although substantial pumping has occurred in the last 40 a, the present plume dimensions (shown in Figs. 1 and 2) have not changed appreciably since 1964, which suggests quasi-steady state conditions.

Work by Dutton et al. (1989) indicates several possible sources of salinity in shallow ground waters in petroleum producing regions of west Texas. These include cross-formational discharge of brines formed by dissolution of underlying Permian bedded evaporites, infiltration from brine pits associated with oil and gas production prior to 1969 (when land disposal was banned) and upward brine movement through poorly plugged oil and gas wells. Nativ and Smith (1987) show that salinity can increase due to possible upward movement of water from underlying Permian formations close to the escarpments of the Southern High Plains. Such regions are > 50 km from the study area and thus cannot be the source of salinity. Evaporation from the water table of the Ogallala aquifer (typically 50–100 m below land surface) is insignificant in the study area, as is natural salinization associated with playas. Playas in the study area focus recharge to the Ogallala aquifer, rather than acting as evaporation pans (Mullican et al., 1997; Scanlon and Goldsmith, 1997; Wood et al., 1997).

The purpose of this paper is to geochemically characterize the saline plume water, identify the probable source(s) and mechanism(s) of salinization, and investigate the physiographic and geologic controls on the plume dimensions.

2. Hydrogeologic setting

The Palo Duro and Anadarko Basins are part of the intracratonic greater Permian Basin, which formed as a result of Late Paleozoic tectonic activity. The two basins are separated by the fault-bounded, structurally

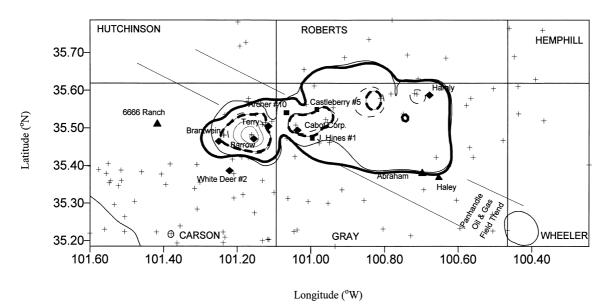


Fig. 2. Plume outline based on Cl and SO₄ concentrations (mg/l). Bold line represents Cl and thin line represent SO₄; solid lines represent 50 mg/l concentration and dashed lines represent 150 mg/l concentration. Diamonds indicate Ogallala wells, triangles indicate Upper Permian wells and squares indicate oil wells. Plus symbols indicate well data taken from TWDB database.

high basement rocks of the Amarillo uplift. The main topographic feature is the High Plains, which is separated from the Pecos Plains to the west by the Pecos River and from the Rolling Plains to the east by the eastern Caprock Escarpment. The Canadian River divides the Southern High Plains from the Central High Plains.

The major hydrostratigraphic units in the northern half of the Southern High Plains are the Deep-Basin Brine aquifer of Wolfcampian, Pennsylvanian and pre-Pennsylvanian age and shallower aquifers in the Neogene Ogallala Formation and Triassic Dockum Group (absent in the study area). Shallower aquifers are separated from the Deep-Basin Brine aquifer by a thick (>500 m) confining unit of Middle and Upper Permian evaporites and siliciclastic red beds (Bassett and Bentley, 1983; Senger, 1993) (Table 1). The available information on the hydrologic characteristics of the hydrostratigraphic units varies greatly in extent and quality. Permeability measurements are most abundant for the shallow fresh-water aquifers $(10^{-12}-10^{-13} \text{ m}^2)$, limited for the Deep-Basin Brine aquifer $(10^{-13}-10^{-20})$ m²), and rare for the confining unit $(10^{-16}-10^{-19} \text{ m}^2)$ (Wirojanagud et al., 1986; Senger, 1993).

The unconfined Ogallala aquifer, which occurs within the lower to middle part of the Ogallala Formation, is the largest aquifer in the continental US (Zwingle, 1993) and the main water supply unit for the Southern High Plains. The Ogallala Formation consists of fluvial sediments (primarily sands and gravels) and fine-grained eolian silts and clays that were deposited during Miocene to Pliocene times. The thickness of the Ogallala Formation ranges from 0 to 250 m in the study area. The chemical composition of Ogallala ground water varies from Ca-HCO₃ to a mixed-cation-HCO₃ water (Nativ, 1988). Ground water in the Ogallala aquifer flows northeastward, following the regional topographic slope for the part of the Southern High Plains shown in Fig. 1, and discharges naturally through springs and seeps along the Canadian River to the north and the Caprock Escarpment to the east. Although most discharge now occurs as a result of pumping for irrigation (which started in 1911 and increased significantly after World War II), the regional ground-water flow direction has not changed appreciably (Knowles et al., 1984). Nevertheless, some areas experienced a water level decline of as much as 15 m between 1940 and 1980 (Dugan et al., 1994).

The principal shallow confined aquifer is in the lower part of the Triassic Dockum Group, which is composed of sandstones and mudstones (Dutton and Simpkins, 1986; 1989). This aquifer system thins northeastward and pinches out approximately 40 km SW of the study area. Because of the erosion of the Pecos and Canadian River valleys during the Pleistocene, the present recharge to the lower Dockum aquifer is primarily through downward leakage from the Ogallala aquifer (Dutton, 1989; 1995). The flow in the lower Dockum Group in the northern part of the Southern High Plains is toward the east. Water quality is

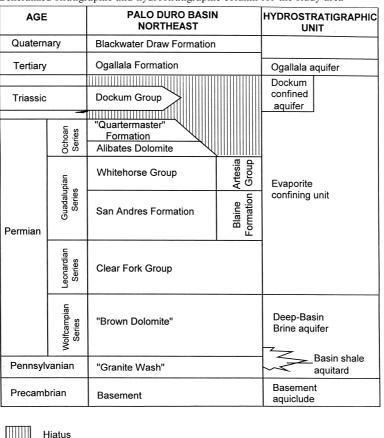


Table 1 Generalized stratigraphic and hydrostratigraphic column for the study area^a

marked by a mixed cation and mixed anion hydrochemical facies (indicative of ion exchange) with TDS < 3000 mg/l (Dutton and Simpkins, 1986).

Middle and Upper Permian evaporite-confining strata consist of halite, anhydrite, dolomite and finegrained siliciclastic red beds (Bassett and Bentley, 1983). Some Upper Permian units, including the Upper Permian Whitehorse Group, are unconformably overlain by the Ogallala Formation and are composed predominantly of siliciclastic red beds with minor evaporites (McGookey et al., 1988). Such units can have significantly higher permeability than underlying evaporitic strata and locally act as aquifers where the Ogallala Formation and Dockum Group are thin or absent, such as at the margins of the Southern High Plains (Long, 1961). Several salt-dissolution zones have been identified within the upper part of the evaporiteconfining unit (Gustavson et al., 1980; McGookev et al., 1988). These zones seem to have developed by shallow, topographically driven circulation of meteoric water (Dutton, 1989).

The regionally confined Deep-Basin Brine aquifer is composed of Pennsylvanian and Permian carbonates, shales and arkosic sands and gravels (commonly referred as granite-wash deposits) (Bassett and Bentley, 1983). The brines typically have TDS between 140 and 290 g/l and have evolved either from halite dissolution by ground water of meteoric origin or from evaporatively concentrated Paleozoic sea water modified by subsequent rock-water interaction (Fisher and Kreitler, 1987; Bein and Dutton, 1993; Stueber et al., 1998). The average equivalent fresh-water head distribution in the Palo Duro Basin indicates that brine generally flows from SW to NE toward highly permeable granite-wash deposits that flank the Amarillo uplift and function as hydrologic sinks (Bassett and Bentley, 1983; Wirojanagud et al., 1986; Fisher and Kreitler, 1987). Although surface discharge of brines is not

^a Data modified from Bassett and Bentley (1983); Gustavson (1986).

Table 2 Chemical analyses of water samples

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 0.50.709964 Samples collected in this Bein and Dutton (1993) Bein and Dutton (1993) a 1 = Ogallala water; 2 = plume water; 3 = lower Dockum water (paleowater); 4 = Upper Permian water; 5 = sult-dissolution zone water; 6 = evaporite-confining unit Dutton (1989) Dutton (1989) Dutton (1987) Nativ (1988) Nativ (1988) Samples ⁸⁷Sr/⁸⁶Sr^bSource Fryar Fryar Fryar - 8.00.708634 S - 8.30.708634 S - 6.7 - 10.8 70912 70732 70725 -8.70.708274.00.70734 - 6.70.7 - 7.2 6.40.7 - 2.5 - 0.4 - 2.9 7.00. - 9.6 - 10.8 - 10.4 - 8.5 - 9.4 - 7.3 - 7.0 6.6 6.0 - 7.3 11.8 - 8.5 1.7 5.1 δ^{18} O (%) T 1 1 1 $\begin{array}{c} 6574 - 60 \\ 4941 - 62 \\ 67086 - 66 \\ 67530 - 72 \\ 95812 - 50 \\ 94917 - 52 \\ 94917 - 52 \\ 2233954 - 50 \end{array}$ $\frac{167743 - 25}{173563 - 25}$ $\frac{173563 - 25}{188532 - 12}$ - 54 - 70 - 88 - 77 - 77 - 75 - 53 - 76 - 76 - 26 - 34 - 26 - 57 - 53 - 52 - 53 - 40 - 58 35526 - 17- 27 216789 - 429 % 287948 - 5293954 - 5 412 -165497 -245936 -227082 -2110 739 384159 160201 TDS (mg/l) 366408422335335422405404405518518395 438 409 432 413 388 910 1075 520 5.38 3.19 4.74 5.05 5.05 6.16 4.50 5.2 4.74 5.81 < 0.5 1
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< 0.5 1</pre> 3.84 5.01 5.53 4.23 3.43 7.48 0.4 2.0 NO₃ (mg/l) 6.44 4.63 < 0.5 5.93 6.0 6.91 50 0.12 0.05 0.13 0.12 0.10 0.05 0.14 0.10 0.33 0.05 0.65 0.32 0.24 0.45 0.58 0.47 0.05 0.14Br (mg/l) $\begin{array}{c} 1.3 \\ 1.4 \\ 7.8 \\ 6.2 \\ 6.2 \\ 52 \\ 52 \\ 58 \\ 58 \end{array}$ 0.4 4.0 0.1300 180 193 273 161 534 118 423 523 ν V ν V V v 135 13.42 HCO₃ 1 (mg/l) (17.17232 16.5 260 16.9 278 15.8 256 15.8 256 19.9 258 19.9 258 19.9 258 19.0 265 11.0 269 11.0 260 607 269 607 269 607 269 607 269 101.05198 75.16237 75.16237 11.10 250 101.05198 75.16237 11.10 250 101.05198 75.16237 11.10 250 11.10 260 81.7 297 95 95 39 39 41.1 66 72.6 135 415 268 326 35 560 161 SO₄ (mg/l) 1502.6 < 5.0 13.18 37.4 48.2 300 230 5900 5610 5100 5760 5700 34 2200 1800 440 169 1320 1540 201 16 572 572 193.7 334.1 266 166 64 302 54.5 56 56 56 56 31.3 31.3 33.19 33.3,19 8.61 6.99 12.5 8.44 27.5 1200 [4.67 [1.4 8.81 9.15 8.78 4.76 8.88 7.9 10.7 Ξ 13 000 35100 36120 53100 54700 205700 94800 104000 166800 170400 98100 131000 CI (mg/l) 250200 148500 139000 107000 114700 1.65 6.70 6.70 5.0 3.7.7 2.3.1 3.7.7 3.7.7 3.7.3 0.80 1.00 1.07 0.81 0.81 0.95 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.00 0.09 0.12 Si Sr (mg/l) (mg/l) 010 1180 1158 1158 560 6 96 109 109 $\begin{array}{c} 12.53 \\ 4.95 \\ 4.86 \\ 5.09 \\ 5.18 \\ 5.18 \\ 3.57 \\ 9.8 \\ 8.6 \\ 8.6 \\ 22.8 \end{array}$ 9.57 222.0 10.0 12.4 78.7 102 98.1 $\begin{array}{c} 12.1 \\ 15.5 \\ 17.4 \\ 15.3 \\ 15.6 \\ 14.0 \\ 14.0 \\ 15.6 \\ 18.6 \\ 18.6 \\ 18.6 \\ 18.6 \\ 18.6 \\ 18.6 \\ 18.6 \\ 18.6 \\ 15.7 \\ 15.7 \end{array}$ 6.79 6.18 5.80 2.34 2.39 2.99 6.67 5.64 5.58 5.58 5.68 6.52 6.49 5.95 5.48 2.02 2.56 6.63 6.36 6.57 6.44 4.85 5.60 5.07 6.81 6.20 1.85 2.44 2.37 4.93 K (mg/l) 8.1 7.2 49 32 32 46 30 1218 1218 3230 700 500 620 459 380 610 580 594 16.25 26.0 584 165.8 57.4 80.7 139.2 172.4 14.4 68.4 1560 1280 24000 117.7 Na (mg/l) 110 208 2239 3326 3318 3391 227 227 108700 110700 68890 76100 56490 62260 23850 35000 33000 21270 54600 54500 77930 60200 49490 Mg (mg/l) 17.8 26.9 27.8 19.7 224.0 224.0 224.0 224.0 224.0 226.1 3923 4040 7860 7400 2000 2360 2110 2600 1600 2668 2095 1978 3.1 103.8 DO Ca (mg/l)(mg/l) 432 78 27 280 280 210 1530 1940 1940 1940 1940 1940 4.7 4.7 47200 7480 15700 22900 6020 7316 8002 8168 87780 5550 4707,4 4708,3 2808,3 390 390 5506,9 4407,9 4400,5 1604,3 1 4207.0 4207.4 3804.6 2607.0 2807.3 2404.7 3507.0 3706.4 7.3 2089.9 2107. -70 - 150 - 150-130120 325 185 ī 7.7 7.7 7.6 7.6 8.2 7.7 9 7.7 4.7 8.2 9.0 4.7 8.0 8.0 7.5 6.3 6.3 7.6 6.6 7.0 5 8.1 33.2 23.0 34.5 18.6 19.0 19.0 15.0 17.9 17.9 21.4 35.3 35.3 17.2 17.2 18.5 23.8 38.2 37.6 68.4 $\begin{array}{c} 2.3.7\\ 1.8.2\\ 1.8.2\\ 1.8.2\\ 1.1.2\\ 1.$ 25.9 23.7 21.4 18.8 29.9 222.5 23.0 223.1 223.1 223.1 223.0 47.3 46.4 101.213 101.561 101.565 101.586 101.586 101.557 101.557 101.557 101.557 101.557 101.557 101.557 101.557 101.555 101.557 101.555 101.556 101.556 101.556 101.556 101.556 101.556 101.557 101.237 101.237 101.237 101.238 102.347 101.752 101.753 102.347 101.752 101.755 101.75 100.989 101.008 101.068 102.46 101.20 101.08 102.46 101.68 100.87 102.40 30-07-199735.417 07-10-199135.326 10-12-199135.326 11-12-199135.354 11-10-199135.351 11-10-199135.351 15-10-199135.347 15-10-199135.347 15-10-199135.347 15-10-199135.347 13-05-199135.347 13-05-199135.266 11-05-199335.266 11-05-199335.251 04-101-199735.481 31-07-199735.515 11-02-198735.515 11-02-198735.515 11-02-198735.515 11-02-198735.515 11-02-198735.515 11-02-198735.515 11-02-198735.515 01-08-199735.543 03-08-199735.545 04-08-199735.491 27-04-198434.896 01-08-199735.539 03-08-199735.399 03-08-199735.410 27-11-198434.854 30-11-198434.734 04-02-199335.254 20-02-198535.294 21-02-198535.341 13-03-198534.546 27-04-198434.904 10-08-198735.44 09-06-198335.41 06-08-198735.09 27-04-198335.08 29-05-198534.66 34.66 12-09-198435.07 35.71 35.08 35.41 35.63 35.07 01-05-198434.52 Type^aDate 9 16 PR-5 PR-6 PR-6 PR-18 PR-18 PR-18 FR-18 FR-18 S. McGregor M.L. Vance M.L. Vance M.L. Vance M.L. Vance M.L. Vance M.L. Vance M.C. Carson M62 Carson M62 Hamly Gray #63 Gray #63 S4a Dockum S5a Dockum S6a Dockum S17 Dockum S11 Dockum S12 Dockum S12 Dockum J. Friemel No. 1 HT601 White Deer #2 #2 Haley Abraham P. Meacham Potter #61 Potter #60 Mansfield Mansfield-b Terry Cabot Corp. Castleberry Barrow Brantwein Archer #10 Hines #1 name Sawyer Sawyer-b Harman SW10 Zeeck No. 0M-39 0M-46 0M-47 **OM-40** RO602 **OL12** DNI Well DSI

^b NBS 987 standard: mean = 0.710259, $2\sigma = 0.000013$, n = 51 (only for samples collected in this study).

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observed within the Palo Duro Basin, Orr et al. (1985) evaluated pressure-depth data from drill-stem tests and concluded that an upward hydraulic gradient exists near the southwestern flanks of the Amarillo uplift (approximately 40 km SW of the study area).

3. Methods

To assess the mechanisms and sources of salinization, water samples were collected from 9 water wells (6 in the Ogallala aquifer and 3 in the underlying Upper Permian Whitehorse Group aquifer where the Ogallala Formation is thin or absent). The Texas Water Development Board (TWDB) database (unpublished) does not list any water wells in confined aquifers within the area of the mapped plume. All samples were collected at the wellheads after pumping the well until pH, Eh and temperature readings stabilized (Table 2) and passing the water through a 0.45-µm cartridge filter. Three oil wells (not known to have been water flooded) producing from Wolfcampian and Upper Permian Formations in the vicinity of the saline plume were also sampled (Fig. 2). The oil-field brines were collected from actively pumping wells following the methods of Lico et al. (1982). Fluids collected in a bucket were passed through a glass separatory funnel filled with fiberglass wool. The separated brine was drained to a filter chamber and forced through a 0.45µm filter with a hand pump. The pH combination electrode was calibrated with pH 4, 7 and 10 buffers and the Eh Pt electrode checked against ZoBell's solution at each site, following Wood (1976). Eh values are reported relative to the standard hydrogen electrode. Alkalinity (reported as HCO₃) was measured by potentiometric titration with 1.6 N H₂SO₄ and dissolved O₂ (except for oil-field brines) according to the modified Winkler method (Brown et al., 1970) at each site (Table 2).

Water samples for cation and silicon analyses were acidified with 6 N HNO₃ (5 ml per 500 ml of water sample) at the well sites. All cations were initially analyzed using atomic absorption spectrometry; where the charge balance error was greater than 5%, cations were re-analyzed using inductively coupled plasma emission spectroscopy (ICAP). Silicon was analyzed by ICAP and anions were analyzed using ion chromatography. Solute concentrations have an accuracy range of $\pm 10\%$. To measure δ^{18} O, water samples were equilibrated with CO₂. To determine δD , H₂ gas was generated by reacting water samples with hot Zn. Samples were analyzed by gas-source mass spectrometry at the University of Georgia with an accuracy of +0.15‰ for δ^{18} O and $\pm 3\%$ for δ D. The results are reported as per mil (‰) deviations from standard mean ocean water (SMOW) (Craig, 1961). Values reported are uncorrected for dissolved salts in brines (Sofer and Gat, 1972). ⁸⁷Sr/⁸⁶Sr isotopic analyses were performed by thermal ionization mass spectrometry at the University of Texas at Austin following methods given in Banner and Kaufman (1994). The mean value obtained for standard NBS SRM 987 is 0.710259 (2σ of $\pm 1.3 \times 10^{-5}$; n = 51). Mineral saturation indices for brines were calculated using Pitzer activity coefficients incorporated in the geochemical modeling program PHRQPITZ (Plummer et al., 1988). Speciation calculations for the remaining water samples were performed using the program NETPATH (Plummer et al., 1994).

Chemical and isotopic data from previous regional studies were incorporated (Dutton and Simpkins, 1986; Dutton, 1987, 1989, 1995; Fisher and Kreitler, 1987; Nativ, 1988; Bein and Dutton, 1993; Fryar and Mullican, 1995) (Table 2). Also included are data from the TWDB database for the period of 1985 to present (data not shown here). For wells sampled more than once, the most recent data were considered. Samples with charge balance error >5% were not considered, nor were samples with charge balance error equal to zero, which indicates that Na and K were determined by difference (Hem, 1985).

4. Results

Plume dimensions plotted by using Cl and SO₄ concentration data from the TWDB database essentially coincide (Fig. 2). Multiple localized zones of high concentration within the plume indicate that the salinization may not result from a single or point source. The Piper trilinear plot (Fig. 3) indicates that for major anions the plume waters are chemically distinct from other water types in the region, with a greater proportion of HCO₃ and SO₄ than brines, a greater proportion of Cl than upgradient Ogallala and Dockum waters, and a greater proportion of HCO₃ and Cl than Upper Permian waters. For cations, the plume waters are less distinctive and may have been influenced by ion-exchange reactions; Na is the dominant cation.

Plume waters are at or near saturation with respect to calcite and dolomite and undersaturated with respect to gypsum, anhydrite and halite, as are most other waters collected in the region. Figure 4 shows Na and Cl concentrations for the plume waters and a line of dilution by fresh water of a brine in equilibrium with halite. All plume waters except one fall on or close to the dilution line for the halite-saturated water, which suggests simple two-end member mixing. (The outlier (Terry) may be contaminated, according to anecdotal evidence of past disposal practices on an

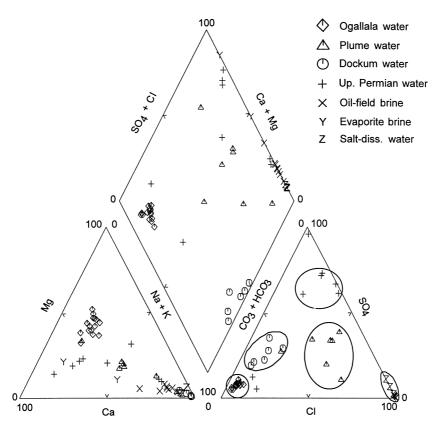


Fig. 3. Piper trilinear plot of the plume waters along with other end-member waters in the region (listed in Table 2).

adjoining property.) However, the SO₄/Cl vs. Cl plot (Fig. 5) indicates that most plume waters do not fall within the mixing band between salt-dissolution zone water and upgradient Ogallala water and may in fact be influenced by waters in the shallow Upper Permian section. Both Cl and SO₄ are assumed to behave conservatively in the Ogallala aquifer because of oxidizing conditions (although SO₄ may not be conservative in deeper, anoxic units, especially the Deep-Basin Brine aquifer). Oil-field brines in the region generally have low SO₄ concentrations; exceptions (e.g., HT601; Table 2) may reflect (1) dissolution of anhydrite or gypsum from relatively shallow depths or (2) mixing with saltdissolution zone waters. The mixing band between oilfield brine and upgradient Ogallala water in Fig. 5 also fails to explain the origin of plume waters. McAdoo et al. (1964) observed that, in almost all brine pits, the Cl greatly exceeds the SO₄ content, whereas in the plume waters Cl approximately equals SO₄ content.

Similarly, the ratio of Br/Cl vs. Cl can be plotted to examine mixing (Fig. 6). Both Br and Cl are assumed to behave conservatively in the absence of evaporites (Whittemore, 1995; Stueber et al., 1998). Only 3 plume water samples that were collected had Br concentrations above the detection limit of 0.05 mg/l (Table 2), which suggests dissolution of halite with a relatively low Br content (typical for recrystallized halite), a large water-rock ratio, or a relatively short residence time (Richter and Kreitler, 1986). Because the plume waters do not fall within the mixing band between salt-dissolution zone waters or brines and upgradient Ogallala water, mixing of more than two end-members is indicated. Other plume water samples that had Br concentrations below detection limit (and less than 0.1 mg/l) are also plotted by considering maximum possible Br concentrations as equal to detection limit (shown inside the square box of Fig. 6). This suggests salt-dissolution zone waters as the probable source.

Plume waters have a wide range of δ^{18} O values (-6.7 to -8.8‰) and δ D values (-42 to -88‰) (Table 2). Four out of 7 plume samples are isotopically depleted compared to the upgradient Ogallala waters (δ^{18} O -3.7 to -7.3‰; δ D -18 to -58‰) (Fig. 7). Of the 3 plume samples that are not isotopically depleted, one sample (Terry) may be contaminated, as noted above. The remaining 2 samples are from City of Pampa municipal wells; owing to analytical difficulties (S.W. Tweedy, Bureau of Economic Geology, personal communication, 1995), the reported δ D value for the sample collected by Dutton (1995) may be several per

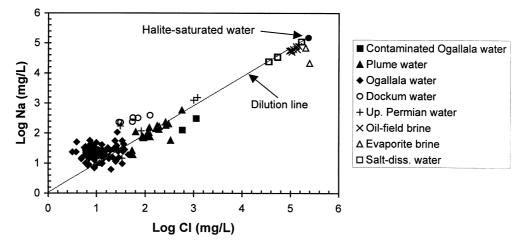


Fig. 4. Na–Cl bivariate plot along with lines representing fresh-water dilution of halite-saturated water (assumed to contain 6.2 mol of halite/kg solution). Data taken from TWDB database and Table 2. Contaminated wells inferred from TWDB database.

mil higher than actual. The salt-dissolution zone waters have δ^{18} O and δ D values in the range of -6.7 to -9.4 and -50 to -72‰, respectively, while oil-field brines have δ^{18} O and δ D values in the range of +6.4 to -5.1 and -12 to -42‰, respectively (Table 2).

The simple mixing between salt-dissolution zone water or oil-field brines (via natural cross-formational flow or artificial contamination) and modern Ogallala water cannot be the source of salinization, as the endmembers have higher δ^{18} O and δ D values than plume waters (Fig. 7). Mixing of brines (either oil-field brines or evaporite-confining unit brines) with a hypothetical water that has very low δ^{18} O and δ D values is unrealistic, because no such water types have been reported in previous regional studies. Furthermore, such mixing fails to explain the high SO₄ and low Br concentrations in the plume. Possible water–rock reactions at the low temperatures characteristic of units above the Amarillo uplift (typically $<40^{\circ}$ C) cannot explain the isotopically depleted plume waters and the offset from the global meteoric water line. However, the depleted signature of plume waters can be explained by the mixing of Permian evaporite (confining unit) brine with water of isotopic composition similar to lower Dockum waters (Fig. 7). Terry's well (outlier plume water mentioned earlier) has the lowest SO₄/Cl and Na/Cl ratios of the plume waters, suggesting that a salinity source has more recently moved into the aquifer, but the maximum Br/Cl ratio is too low for oil-field brine to be a substantial contributor.

The range of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values in 5 plume water samples (0.7078 to 0.7089) overlaps the range of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ in 3 oil-field brines (0.7084 to 0.7103) (Table 2) and the range of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values in salt dissolution

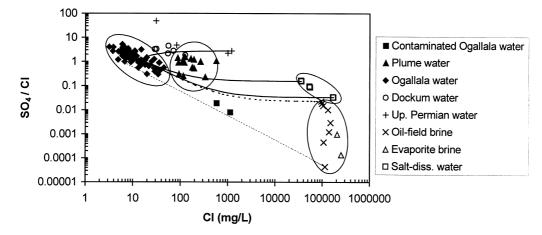


Fig. 5. SO_4/Cl vs. Cl bivariate plot for end-member waters in the region. Data taken from TWDB database and Table 2. Contaminated wells inferred from TWDB database.

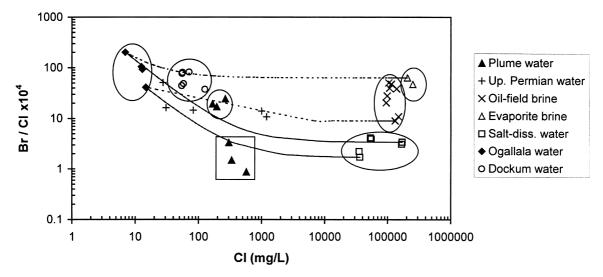


Fig. 6. Br/Cl vs. Cl relationship for end-member waters along with selected mixing lines to explain the origin of plume waters. Plume waters that had Br concentrations below detection limit (and < 0.1 mg/l) are plotted as equal to detection limit inside the square box. Data taken from Table 2.

zone waters (0.7072 to 0.7083 [unpublished data, A. Dutton]). On a plot of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ vs. 1/Sr (not shown), the plume waters fall between the salt-dissolution zone waters, evaporite-confining unit brines and fresh Ogallala water, which may indicate that oil-field brines are not the primary source of salinity. However, mixing calculations using ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values are precluded by the lack of data for the lower Dockum waters and limited data for the upgradient Ogallala waters. Musgrove and Banner (1993) observed that, probably because of water–rock interaction, ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ data were less definitive than Cl⁻, δ^{18} O and δ D data in delineating mixing.

5. Discussion

5.1. Mixing models

It is hypothesized that the isotopically depleted saline plume waters may partly represent paleowaters recharged during Middle to Late Wisconsinan time (15 to 35 ka before present), when the temperatures were cooler than average Holocene temperatures by 5 to 8°C. On the basis of values of $\delta^{18}O$ (-5.9 to -12.7‰), δD (-40 to -85‰) and ¹⁴C (<1 to 13% modern ¹⁴C activity), Dutton (1989, 1995) and Dutton and Simpkins (1986, 1989) inferred the presence of such paleowaters in the confined lower Dockum aquifer and the salt dissolution zone SW of the study area. The depleted isotopic composition cannot be explained by recharge at higher altitudes because the Pecos River has functioned as a hydrologic divide to the west (dividing the Southern High Plains from the Rocky Mountains) since its incision during the Pliocene (Gustavson and Finley, 1985; Senger, 1993). Similarly, eastward erosion of the Colorado Piedmont in the Central High Plains has isolated confined ground waters (15 to 40 ka old) in the Dakota Formation (Cretaceous) from recharge along the Rocky Mountain front (Davisson et al., 1993).

It is proposed that paleowaters with relatively low δ^{18} O and δ D values (1) acquire salinity by mixing with salt-dissolution zone waters present in the upper part of the evaporite-confining unit, (2) possibly mix with small proportions of modified-connate brine present in Permian evaporite-confining units and (3) subsequently mix with Ogallala water as a result of topographically driven circulation. Several zones of active salt dissolution resulting from the topographically driven circulation of meteoric waters have already been recognized in the study area (Gustavson et al., 1980; McGookey et al., 1988; Dutton, 1989). Cross-formational flow and chemical evolution have been invoked to explain the composition of ground water to the east in Oklahoma, Kansas and Missouri (e.g., Banner et al., 1989; Musgrove and Banner, 1993).

To investigate the authors' hypothesis, mixing between end-member waters has been modeled using δ^{18} O and Cl (Fig. 8) and δ D and Cl (Fig. 9). These constituents are assumed to behave conservatively in the relatively shallow units above the Upper Permian evaporites. The hypothetical trajectories shown are based on the initial mixing of Dockum water with saltdissolution zone water and evaporite-confining unit (modified-connate) brine followed by mixing with upgradient Ogallala water. Sampled wells within the

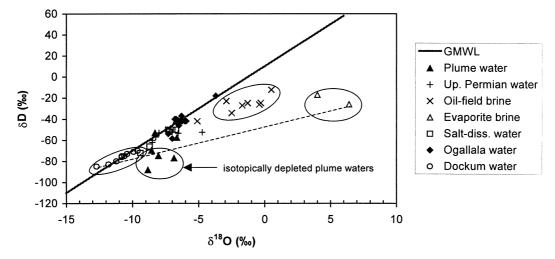


Fig. 7. $\delta^{18}O - \delta D$ relationship for end-member waters in the region. GMWL represents global meteoric water line given by the equation $\delta D = 8\delta^{18}O + 10$ (Craig, 1961).

plume indicate various flow paths and different mixing percentages among the end-members (salt-dissolution zone water, evaporite-confining unit brine, Dockum water and Ogallala water) (Figs. 8 and 9).

Mixing percentages based on δ^{18} O, δ D and Cl plots were used in the geochemical modeling programs PHRQPITZ and NETPATH to predict the major ion composition of plume waters for comparison with observed values. Mixing calculations were performed in a closed system by taking the Mansfield well (saltdissolution zone), the Dockum well S12 and the upgradient Ogallala well White Deer #2 as end members and allowing ion exchange (Na^+/Ca^{2+}) and $Na^+/$ Mg^{2+}). Ion exchange reactions are plausible because of the presence of illite, chlorite, smectite and vermiculite in the confining unit (Dutton, 1987; Fisher, 1988) and montmorillonite (smectite) and illite in the Ogallala aquifer (Fryar and Mullican, 1995). However, the exact mechanisms for ion exchange processes along the various flow paths cannot be differentiated because of the lack of petrographic data and well control, especially in the Upper Permian units. Activity ratios of 0.2 to 0.8 for Na^+/Ca^{2+} and 0.1 to 0.8 for $Na^+/$ Mg^{2+} provided the best fit between the modeled and observed concentrations. These ratios are in the range of experimentally determined values for clay minerals like those found in the study area (Bruggenwert and Kamphorst, 1982; Appelo and Postma, 1994). Model results are presented in Table 3 for the 4 isotopically depleted plume samples. The proportion of salt-dissolution zone water mixing with the Dockum and modern Ogallala waters is < 2% in all cases. A reasonable match exists between the observed and simulated values for the major ions, but the simulated isotopic values do not match as well for the isotopic parameter

not considered in the mixing calculations and the mixing percentages vary for the two simulations (a and b). These differences are probably artifacts of the isotopic variations between the actual end-member compositions along the flow paths and those used in the simulations. In general, the calculations appear to work better when δ^{18} O is the mixing parameter (simulation a) compared to δD (simulation b). This is probably due to greater accuracy in determination of δ^{18} O values ($\pm 0.15\%$) compared to δD values ($\pm 3\%$).

5.2. Geologic controls on salinization

The presence of the Amarillo uplift has strongly affected the regional hydrodynamics of fluids in both the Palo Duro and Anadarko Basins (Fig. 10). Fluid flow in the Paleozoic strata of the Palo Duro Basin is from W to E-NE, with granite-wash sediments around the Amarillo uplift acting as a hydrologic sink (Senger, 1993). In addition, the potential for upward cross-formational flow exists in the Deep-Basin Brine aquifer near the Amarillo uplift, as shown by Orr et al. (1985). The Amarillo uplift (along with the Bush dome) has also influenced the style of deposition of Permian sediments, which follow the subsurface rise caused by the uplift and thin at higher elevations near the margins of the adjoining basins (Fig. 10). Consequently, the Middle and Upper Permian evaporite deposits present at higher elevations near the basin margins have undergone dissolution by circulating meteoric waters since the Middle Tertiary (Gustavson, 1986; Dutton, 1989). This has resulted in disturbed overlying strata, with dissolution-related subsidence, chaotic bedding, faults and numerous joints that have affected both the

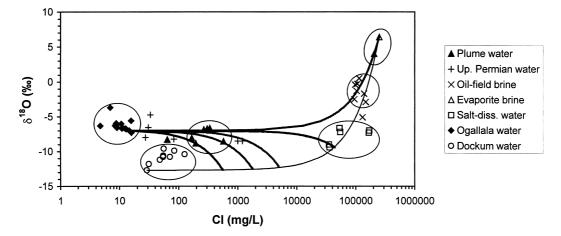


Fig. 8. δ^{18} O–Cl relationship for end-member waters with selected mixing lines to explain the origin of plume waters.

thickness of the Ogallala Formation and the present topography (Gustavson et al., 1980; Gustavson, 1986).

The hydrology of the region at shallower depths has also been indirectly influenced by the Amarillo uplift through lithological and structural effects on underlying units. Grain size distribution and thickness variation of the Ogallala Formation may have been influenced by the dissolution of underlying Permian evaporites. Coarse fluvial sediments were deposited in paleovalleys, whereas finer eolian sediments covered paleoupland areas (Gustavson and Winkler, 1988). Upward cross-formational flow into the Ogallala Formation from underlying units tends to occur in paleoupland regions, where the aquifer is thin and less permeable (Nativ and Smith, 1987). However, it can also occur due to pinchout of underlying formations; as where the Dockum Group pinches out in southwestern Carson County (Fig. 10). Some water in the lower Dockum aquifer may also pass laterally northeastward into the Upper Permian red beds. Meteoric waters recharged upgradient move from W to E–NE in the Ogallala aquifer and the lower Dockum aquifer, consistent with the topographic slope and regional flow. Some of the water leaks to the underlying evaporite-confining unit. It is assumed that horizontal flow in this unit is almost negligible (Senger, 1993), but ground water may flow laterally in the siliciclastic red beds in the Upper Permian section.

The end-member waters mix in various proportions, indicated by the mixing lines in Figs. 8 and 9, as a result of topographically driven circulation along the inferred flow paths shown in Fig. 10. The salinity distribution within the Ogallala aquifer may be influenced by the variations in its saturated thickness as well as by the variable flux of saline paleowaters. Because the probability of fractures and joints is high in this region, owing to the presence of salt-dissolution zones, saline water could rise from the Upper Permian units

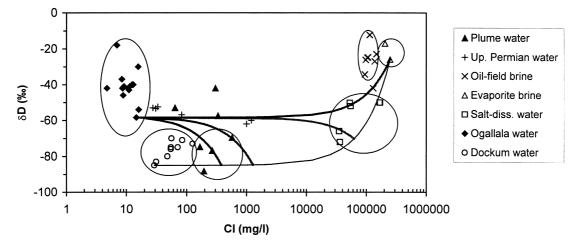


Fig. 9. δD -Cl relationship for end-member waters with selected mixing lines to explain the origin of plume waters.

Constituent Barrow	Barrow			Brantwein			Cabot Corp.	·		Harnly		
	Observed	Simulation a	Simulation b	Observed	Simulation a	Simulation b	Observed	Simulation a	Simulation b	Observed	Simulation a	Simulation b
Ca	1.22	1.39	1.50	0.80	0.80	3.01	2.46	1.77	2.46	2.01	1.11	1.48
Mg	0.48	0.80	0.72	0.64	0.32	0.75	1.43	1.77	1.54	1.35	1.17	1.48
Na	25.40	19.70	20.39	7.21	9.81	7.36	7.86	5.84	8.40	6.05	5.88	6.63
K	0.05	0.13	0.12	0.11	0.10	0.07	0.16	0.13	0.09	0.16	0.12	0.09
CI	16.13	16.13	16.16	5.46	5.45	5.23	7.50	7.55	7.52	4.68	4.69	4.69
HCO ₃	4.10	4.04	4.77	3.24	4.66	5.95	3.42	3.81	5.47	4.08	4.22	5.26
SO_4	6.32	1.34	1.45	1.05	0.74	1.17	2.72	0.64	1.15	2.24	0.57	0.89
Hd	7.76	7.93	8.03	7.70	7.85	8.20	7.20	7.35	7.64	7.39	7.68	7.83
δ ¹⁸ O (‰)	-8.6	- 8.4	-9.2	- 8.8	- 8.9	-12.1	- 6.9	-7.2	-10.9	-8.0	-8.0	-10.3
$\delta D (\%_0)$	- 70	- 65	- 70	- 88	-67	-82	- 77	- 59	- 77	- 75	- 63	- 74
Mixing												
percentages												
Ogallala		73.7	60.6		67	10		96.4	31		83	41.7
(White Deer #2)												
Docknim (S		747	37.8		375	80.5		96	68 3		16.6	57.9
12)		1				2		i				
Salt		1.6	1.6		0.5	0.5		0.7	0.7		0.4	0.4
dissolution												
(Mansfield)												

Table 3 Result of mixing calculations (observed waters compared with simulated waters)^a; concentrations are given in mmol/kg

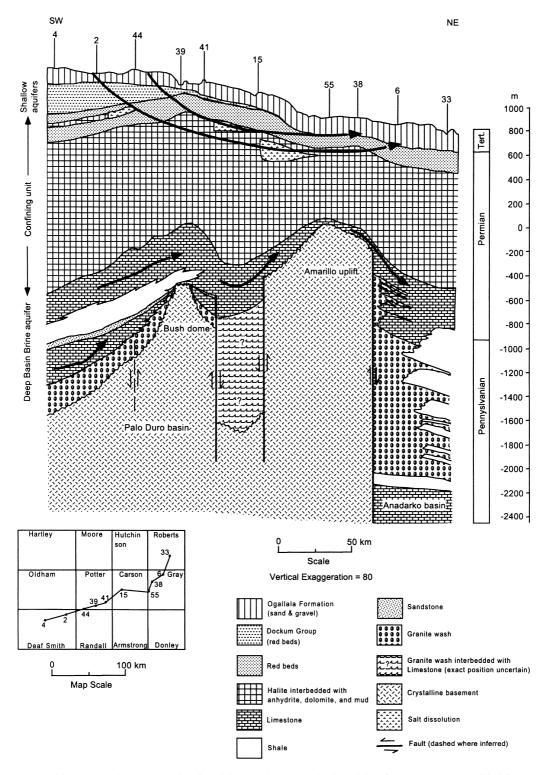


Fig. 10. Stratigraphic cross section along with inferred flow paths to explain the origin of plume waters. Modified from Dutton et al. (1982).

into the Ogallala aquifer in the study area. It is unlikely that brine (either oil-field brine or evaporite-confining unit brine) could rise from Middle and Lower Permian units all the way into the Ogallala aquifer or Upper Permian units through the thick evaporite-confining unit. Although the hydraulic gradient may be upward close to the Amarillo uplift in the Deep-Basin Brine aquifer, the hydraulic heads in the Ogallala aquifer and Upper Permian units are much higher than those in the Deep-Basin Brine aquifer (Bair, 1987; Senger, 1993).

The spatial distribution of the saline plume is controlled and limited by the extent of the Ogallala Formation and the distance to the Canadian River (Fig. 1). The Ogallala Formation is either thin or absent E and SE of the study area because of retreat of the eastern Caprock Escarpment. The Canadian River, which is fed partly by the discharge from the Ogallala aquifer (Mullican et al., 1997), controls the northern limit of the saline plume. It is possible that as the plume moves N–NE, it is further diluted by meteoric recharge where the Ogallala Formation is exposed in the Canadian River valley. The upward flux of saline water may also become insignificant outside the mapped plume area.

6. Conclusion

A saline plume in the regionally important Ogallala aquifer in the Southern High Plains, Texas, lies above the Panhandle oil and gas field in the vicinity of the Amarillo uplift, which divides the Palo Duro Basin from the Anadarko Basin. Prior to this study, little information was available regarding the source or the mechanism of salinization. Because ground water is the major source of water in this semi-arid region, it is important to determine whether the increased salinity is due to artificial or natural causes. The authors have documented that oil-field brines are not the primary source of salinity, as the saline plume waters tend to be depleted in δ^{18} O and δ D and high in SO₄. Instead, the saline plume originated from upward, topographically driven, cross-formational discharge of waters that were probably recharged during Middle to Late Wisconsinan time and that mixed with salt-dissolution zone waters present in the upper part of the evaporiteconfining unit. The discharge of paleowaters in the study area is controlled by the geometry of the underlying units, pinchout of the lower Dockum aquifer, variations in the saturated thickness within the Ogallala aquifer and presence of joints, fractures and other potential pathways associated with salt dissolution. The distribution of Cl and SO₄ indicates that the flux of saline water is variable within the study area. Even though significant pumping has occurred, the overall shape of the saline plume has not changed appreciably since the plume was first mapped by McAdoo et al. (1964).

Natural salinization can be important in degrading water quality, even in areas of active petroleum production. Saline plumes in similar areas cannot be considered a priori to be the result of oil-field contamination; rather, the source should be investigated thoroughly. This is also critical in assessing the potential for further degradation of the Ogallala aquifer: as the water table declines with continued pumpage for irrigation, salinity could increase in the vicinity of the plume.

Acknowledgements

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References

- Appelo, C.A.J., Postma, D., 1994. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam.
- Bair, E.S., 1987. Regional hydrodynamics of the proposed high-level nuclear-waste repository sites in the Texas Panhandle. J. Hydrol. 92, 149–172.
- Banner, J.L., Kaufman, J., 1994. The isotopic record of ocean chemistry and diagenesis preserved in non-luminescent brachiopods from Mississippian carbonate rocks, Illinois and Missouri. Geol. Soc. Am. Bull. 106, 1074–1082.
- Banner, J.L., Wasserburg, G.J., Dobson, P.F., Carpenter, A.B., Moore, C.H., 1989. Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri. Geochim. Cosmochim. Acta 53, 383–398.
- Bassett, R.L., Bentley, M.E., 1983. Deep brine aquifers in the Palo Duro Basin: regional flow and geochemical constraints. Univ. of Texas at Austin, Bureau of Economic Geology Report of Investigations 130.
- Bein, A., Dutton, A.R., 1993. Origin, distribution, and movement of brine in the Permian Basin (USA): a model for displacement of connate brine. Geol. Soc. Am. Bull. 105, 695–707.
- Brown, E., Skougstad, M.W., Fishman, M.J., 1970. Methods

for collection and analysis of water samples for dissolved minerals and gases. In: US Geol. Surv. Techniques of Water Resources Investigations (Book 5, Chapter A-1).

- Bruggenwert, M.G.M., Kamphorst, A., 1982. Survey of experimental information on cation exchange in soil systems. In: Bolt, G.H. (Ed.), Soil Chemistry, B. Physico-Chemical Models. Elsevier, Amsterdam, pp. 141–203.
- Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703.
- Davisson, M.L., Smith, D.K., Macfarlane, P.A., Whittemore, D.O., Hudson, G.B., Caffee, M., 1993. Isotopic indications of age and flow characteristics of ground water in the Dakota aquifer, eastern Colorado through central Kansas. Geol. Soc. Am., Abstracts with Programs 25, 145.
- Dugan, J.T., McGrath, T., Zelt, R.B., 1994. US Geol. Surv. Water-Resources Investigations Report 94-4027.
- Dutton, A.R., 1987. Origin of brine in the San Andres Formation, evaporite confining system, Texas Panhandle and eastern New Mexico. Geol. Soc. Am. Bull. 99, 103– 112.
- Dutton, A.R., 1989. Hydrogeochemical processes involved in salt-dissolution zones, Texas Panhandle, USA. Hydrol. Proc. 3, 75–89.
- Dutton, A.R., 1995. Groundwater isotopic evidence for paleorecharge in US High Plains aquifers. Quatern. Res. 43, 221–231.
- Dutton, A.R., Simpkins, W.W., 1986. Hydrogeochemistry and water resources of the Triassic lower Dockum Group in the Texas Panhandle and eastern New Mexico. Univ. Texas at Austin, Bureau of Economic Geology Report of Investigations 161.
- Dutton, A.R., Simpkins, W.W., 1989. Isotopic evidence for paleohydrologic evolution of ground-water flow paths, Southern Great Plains, USA. Geology 17, 653–656.
- Dutton, S.P., Goldstein, A.G., Ruppel, S.C., 1982. Petroleum potential of the Palo Duro Basin, Texas Panhandle. Univ. Texas at Austin, Bureau of Economic Geology Report of Investigations 123.
- Dutton, A.R., Richter, B.C., Kreitler, C.W., 1989. Brine discharge and salinization, Concho River watershed, West Texas. Ground Water 27, 375–383.
- Eifler Jr., G.K., Barnes, V.E., 1969. Amarillo sheet. In: Geologic Atlas of Texas, Scale 1:250,000. Univ. Texas at Austin, Bureau of Economic Geology.
- Fisher, R.S., 1988. Clay minerals in evaporite host rocks, Palo Duro Basin, Texas. J. Sed. Pet. 58, 836–844.
- Fisher, R.S., Kreitler, C.W., 1987. Geochemistry and hydrodynamics of deep-basin brines, Palo Duro Basin, Texas. Appl. Geochem. 2, 459–476.
- Fryar, A.E., Mullican III, W.F., 1995. Delineating controls on the composition of ground water in the vicinity of the Pantex Plant, Southern High Plains, Texas. Univ. Texas at Austin, Bureau of Economic Geology, report prepared for the US Department of Energy under subgrant to grant no. DE-FG04-90AL65847.
- Gustavson, T.C., Finley, R.J., 1985. Late Cenozoic geomorphic evolution of the Texas Panhandle and northeastern New Mexico: case studies of structural controls on regional drainage development. Univ. Texas at Austin, Bureau of Economic Geology Report of Investigations 148.

- Gustavson, T.C., 1986. Geomorphic development of the Canadian River Valley, Texas Panhandle: an example of regional salt dissolution and subsidence. Geol. Soc. Am. Bull. 97, 459–472.
- Gustavson, T.C., Winkler, D.A., 1988. Depositional facies of the Miocene–Pliocene Ogallala Formation, northwestern Texas and eastern New Mexico. Geology 16, 203–206.
- Gustavson, T.C., Finley, R.J., McGillis, K.A., 1980. Regional salt dissolution in the Anadarko, Dalhart, and Palo Duro Basins of the Texas Panhandle. Univ. Texas at Austin, Bureau of Economic Geology Report of Investigations 106.
- Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. US Geol. Surv. Water-Supply Paper 2254.
- Knowles, T., Nordstrom, P., Klemt, W.B., 1984. Evaluating the ground-water resources of the High Plains of Texas, vol. 1. Texas Dept. of Water Resources Report 288.
- Lico, M.S., Kharaka, Y.K., Carothers, W.W., Wright, V.A., 1982. Methods for collection and analysis of geopressured geothermal and oil field waters. US Geol. Surv. Water-Supply Paper 2194.
- Long Jr., A.T., 1961. Geology and ground-water resources of Carson and part of Gray County, Texas, progress report no. 1. Texas Board Water Engineers Bull. 6102.
- McAdoo, G.D., Leggat, E.R., Long, A.T., 1964. Geology and ground-water resources of Carson County and part of Gray County, Texas, progress report no. 2. Texas Water Commission Bull. 6402.
- McGookey, D.A., Gustavson, T.C., Hoadley, A.D., 1988. Regional stratigraphic cross sections, Mid-Permian to Quaternary strata, Texas Panhandle and Eastern New Mexico: distribution of evaporites and areas of evaporite dissolution and collapse. Univ. of Texas at Austin, Bureau of Economic Geology Cross Sections 8.
- Mullican III, W.F., Johns, N.D., Fryar, A.E., 1997. Playas and recharge of the Ogallala aquifer on the Southern High Plains of Texas — an examination using numerical techniques. Univ. of Texas at Austin, Bureau of Economic Geology Report of Investigations 242.
- Musgrove, M., Banner, J.L., 1993. Regional ground-water mixing and the origin of saline fluids: Midcontinent, United States. Science 259, 1877–1882.
- Nativ, R., 1988. Hydrogeology and hydrochemistry of the Ogallala aquifer, Southern High Plains, Texas Panhandle and Eastern New Mexico. Univ. Texas at Austin, Bureau of Economic Geology Report of Investigations 177.
- Nativ, R., Smith, D.A., 1987. Hydrogeology and geochemistry of the Ogallala aquifer, Southern High Plains. J. Hydrol. 91, 217–253.
- Orr, E.D., Kreitler, C.W., Senger, R.K., 1985. Investigation of underpressuring in the Deep-Basin Brine aquifer, Palo Duro Basin, Texas. Univ. Texas at Austin, Bureau of Economic Geology Geological Circular 85-1.
- Plummer, L.N., Parkhurst, D.L., Fleming, G.W., Dunkle, S.A., 1988. A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines. US Geol. Surv. Water-Resources Investigations Report 88-4153.
- Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1994. An interactive code (NETPATH) for modeling net geochem-

ical reactions along a flow path, version 2.0. US Geol. Surv. Water-Resources Investigations Report 94-4169.

- Richter, B.C., Kreitler, C.W., 1986. Geochemistry of salt water beneath the Rolling Plains, north-central Texas. Ground Water 24, 735–742.
- Scanlon, B.R., Goldsmith, R.S., 1997. Field study of spatial variability in unsaturated flow beneath and adjacent to playas. Water Resour. Res. 33, 2239–2252.
- Senger, R.K., 1993. Paleohydrology of variable-density ground-water flow systems in mature sedimentary basins: example of the Palo Duro basin, Texas, USA. J. Hydrology 151, 109–145.
- Sofer, Z., Gat, J.R., 1972. Activities and concentrations of oxygen-18 in concentrated aqueous salt solutions: analytical and geophysical implications. Earth Planet. Sci. Lett. 15, 232–238.
- Spangler, L.E., Naftz, D.L., Peterman, Z.E., 1996. Hydrology, chemical quality, and characterization of salinity in the Navajo aquifer in and near the Greater Aneth Oil Field, San Juan County, Utah. US Geol. Surv. Water-Resources Investigations Report 96-4155.
- Stueber, A.M., Saller, A.H., Ishida, H., 1998. Origin, migration, and mixing of brines in the Permian Basin: geo-

chemical evidence from the eastern Central Basin platform, Texas. Am. Assoc. Petrol. Geol. Bull. 82, 1652–1672.

- Whittemore, D.O., 1995. Geochemical differentiation of oil and gas brine from other saltwater sources contaminating water resources: case studies from Kansas and Oklahoma. Environ. Geosci. 2, 15–31.
- Wirojanagud, P., Kreitler, C.W., Smith, D.A., 1986. Numerical modeling of regional ground-water flow in the Deep-Basin Brine aquifer of the Palo Duro Basin, Texas Panhandle. Univ. Texas at Austin, Bureau of Economic Geology Report of Investigations 159.
- Wood, W.W., 1976. Guidelines for collection and field analysis of ground-water samples for selected unstable constituents. In: US Geol. Surv. Techniques of Water-Resources Investigations (Book 1, Chapter D2).
- Wood, W.W., Sanford, W.E., 1995. Eolian transport, saline lake basins, and groundwater solutes. Water Resour. Res. 31, 3121–3129.
- Wood, W.W., Rainwater, K.A., Thompson, D.B., 1997. Quantifying macropore recharge: examples from a semiarid area. Ground Water 35, 1097–1106.
- Zwingle, E., 1993. Ogallala aquifer, wellspring of the High Plains. National Geographic 183, 80–109.