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

Sunil Mehta^{a,*}, Alan E. Fryar^a, Jay L. Banner^b

^aDepartment of Geological Sciences, University of Kentucky, Lexington, KY 40506-0053, USA

^bDepartment of Geological Sciences, The University of Texas at Austin, Austin, TX 78712, USA

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Abstract

An extensive saline plume ($>250 \text{ km}^2$) 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 $\delta^{18}\text{O}$ (-6.7 to -8.8‰) and δD (-42 to -88‰) values that tend to be depleted and have higher Cl ($>150 \text{ mg/l}$) and SO_4 ($>75 \text{ mg/l}$) 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 $>3000 \text{ mg/l}$) 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 $<400 \text{ mg/l}$. 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).

* Corresponding author. Fax: +1-606-323-1938.

E-mail address: smeht0@pop.uky.edu (S. Mehta).

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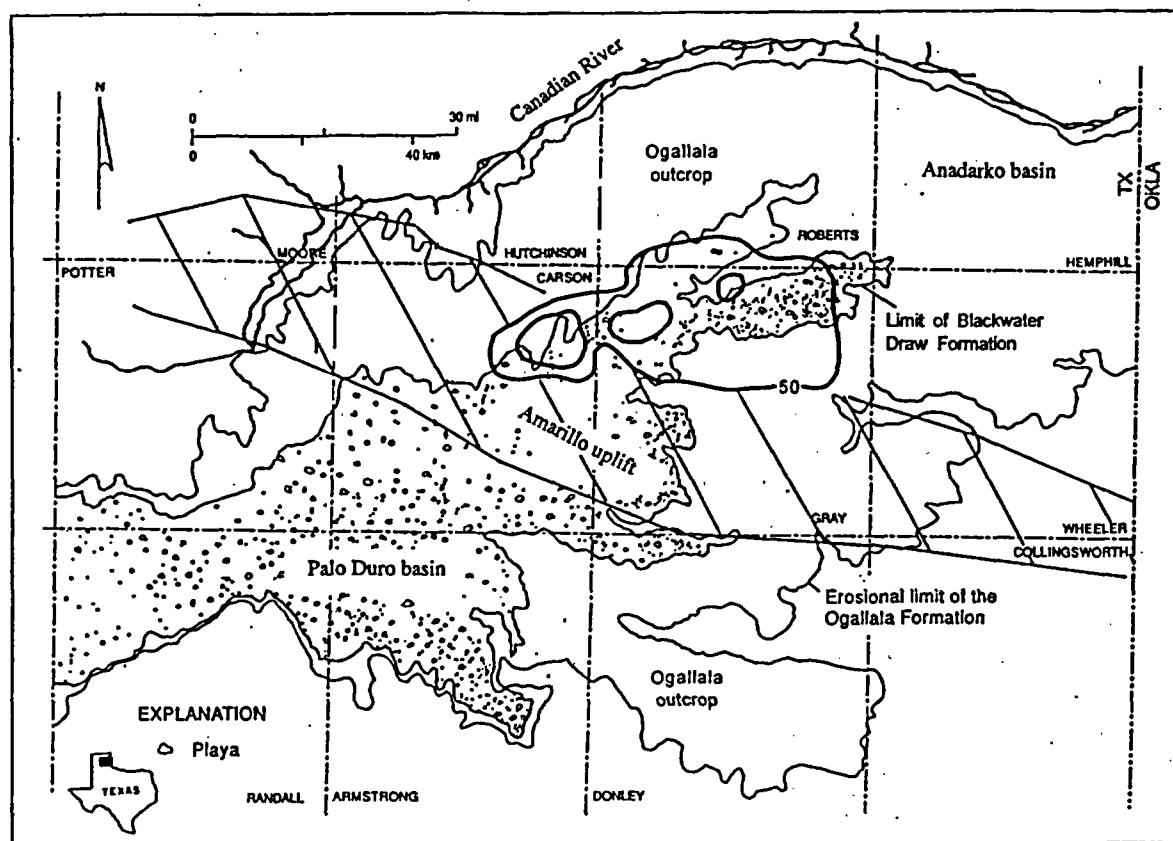


Fig. 1. Location of saline plume in the study area. The Cl concentration contours are 50 and 150 mg/l. The Amarillo uplift is hachured. The geologic map is modified from Eifler and Barnes (1969); Mullican et al. (1997).

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

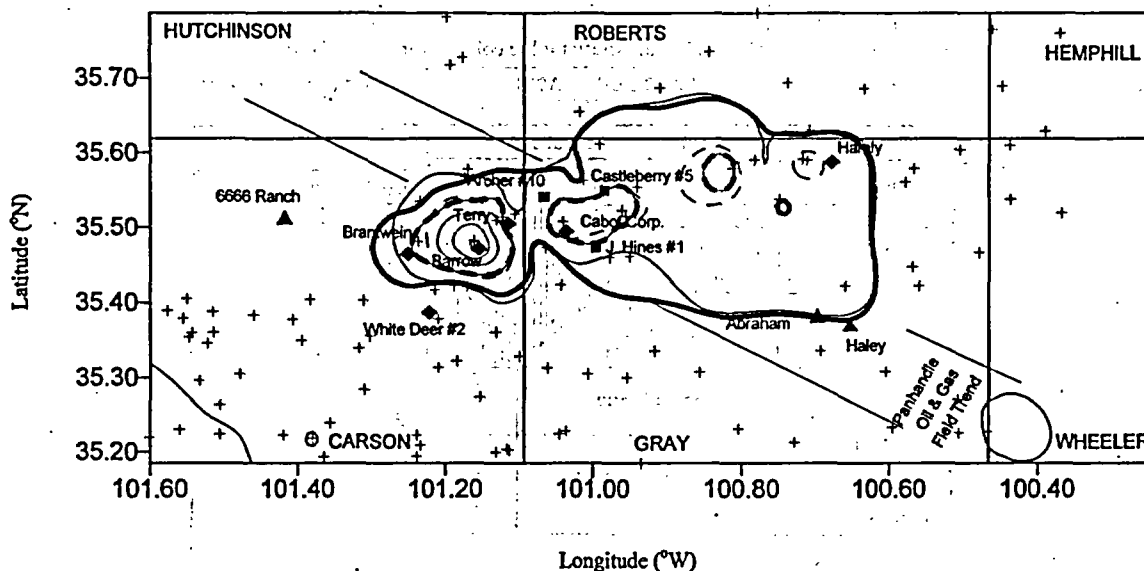


Fig. 2. Plume outline based on Cl and SO₄ concentrations (mg/l). Bold line represents Cl and thin line represents SO₄; solid lines represent 50 mg/l concentration and dashed lines represent 150 mg/l concentration. Diamonds indicate Ogallala wells, triangles indicate Upper Permian wells and squares indicate 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} m²), limited for the Deep-Basin Brine aquifer (10^{-13} – 10^{-20} m²), and rare for the confining unit (10^{-16} – 10^{-19} m²) (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

AGE		PALO DURO BASIN NORTHEAST		HYDROSTRATIGRAPHIC UNIT
Quaternary		Blackwater Draw Formation		
Tertiary		Ogallala Formation		Ogallala aquifer
Triassic		Dockum Group		Dockum confined aquifer
Permian	Ochoan Series	"Quartermaster" Formation	Artesia Group	Evaporite confining unit
		Alibates Dolomite		
	Guadalupean Series	Whitehorse Group	Blaine Formation	
		San Andres Formation		
	Leonardian Series	Clear Fork Group		
Wolfcampian Series	"Brown Dolomite"		Deep-Basin Brine aquifer	
Pennsylvanian		"Granite Wash"		Basin shale aquitard
Precambrian		Basement		Basement aquiclude

 Hiatus

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

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 fine-grained 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 evaporite-confining unit (Gustavson et al., 1980; McGookey et al., 1988). These zones seem to have developed by shal-

low, 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

Table 2
Chemical analyses of water samples

Well name	Type	Date	Latitude (°N)	Longitude (°W)	Temperature (°C)	pH	Eh (mV)	DO (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Si (mg/l)	Sr (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	HCO ₃ (mg/l)	Br (mg/l)	NO ₃ (mg/l)	TDS (mg/l)	δD (‰)	δ ¹⁸ O (‰)	⁸⁷ Sr/ ⁸⁶ Sr	Source
White Deer #2	1	30-07-1997	35.417	101.213	23.7	7.6	4707.4	45.1	17.8	17.6	4.94	12.1	0.80	14.67	17.17232	0.06	3.84	366 - 58	-7.00.70912	Samples collected in this study				
OM-39	1	07-10-1991	35.332	101.561	19.6	7.7	4708.3	41.5	26.9	20.4	5.60	15.5	1.00	11.4	21.6 260	< 0.10	4.20	408 - 41	-6.6	Fryar and Mullican (1995)				
OM-40	1	14-10-1991	35.326	101.560	18.2	7.6	2808.3	38.4	26.9	23.9	6.07	17.4	1.02	8.81	16.9 278	< 0.10	5.01	422 - 42	-6.0	Fryar and Mullican (1995)				
OM-46	1	10-12-1991	35.350	101.583	18.4	7.7	410	33.8	27.8	25.1	6.81	15.3	1.07	9.15	15.8 256	< 0.10	5.38	396 - 41	-6.6	Fryar and Mullican (1995)				
OM-47	1	11-12-1991	35.347	101.586	16.8	7.7	390	39.6	19.7	12.1	6.67	14.0	0.81	4.76	9.49225	< 0.10	3.19	335 - 42	-6.3	Fryar and Mullican (1995)				
PR-2	1	11-10-1991	35.351	101.558	19.9	7.8	5306.9	38.7	23.4	30.1	5.64	14.0	0.88	8.88	18.7 277	< 0.10	4.74	422 - 46	-6.5	Fryar and Mullican (1995)				
PR-6	1	15-10-1991	35.340	101.557	18.6	7.6	4607.9	42.7	24.9	21.1	5.61	15.6	0.99	11	20.1 258	< 0.10	4.60	405 - 43	-6.7	Fryar and Mullican (1995)				
PR-18	1	08-10-1991	35.351	101.547	20.2	7.4	450	42.5	24.0	25.9	5.58	14.5	0.96	8.61	19.9 258	< 0.10	4.22	404 - 42	-6.2	Fryar and Mullican (1995)				
PR-41	1	15-10-1991	35.347	101.555	20.3	7.5	4409.5	42.9	26.1	23.8	5.68	14.2	1.01	10.7	20.8 274	< 0.10	5.05	424 - 42	-6.0	Fryar and Mullican (1995)				
F. Wink	1	09-10-1992	35.247	101.555	19.5	7.7	4708.0	42.6	40.7	20.4	6.52	22.5	1.49	6.99	18.6 352	0.14	6.07	518 - 18	-3.7	Fryar and Mullican (1995)				
D. Gabel	1	13-05-1993	35.280	101.546	17.9	7.7	1604.3	33.1	27.4	20.3	6.49	18.6	1.10	12.5	16.6 252	0.13	6.44	395 - 40	-6.7	Fryar and Mullican (1995)				
S. McGregor	1	12-05-1993	35.266	101.604	19.4	7.6	2107.3	36.5	29.7	19.5	6.36	25.0	1.24	8.44	20.9 286	< 0.10	4.63	438 - 37	-6.3	Fryar and Mullican (1995)				
M.L. Vance	1	11-05-1993	35.272	101.568	17.2	7.6	2306.6	32.2	28.5	16.4	5.95	24.9	1.20	13	19.0 262	0.12	5.53	409 - 40	-6.8	Fryar and Mullican (1995)				
FPOP-MW-04	1	04-11-1994	35.272	101.600	13.9	7.6	4107.7	37.4	30.9	22.29	5.48	25.7	0.98	8.78	26.7 270	< 0.10	4.23	432 - 42	-6.4	Fryar and Mullican (1995)				
J. Urbanczyk	1	28-07-1994	35.380	101.486	18.8	7.6	7.3	40.3	26.7	16.25	6.57	15.7	0.97	7.9	11.9 282	< 0.10	4.50	413		Fryar and Mullican (1995)				
Carson #62	1	20-02-1985	35.359	101.544		8.2		42	25	26.0	6.20		0.90	16	17.0 250	< 0.4	5.2	388 - 54	-7.3	Nativ (1988)				
Barrow	2	30-07-1997	35.482	101.162	25.9	7.8	4207.0	49	11.6	584	2.02	9.57	0.90	572	607 269	< 0.05	4.74	2110 - 70	-8.60.707815	Samples collected in this study				
Brantwein	2	31-07-1997	35.481	101.237	23.7	7.7	4207.4	32.1	15.5	165.8	4.32	22.0	0.82	193.7	101.05198	0.33	5.81	739 - 88	-8.80.708744	Samples collected in this study				
Terry	2	31-07-1997	35.514	101.123	21.4	7.3	3804.6	131.6	55.2	57.4	6.79	10.0	2.59	334.1	75.16237	< 0.05	< 0.5	910 - 37	-6.70.708906	Samples collected in this study				
Cabot Corp.	2	04-08-1997	35.508	101.041	18.8	7.2	2607.0	98.6	34.7	180.7	6.44	10.1	1.59	266	261.33208.6	0.65	6.16	1075 - 77	-6.90.708791	Samples collected in this study				
Harnly	2	02-08-1997	35.591	100.713	29.9	7.4	2807.3	80.8	32.8	139.2	6.18	12.4	1.59	166	215.18249	0.32	5.93	909 - 75	-8.00.708634	Samples collected in this study				
Gray #63	2	19-02-1985	35.515	100.955		8.5		70	21	110	5.80		0.80	64	110 270	< 0.4	6.0	658 - 53	-8.3	Nativ (1988)				
Pampa-Dutton	2	17-08-1992	35.515	100.963	18.6	7.1	2089.9	115	44.5	208	8.10	12.53	1.86	302	286 219	< 0.1	< 0.5	1197 - 42	-6.7	Dutton (1995); Dutton unpublished data				
S4a Dockum	3	12-03-1985	35.122	102.502	19.0	8.2	-130	15.4	6.1	239	2.34	4.95	0.31	54.5	116 428	0.24		867 - 76	-10.8	Dutton and Simpkins (1989)				
S5a Dockum	3	27-11-1984	34.854	102.347	19.0	8.2		4.6	1.4	326	2.39	4.86	0.12	56	251 503	0.45		1150 - 70	-9.6	Dutton and Simpkins (1989)				
S6a Dockum	3	30-11-1984	34.734	101.864	20.5	8.1	-120	4.7	2.6	318	2.99	5.09	0.12	71.1	194 529	0.58		1128 - 75	-10.8	Dutton and Simpkins (1989)				
S7a Dockum	3	13-03-1985	34.546	101.769	15.0	8.4		4.7	1.9	391	1.85	4.77	0.16	126	232 510	0.47		1273 - 73	-10.4	Dutton and Simpkins (1989)				
S11 Dockum	3	27-04-1984	34.904	102.317	17.9	8.5		7.3	3.5	227	2.44	5.18		31.3	104 447			828 - 83	-11.8	Dutton and Simpkins (1989)				
S12 Dockum	3	27-04-1984	34.896	102.181	17.9	9.0		3.1	2.0	230	2.37	3.57		29	94.2 464			828 - 85	-12.7	Dutton and Simpkins (1989)				
6666 Ranch	4	01-08-1997	35.539	101.389	21.4	7.4	3706.4	103.8	32.3	117.7	4.85	10.5	1.65	82.61	393.79190.3	0.12	4.45	942 - 37	-8.20.708426	Samples collected in this study				
Hailey	4	03-08-1997	35.399	100.704	35.3	7.7	2404.7	432	81	172.4	4.93	9.8	6.70	30.681502.6	48.8	0.05	3.43	2292 - 53	-6.60.708019	Samples collected in this study				
Abraham	4	03-08-1997	35.410	100.742	26.9	7.2	3507.0	78	9.0	14.4	2.56	8.6	0.26	33.19	13.18246.4	< 0.05	6.91	412 - 52	-4.70.709167	Samples collected in this study				
P. Meacham	4	04-02-1993	35.254	101.723	17.2	8.0	2107.1	27	24.8	68.4	6.63	22.8	1.05	27.5	37.4 297	0.14	7.48	520 - 53	-8.0	Fryar and Mullican (1995)				
Potter #61	4	20-02-1985	35.294	101.752		8.0		280	122	1560	8.1		7.20	1200	3300 95	1.3	< 0.4	6574 - 60	-8.5	Nativ (1988)				
Potter #60	4	21-02-1985	35.341	101.919		8.2		210	85	1280	7.2		5.0	1000	2230 120	1.4	2.0	4941 - 62	-8.5	Nativ (1988)				
Mansfield	5	10-08-1987	35.44	102.38	22.5	7.5		1530	430	24000	49		29.8	35100	5900 39	7.8		67086 - 66	-8.70.70827	Dutton (1989); Dutton unpublished data				
Mansfield-b	5	09-06-1983	35.41	102.40	23.0	7.2	-325	1460	388	23850	32		23.1	36120	5610 41.1	6.2		67530 - 72	-9.4	Dutton (1989)				
Sawyer	5	06-08-1987	35.09	100.83	22.5	6.6		1940	500	35000	46		37.7	53100	5100 66	22		95812 - 50	-6.70.70732	Dutton (1989); Dutton unpublished data				
Sawyer-b	5	27-04-1983	35.08	100.87	23.1	6.3	-185	1860	480	33000	30		27.8	54700	4725 72.6	21.4		94917 - 52	-7.2	Dutton (1989)				
Harman	5	29-05-1985	34.66	101.75	23.0	6.3		1466	3923	108700	1218		28.5	166800	5760	52		287948 - 50	-7.3	Dutton (1989)				
SW10	5		34.66	101.75	25.6			1731	4040	110700	1293		32	170400	5700	58		293954 - 50	-7.0	Dutton (1987)				
Zeek No. 1	6	01-05-1984	34.52	101.68	18.5	7.6		47200	7860	68890	3230		1010	205700	201 135 1300			335526 - 17	4.00.70734	Dutton (1987);				
J. Friemel No. 16	7	12-09-1984	35.07	102.46	23.8	6.6		87780	17400	21270	3700		2180	250200	34 415 1180			384159 - 26	6.40.70725	Dutton unpublished data				
HT601	7		35.71	101.20	38.2			5550	2000	54600	490		100	94800	2200 268 193			160201 - 34	-2.5	Dutton (1987); Dutton unpublished data				
RO602	7		35.63	101.08	37.6			7480	2360	54500	500		158	98100	1800 326 273			165497 - 26	-0.4	Bein and Dutton (1993)				
DS1	7		35.07	102.46	68.4			15700	2110	77930	620		440	148500	440 35 161			245936 - 23	-2.9	Fisher and Kreidler (1987) as cited by Bein and Dutton (1993)				
DNI	7		35.08	100.87	47.3			22900	2600	60200	459		660	139000	169 560 534			227082 - 27	-1.7	Fisher and Kreidler (1987) as cited by Bein and Dutton (1993)				
OL12	7		35.41	102.40	46.4			6020	1600	76100	380		90	131000	1320 161 118			216789 - 42	-5.1	Fisher and Kreidler (1987) as cited by Bein and Dutton (1993)				
Archer #10	7	01-08-1997	35.543	101.068	33.2	7.0	-70	7316	2668	49490	610	78.7	109	107000	48.2 81.7 423	< 0.5	167743 - 25	-0.30.710313	Samples collected in this study					
Castleberry #5	7	03-08-1997	35.545	100.989	23.0	7.3	-150	8002	2095	56490	580	102	96	104000	1540 135 523	< 0.5	173563 - 25	-1.30.708437	Samples collected in this study					
J. Hines #1	7	04-08-1997	35.491	101.008	34.5	5.6	200	8168	1978	62260	594	98.1	164	114700	< 5.0 13.42 544	< 0.5	188532 - 12	0.50.709964	Samples collected in this study					

* 1 = Ogallala water; 2 = plume water; 3 = lower Dockum water (paleowater); 4 = Upper Permian water; 5 = salt-dissolution zone water; 6 = evaporite-confining unit brine; 7 = oil-field brine.

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

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- μ m 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 0.45- μ m 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 HCO_3^-) was measured by potentiometric titration with 1.6 N H_2SO_4 and dissolved O_2 (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 HNO_3 (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 $\delta^{18}\text{O}$, water samples were equilibrated with CO_2 . To determine δD , H_2 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 $\pm 0.15\%$ for $\delta^{18}\text{O}$ and $\pm 3\%$ for δD . 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). $^{87}\text{Sr}/^{86}\text{Sr}$ 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 Mulligan, 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 SO_4 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 HCO_3^- and SO_4^{2-} than brines, a greater proportion of Cl than upgradient Ogallala and Dockum waters, and a greater proportion of HCO_3^- 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

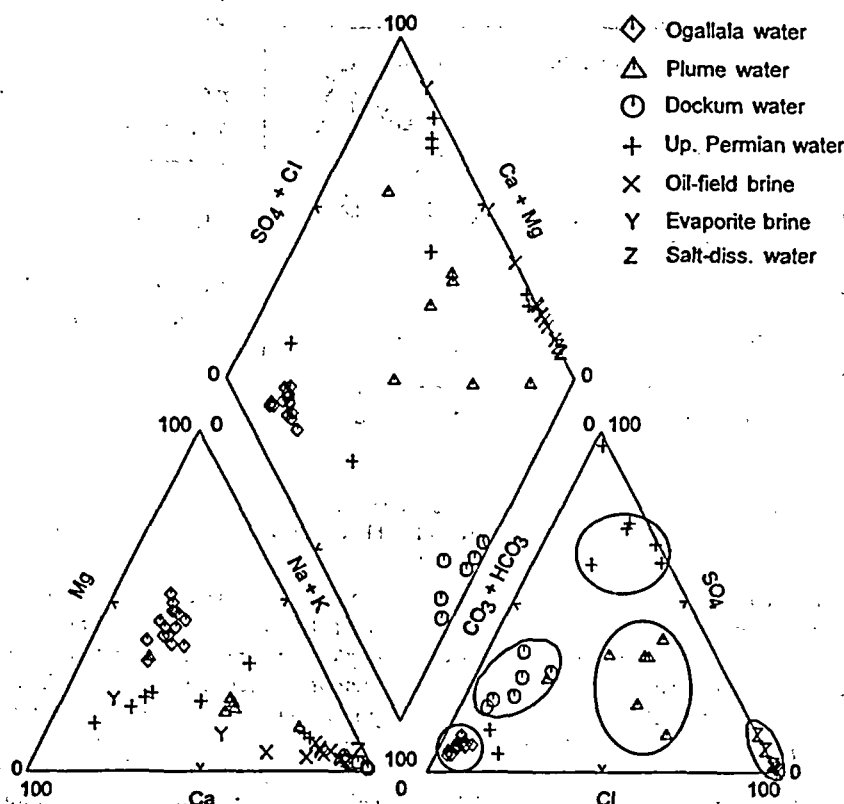


Fig. 3. Piper trilinear plot of the plume waters along with other end-member waters in the region (listed in Table 2).

adjoining property.) However, the SO_4/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 SO_4 are assumed to behave conservatively in the Ogallala aquifer because of oxidizing conditions (although SO_4 may not be conservative in deeper, anoxic units, especially the Deep-Basin Brine aquifer). Oil-field brines in the region generally have low SO_4 concentrations; exceptions (e.g., HT601; Table 2) may reflect (1) dissolution of anhydrite or gypsum from relatively shallow depths or (2) mixing with salt-dissolution zone waters. The mixing band between oil-field 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 SO_4 content, whereas in the plume waters Cl approximately equals SO_4 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 $\delta^{18}\text{O}$ values (−6.7 to −8.8‰) and δD values (−42 to −88‰) (Table 2). Four out of 7 plume samples are isotopically depleted compared to the upgradient Ogallala waters ($\delta^{18}\text{O}$ −3.7 to −7.3‰; δD −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 δD value for the sample collected by Dutton (1995) may be several per

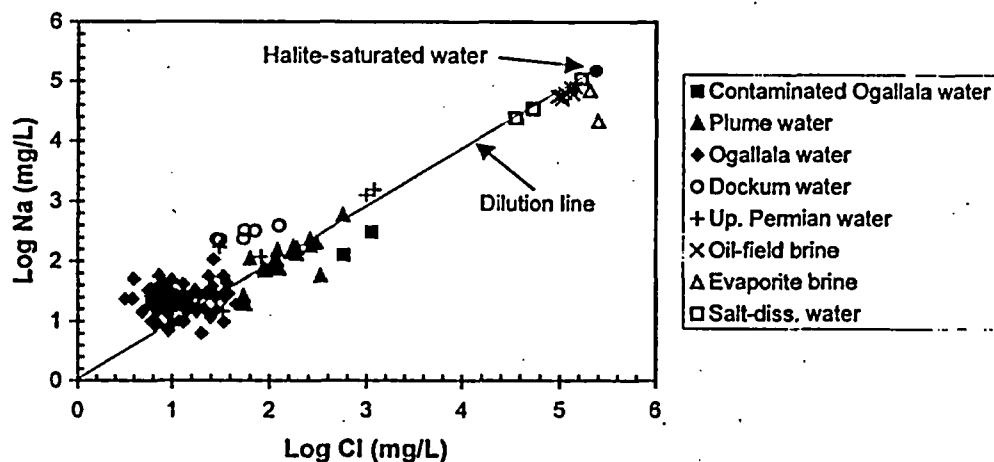


Fig. 4. Na-Cl bivariate plot along with lines representing fresh-water dilution of halite-saturated water (assumed to contain 6.2 mol of halite/kg solution). Data taken from TWDB database and Table 2. Contaminated wells inferred from TWDB database.

mil higher than actual. The salt-dissolution zone waters have $\delta^{18}\text{O}$ and δD values in the range of -6.7 to -9.4 and -50 to -72‰ , respectively, while oil-field brines have $\delta^{18}\text{O}$ and δD 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 end-members have higher $\delta^{18}\text{O}$ and δD 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 $\delta^{18}\text{O}$ and δD values is unrealistic, because no such water types have been reported in previous regional studies. Furthermore, such mixing fails to explain the high SO_4 and low Br concentrations in the plume. Possible water-rock reactions at the low

temperatures characteristic of units above the Amarillo uplift (typically $<40^\circ\text{C}$) 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 SO_4/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

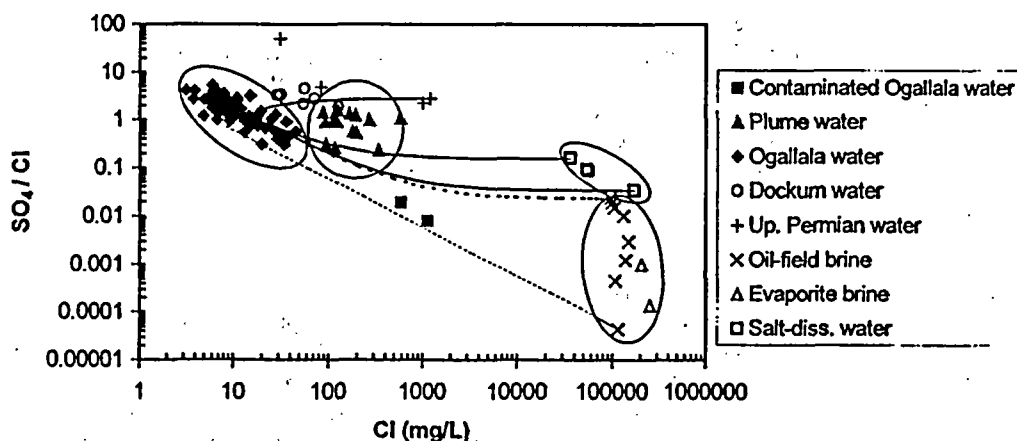


Fig. 5. SO_4/Cl vs. Cl bivariate plot for end-member waters in the region. Data taken from TWDB database and Table 2. Contaminated wells inferred from TWDB database.

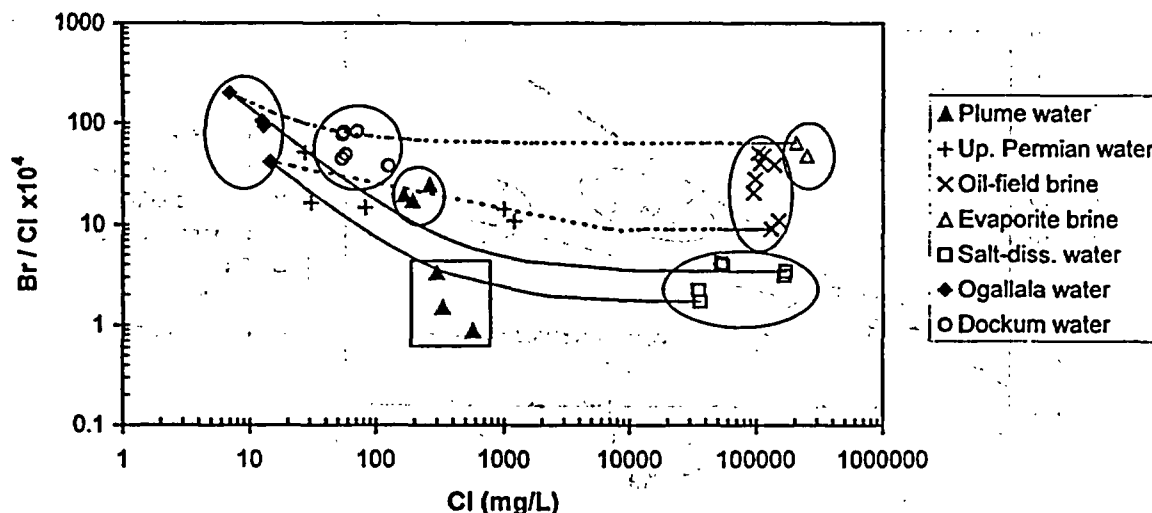


Fig. 6. Br/Cl vs. Cl relationship for end-member waters along with selected mixing lines to explain the origin of plume waters. Plume waters that had Br concentrations below detection limit (and <0.1 mg/l) are plotted as equal to detection limit inside the square box. Data taken from Table 2.

zone waters (0.7072 to 0.7083 [unpublished data, A. Dutton]). On a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ (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^- , $\delta^{18}\text{O}$ and δD 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 $\delta^{18}\text{O}$ (–5.9 to –12.7‰), δD (–40 to –85‰) and ^{14}C (<1 to 13% modern ^{14}C 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 $\delta^{18}\text{O}$ and δD 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 $\delta^{18}\text{O}$ and Cl (Fig. 8) and δD 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 salt-dissolution zone water and evaporite-confining unit (modified-connate) brine followed by mixing with upgradient Ogallala water. Sampled wells within the

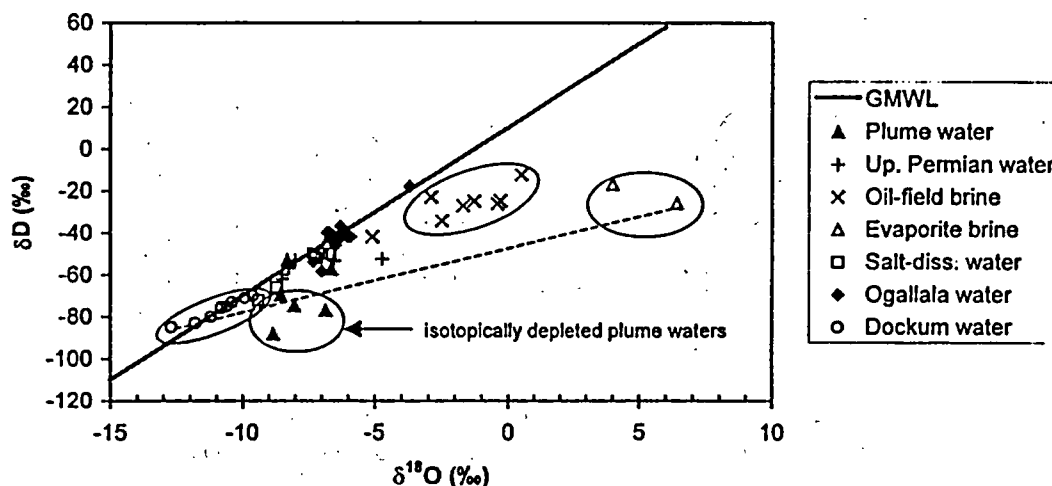


Fig. 7. $\delta^{18}\text{O}$ – δD relationship for end-member waters in the region. GMWL represents global meteoric water line given by the equation $\delta\text{D} = 8\delta^{18}\text{O} + 10$ (Craig, 1961).

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 $\delta^{18}\text{O}$, δD 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 (salt-dissolution zone), the Dockum well S12 and the upgradient Ogallala well White Deer #2 as end members and allowing ion exchange ($\text{Na}^+/\text{Ca}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}$). 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 $\text{Na}^+/\text{Ca}^{2+}$ and 0.1 to 0.8 for $\text{Na}^+/\text{Mg}^{2+}$ 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 $\delta^{18}\text{O}$ is the mixing parameter (simulation a) compared to δD (simulation b). This is probably due to greater accuracy in determination of $\delta^{18}\text{O}$ values ($\pm 0.15\text{‰}$) compared to δD values ($\pm 3\text{‰}$).

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

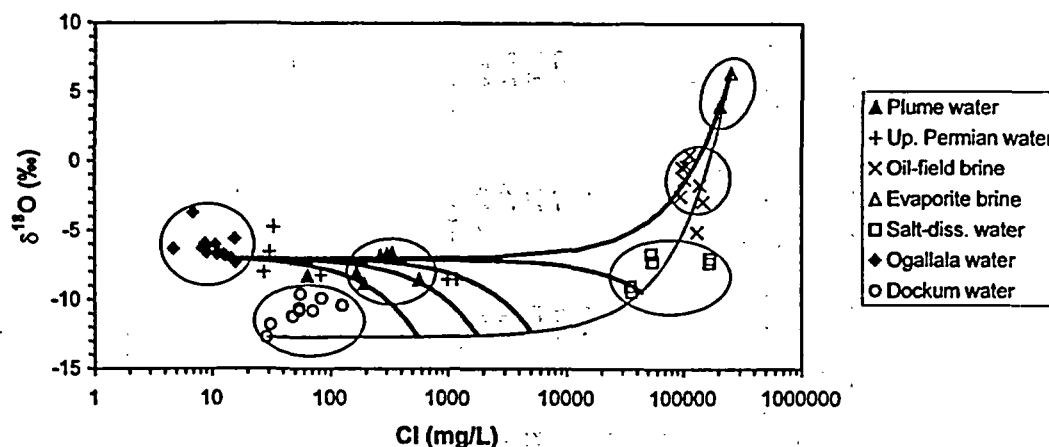


Fig. 8. $\delta^{18}\text{O}$ -Cl relationship for end-member waters with selected mixing lines to explain the origin of plume waters.

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 paleoplains areas (Gustavson and Winkler, 1988). Upward cross-formational flow into the Ogallala Formation from underlying units tends to occur in paleoplains 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

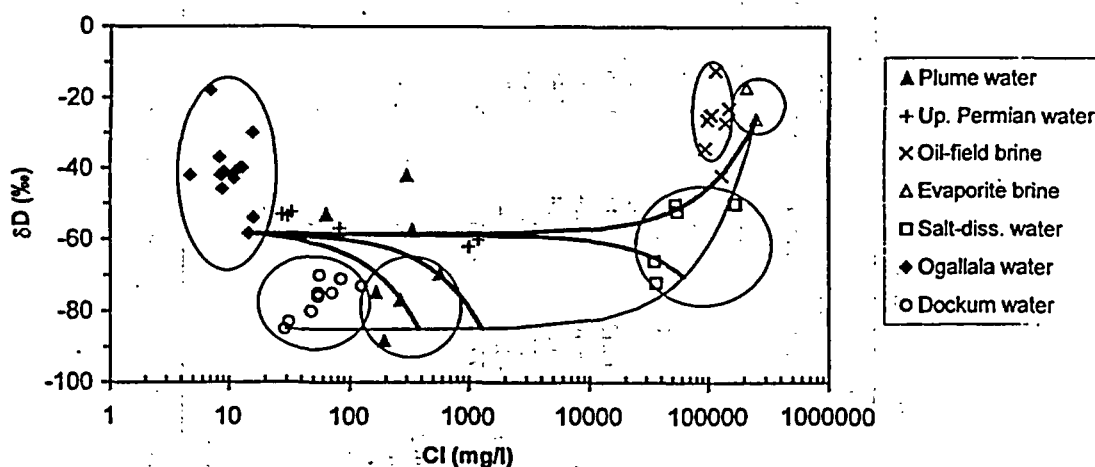


Fig. 9. δD -Cl relationship for end-member waters with selected mixing lines to explain the origin of plume waters.

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

Constituent	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
Cl	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
pH	7.76	7.93	8.03	7.70	7.85	8.20	7.20	7.35	7.64	7.39	7.68	7.83
$\delta^{18}\text{O}$ (‰)	−8.6	−8.4	−9.2	−8.8	−8.9	−12.1	−6.9	−7.2	−10.9	−8.0	−8.0	−10.3
δD (‰)	−70	−65	−70	−88	−67	−82	−77	−59	−77	−75	−63	−74
Mixing percentages												
Ogallala (White Deer #2)		73.7	60.6		67	10		96.4	31		83	41.7
Dockum (S 12)		24.7	37.8		32.5	89.5		2.9	68.3		16.6	57.9
Salt dissolution (Mansfield)		1.6	1.6		0.5	0.5		0.7	0.7		0.4	0.4

* Simulation a: simulated waters using Cl and $\delta^{18}\text{O}$ as mixing parameters. Simulation b: simulated waters using Cl and δD as mixing parameters.

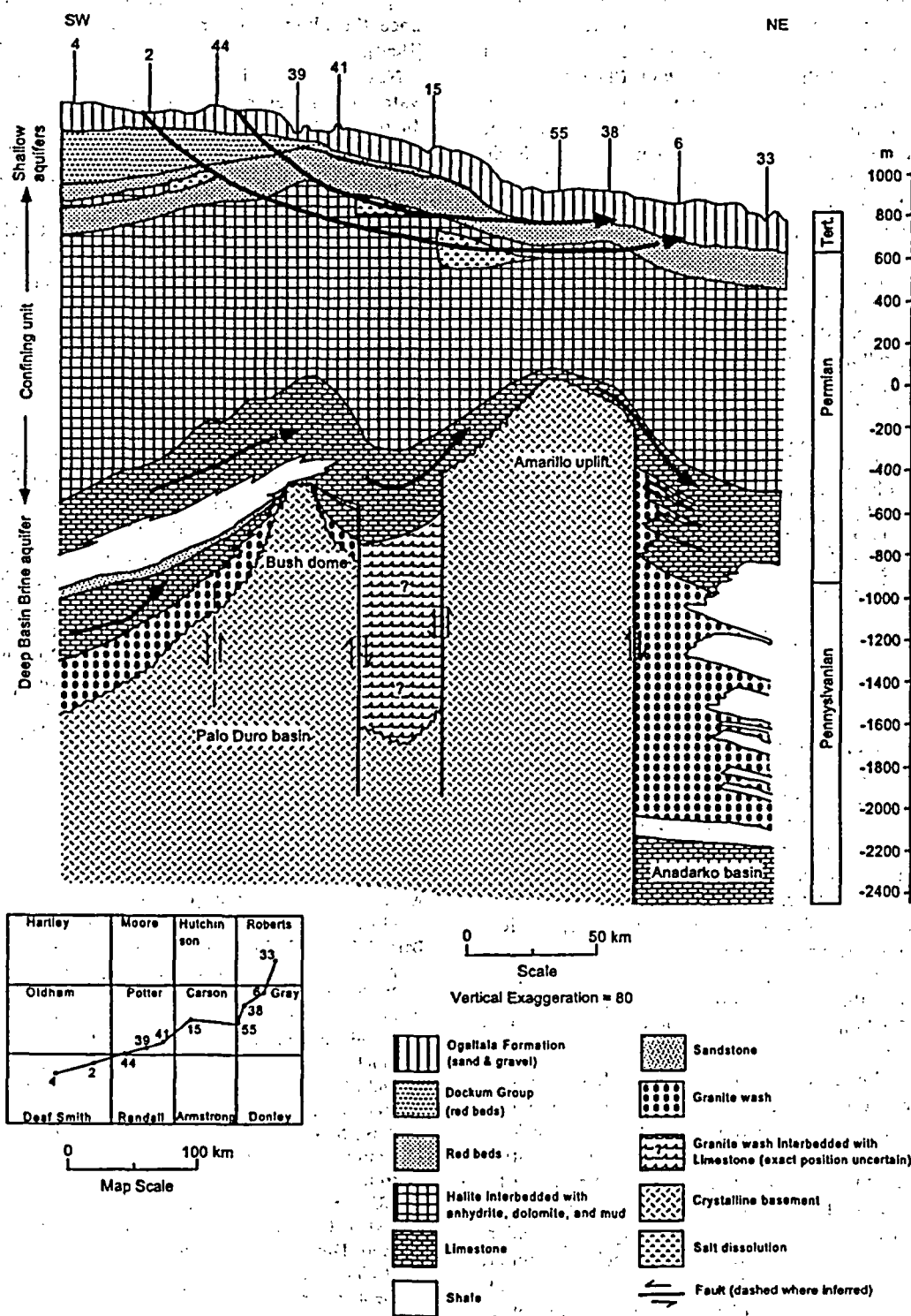


Fig. 10. Stratigraphic cross section along with inferred flow paths to explain the origin of plume waters. Modified from Dutton et al. (1982).

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 $\delta^{18}\text{O}$ and δD and high in SO_4 . 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 evaporite-confining 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 SO_4 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 pumping for irrigation, salinity could increase in the vicinity of the plume.

Acknowledgements

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