GEOCHEMICAL IDENTIFICATION OF THE SOURCE OF SALINITY IN GROUNDWATERS OF SOUTHEASTERN SEWARD COUNTY

A Report for
Southwest Kansas Groundwater
Management District No. 3

by

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INTRODUCTION

Irrigation wells screened in the middle of unconsolidated sediments of Quarternary and Tertiary age in southeastern Seward and southwestern Meade counties have encountered saline water. Previous studies suggest that the salinity source is salt water from the underlying bedrock of Upper Permian age (Gutentag et al., 1981; Krothe and Oliver, 1982). However, groundwaters containing greater than 200 mg/L dissolved chloride in the unconsolidated aquifer in southeastern Seward County have sodium/chloride ratios ranging from 0.44 to 0.62. If unaltered halite solutions from the Permian rocks were the salinity source, this ratio would be expected to be near 0.65. Much oil and gas is produced in Seward County and brines accompanying the oil have sodium/chloride ratios generally within the range 0.50 ± 0.05 (based on data from the KGS brine file). Thus, the question of whether or not oilfield brine pollution of the groundwaters was an important salinity source needed to be answered.

The Southwest Kansas Groundwater Management District No. 3 requested that geochemical identification of the salinity source in southeastern Seward County be made. The district collected groundwaters in July and August 1983, and sent samples to the Kansas Department of Health and Environment (KDHE) laboratories in Topeka for partial chemical analysis and to the Kansas Geological Survey (KGS) for salinity identification by the methods of Whittemore et al. (1981); Whittemore (1984). The district also sent two oilfield brine samples collected by the district office of the KDHE. All sample locations are within the study area bounded by T.34S., R.31W. and R.32W, and T.35S., R.31W. and R.32W.

PROCEDURE

Concentrations of chloride, bromide, and iodide were determined in all samples at the KGS by automated methods on a Technicon Auto-Analyzer. A phenol red method was used for bromide (Basel et al., 1982) and ceric-arsenious acid oxidation for iodide measurements. Major dissolved constituents were determined by the KDHE laboratories.

RESULTS AND DISCUSSION

Chemical analyses of groundwater samples collected for this study are given in Table 1, and hardness values and chemical weight ratios in Table 2. Data for earlier samples collected from some of the same and a few different wells in the study area are also listed in these tables along with the water chemistry for three observation wells drilled by the KGS in the early 1970's in a cooperative project with the U.S. Geological Survey. One of these latter wells is located just to the north of the study area.

Concentrations of dissolved chloride range from 14 to about 800 mg/L and sulfate from 22 to 130 mg/L in samples from water-supply wells in the study area (Table 1). Groundwaters from supply wells in the rest of Seward County contain 8 to 60 mg/L of dissolved chloride (excluding a couple wells with known oilfield brine pollution) and 33 to 177 mg/L dissolved sulfate (Byrne and McLaughlin, 1948; Hathaway et al., 1978; Gutentag et al., 1981; Krothe and Oliver, 1982; U.S. Geological Survey computer files, 1976). Sulfate/chloride ratios are less than 1.0 in most of the supply groundwaters (and in all well waters with greater than 60 mg/L chloride) in the study area, and greater than 1.0 in all

Table 1. Dissolved Constituent Concentrations in Well Waters from Southeastern Seward County.

LOCATION AND WELL NUMBER	DATE OF SAMPLE	WELL NAME	DATA SOURCE, LAB NO.	SPECIFIC CONDUCTANCE, LAB (UMHOS)	CALCIUM MG/L CA	MAGNESIUM MG/L MG	SODIUM MG/L NA	BICARBONATE MG/L HCO3	SULFATE MG/L SO4	CHLORIDE MG/L CL	NITRATE MG/L N	BROMIDE MG/L BR	IODIDE UG/L I
34S 31W 22DBD 1	83-07-27		KGS83361	1060	-	-	-	-	86	170	-	.19	3.0
34S 32W 05DDC 1	83-07-27	AMIGO CIR#1	KGS83363	550	-	-	-	-	54	23	-	.16	3.4
34S 32W 06BAC 1	83-07-27	AMIGO RANCH	KDHE162	617	70	23	33	215	113	27	4.1	-	-
34S 32W 17BAB 1	83-07-27	COPE	KGS83366	1140	-	-	-	-	125	173	-	.21	3.8
34S 32W 27CBD 1	83-07-27	PUBLIC W.S.	KGS83354	715	-	-	-	-	60	72	-	.18	3.4
34S 32W 28BAA 1	83-07-27		KGS83356	2540	-	-	-	-	121	607	-	.30	4.8
34S 32W 28BAA 1	83-07-27		KDHE161	2310	139	55	264	217	120	603	3.1	-	-
34S 32W 28BBB 1	83-07-27		KDHE163	1000	77	32	90	220	98	158	2.8	-	-
34S 32W 29BAA 1	83-07-27	COPE #2	KGS83355	770	-	-	-	-	72	89	-	.20	4.0
34S 32W 31BDD 1	83-07-27		KDHE168	596	56	21	44	233	49	48	3.6	-	-
34S 32W 32DDB 1	83-07-27		KGS83362	1400	-	-	-	-	89	266	-	.19	4.6
34S 32W 32DDB 1	83-07-27		KDHE159	1330	73	32	167	231	91	268	2.8	-	-
35S 31W 04BDB 1	83-07-27	FRANTZ	KGS83357	850	-	-	-	-	48	112	-	.17	3.7
35S 31W 04BDB 1	83-07-27	FRANTZ	KDHE167	790	60	14	53	244	48	110	3.6	-	-
35S 31W 04BDD 1	83-07-27	FRANTZ	KGS83367	855	-	-	-	-	40	120	-	.12	4.0
35S 31W 04BDD 1	82-08-13	FRANTZ	KDHE449	-	78	16	77	224	47	121	10.0	-	-
35S 31W 04CDB 1	82-04-22	FRANTZ	KDHE2114	699	71	14	73	242	34	108	2.9	-	-
35S 31W 04DDB 1	83-07-27	FRANTZ	KGS83359	990	-	-	-	-	47	162	-	.15	4.1
35S 31W 05ABD 1	83-07-27	FRANTZ	KGS83358	1210	-	-	-	-	61	219	-	.17	3.8
35S 31W 05ABD 1	83-07-27	FRANTZ	KDHE165	1090	72	24	126	232	59	203	3.4	-	-
35S 31W 05ABD 1	82-04-22	FRANTZ	KDHE2115	1010	74	24	126	244	55	207	3.0	-	-
35S 31W 05BAB 1	82-02-19	HOLMES	KDHE1570	-	75	23	89	220	57	155	3.6	-	-
35S 31W 05DBD 1	83-07-27	FRANTZ	KGS83360	1830	-	-	-	-	93	429	-	.22	6.0
35S 31W 05DBD 1	83-07-27	FRANTZ	KDHE166	1780	87	34	238	228	92	428	2.5	-	-
35S 31W 05DBD 1	82-09-18	FRANTZ	KDHE445	-	83	33	243	201	93	420	2.4	-	-

Table 1. Dissolved Constituent Concentrations in Well Waters from Southeastern Seward County. (continued)

LOCATION AND WELL NUMBER	DATE OF SAMPLE	WELL NAME	DATA SOURCE, LAB NO.	SPECIFIC CONDUCTANCE, LAB (UMHOS)	CALCIUM MG/L CA	MAGNESIUM MG/L MG	SODIUM MG/L NA	BICARBONATE MG/L HCO3	SULFATE MG/L SO4	CHLORIDE MG/L CL	NITRATE MG/L N	BROMIDE MG/L BR	IODIDE UG/L I
35S 31W 07DCC 1	82-08-18		KDHE447	-	62	22	83	239	58	112	2.5	-	-
35S 31W 10ACA 1	82-04-22	LAUDERBACK	KDHE2116	698	64	19	74	253	46	99	3.3	-	-
35S 31W 18ADD 1	83-07-27	DIP SAMP,OWS	KGS83364	626	-	-	-	-	36	58	-	.13	5.0
35S 32W 01CDB 1	83-08-29		KGS83383	565	-	-	-	-	28	47	-	.16	3.4
35S 32W 01CDB 1	83-08-29		KDHE508	545	67	12	35	220	31	49	5.6	-	-
35S 32W 02AAA 1	83-07-27	PE COMPR PLT	KGS83365	1150	-	-	-	-	72	189	-	.24	3.7
35S 32W 02AAA 1	83-07-27	COMPR PIT	KDHE164	1090	83	25	114	232	65	201	2.9	-	-
35S 32W 02DAD 1	83-08-29	ABANDONED	KGS83382	3080	-	-	-	-	130	783	-	.28	43.0
35S 32W 02DAD 1	83-08-29	ABANDONED	KDHE507	2800	91	44	439	195	126	814	.3	-	-
35S 32W 05ABB 1	83-07-27	FEED YARD	KGS83353	690	-	-	-	-	22	60	-	.18	8.3
35S 32W 12ADB 1	83-07-27		KDHE160	1090	84	26	114	229	65	206	2.8	-	-
34S 31W 30BBB 2	74-10-22	MID OGALLALA	USGS	4500	152	50	670	95	200	1270	.6	-	-
34S 31W 30BBB 1	74-10-18	UPPR PERMIAN	USGS	-	1270	640	5000	144	1060	11100	.2	-	-
33S 32W 28CDD 1	74-10-10	UPPR PERMIAN	USGS	-	3600	1800	6100	156	1260	20300	-	-	-

Table 2. Weight Ratios of Dissolved Constituents and Hardness in Well Waters from Southeastern Seward County.

LOCATION AND WELL NUMBER		DATE OF SAMPLE	WELL NAME	CA/MG	CA/CL	MG/CL	NA/CL	SO4/CL	BR/CL X 10E4	I/CL X 10E6	TOTAL HARD- NESS	NON- CAR- BONATE HARDNESS	NON- CARBONATE HARDNESS /SO4
34S 31W 22DBC	1	83-07-27		-	-	-	-	.5059	11.2	17.6	-	-	-
34S 32W 05DCC	1	83-07-27	AMIGO CIR #1	-	-	-	-	2.3478	69.6	147.8	-	-	-
34S 32W 06BAC	1	83-07-27	AMIGO RANCH	3.04	2.593	.852	1.222	4.1852	-	-	269	93	.82
34S 32W 17BAB	1	83-07-27	COPE	-	-	-	-	.7225	12.1	22.0	-	-	-
34S 32W 27CBD	1	83-07-27	PUBLIC W.S.	-	-	-	-	.8333	25.0	47.2	-	-	-
34S 32W 28BAA	1	83-07-27		-	-	-	-	.1993	4.9	7.9	-	-	-
34S 32W 28BAA	1	83-07-27		2.53	.231	.091	.438	.1990	-	-	573	395	3.30
34S 32W 28BBB	1	83-07-27		2.41	.487	.203	.570	.6203	-	-	324	144	1.46
34S 32W 29BAA	1	83-07-27	COPE #2	-	-	-	-	.6090	22.5	44.9	-	-	-
34S 32W 31BCD	1	83-07-27		2.67	1.167	.437	.917	1.0208	-	-	226	35	.72
34S 32W 32DCB	1	83-07-27		-	-	-	-	.3346	7.1	17.3	-	-	-
34S 32W 32DCB	1	83-07-27		2.28	.272	.119	.623	.3396	-	-	314	125	1.37
35S 31W 04BCB	1	83-07-27	FRANTZ	-	-	-	-	.4286	15.2	33.0	-	-	-
35S 31W 04BCB	1	83-07-27	FRANTZ	4.29	.545	.127	.845	.4364	-	-	207	7	.15
35S 31W 04BCD	1	83-07-27	FRANTZ	-	-	-	-	.3333	10.0	33.3	-	-	-
35S 31W 04BCD	1	82-08-18	FRANTZ	4.87	.645	.132	.636	.3884	-	-	261	77	1.64
35S 31W 04CDB	1	82-04-22	FRANTZ	5.07	.657	.130	.676	.3148	-	-	235	36	1.07
35S 31W 04DCB	1	83-07-27	FRANTZ	-	-	-	-	.2901	9.3	25.3	-	-	-
35S 31W 05ABC	1	83-07-27	FRANTZ	-	-	-	-	.2785	7.8	17.4	-	-	-
35S 31W 05ABD	1	83-07-27	FRANTZ	3.00	.355	.118	.621	.2906	-	-	279	88	1.50
35S 31W 05ABD	1	82-04-22	FRANTZ	3.08	.357	.116	.609	.2657	-	-	284	83	1.52
35S 31W 05BAB	1	82-02-19	HOLMES	3.26	.484	.148	.574	.3677	-	-	282	101	1.78
35S 31W 05DBC	1	83-07-27	FRANTZ	-	-	-	-	.2168	5.1	14.0	-	-	-
35S 31W 05DBD	1	83-07-27	FRANTZ	2.56	.203	.079	.556	.2150	-	-	357	170	1.85
35S 31W 05DBD	1	82-08-18	FRANTZ	2.52	.198	.075	.579	.2214	-	-	343	178	1.92

Table 2. Weight Ratios of Dissolved Constituents and Hardness in Well Waters from Southeastern Seward County. (continued)

LOCATION AND WELL NUMBER		DATE OF SAMPLE	WELL NAME	CA/MG	CA/CL	MG/CL	NA/CL	SO4/CL	BR/CL X 10E4	I/CL X 10E6	TOTAL HARD-NESS	NON-CAR-BONATE HARDNESS	NON-CARBONATE HARDNESS /SO4
35S 31W 07DCC	1	82-08-18		2.82	.554	.196	.741	.5179	-	-	245	49	.85
35S 31W 10ACA	1	82-04-22	LAUDERBACK	3.37	.646	.192	.747	.4646	-	-	238	31	.66
35S 31W 18ACD	1	83-07-27	DIP SAMP,OWS	-	-	-	-	.6207	22.4	86.2	-	-	-
35S 32W 01CDB	1	83-08-29		-	-	-	-	.5957	34.0	72.3	-	-	-
35S 32W 01CDB	1	83-08-29		5.58	1.367	.245	.714	.6327	-	-	217	36	1.17
35S 32W 02AAA	1	83-07-27	PE COMPR PLT	-	-	-	-	.3810	12.7	19.6	-	-	-
35S 32W 02AAA	1	83-07-27	COMPR PIT	3.32	.413	.124	.567	.3234	-	-	310	120	1.84
35S 32W 02DAD	1	83-08-29	ABANDONED	-	-	-	-	.1660	3.6	54.9	-	-	-
35S 32W 02DAD	1	83-08-29	ABANDONED	2.07	.112	.054	.539	.1548	-	-	408	248	1.97
35S 32W 05ABB	1	83-07-27	FEED YARD	-	-	-	-	.3667	30.0	138.3	-	-	-
35S 32W 12ADB	1	83-07-27		3.23	.408	.126	.553	.3155	-	-	317	129	1.98
34S 31W 30BBB	2	74-10-22	MID OGALLALA	3.04	.120	.039	.528	.1575	-	-	585	507	2.54
34S 31W 30BBB	1	74-10-18	UPPR PERMIAN	1.98	.114	.058	.450	.0955	-	-	5805	5687	5.37
33S 32W 28CDD	1	74-10-10	UPPR PERMIAN	2.00	.177	.089	.300	.0621	-	-	16398	16270	12.91

supply waters unpolluted by anthropogenic activities in the rest of Seward County. Sodium/chloride ratios range from 0.44 to 0.62 for well waters with chloride concentrations greater than 200 mg/L, and from 0.57 to 0.86 for groundwaters with dissolved chloride of between 100 and 200 mg/L, values lower than usual for natural waters of Kansas. Thus, the source of higher dissolved solids in the groundwater supply appears to be salt water with a low sulfate/chloride ratio and a lower sodium/chloride ratio than in unaltered halite-solution brine.

Weight ratios of bromide/chloride and iodide/chloride indicate that the saltwater source is similar to halite solutions. Mixing zone curves of bromide/chloride and iodide/chloride versus chloride concentration were used for the identification (Figures 1 and 2). The individual curves were calculated by selecting freshwater and saltwater endpoints that would produce lines that bracket the data points. The saltwater endpoints chosen were also based on the chemistry of halite-solution brines from other areas that I had analyzed for several previous reports. The bromide/chloride endpoints used for the saltwater source were 1.2×10^{-4} and 2.0×10^{-4} and the iodide/chloride endpoints 1.0×10^{-6} and 3.0×10^{-6} at a chloride concentration of 100,000 mg/L.

Bromide/chloride and iodide/chloride ratios for the two oilfield brines analyzed from Seward County are much higher than for halite solutions as expected (Table 3). However, the two oil brines differ markedly in their ratios indicating appreciable differences in the history or origin of waters in the two groups of formations.

The only point falling outside the freshwater and halite-brine mixing zones in Figure 2 was for the irrigation well (now abandoned)

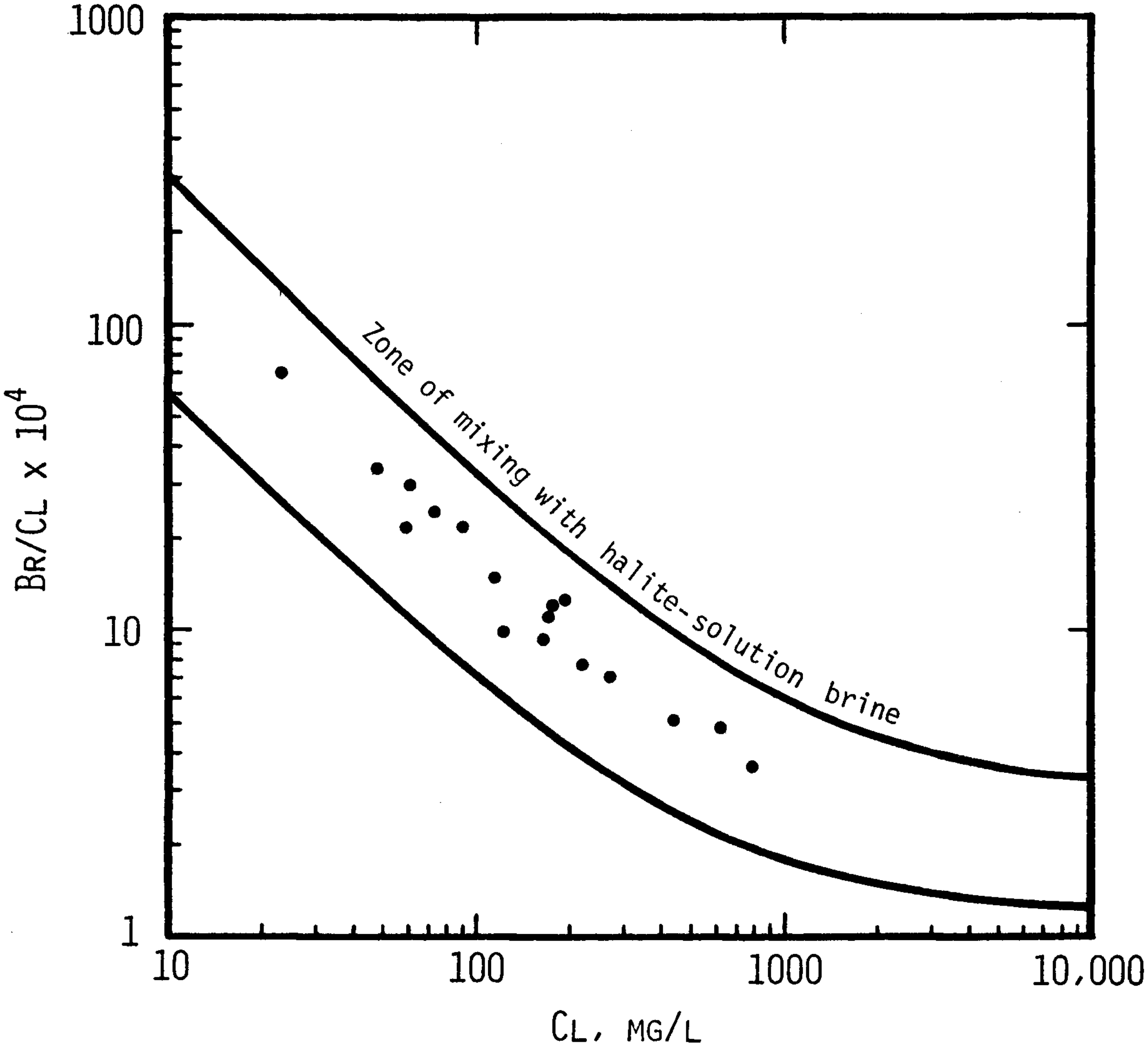

Figure 1. Weight Ratio of Bromide/Chloride versus Chloride Concentration.

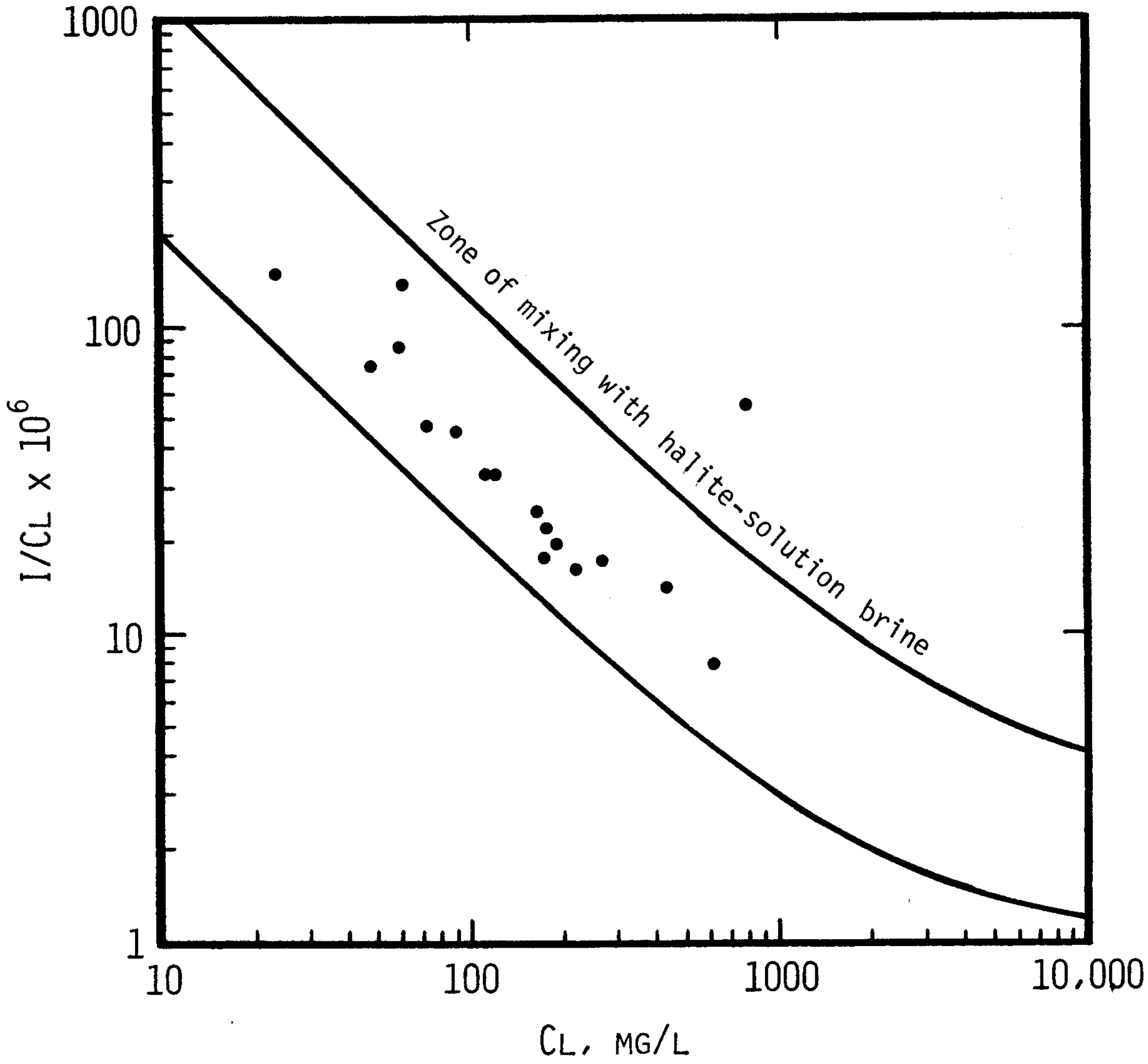

Figure 2. Weight Ratio of Iodide/Chloride versus Chloride Concentration.

Table 3. Dissolved Constituent Concentrations and Weight Ratios for Oilfield Brines from Southeastern Seward County.

	Oilfield Brine	
	1	2
Location	34S 32W 26CB	35S 32W 1BA
Name	Thompson #1-26	-
Producing horizon	Mississippian-Morrowan	Kansas City Group
Specific conductance, μmho/cm at 25°C	191,000	235,000
SO_4, mg/L	277	297
Cl, mg/L	100,700	149,700
Br, mg/L	472	203
I, mg/L	122	8.9
SO_4/Cl	0.0027	0.0020
Br/Cl x 10^4	47	13.6
I/Cl x 10^6	1210	59

containing the highest chloride content. The bromide/chloride ratio for this water fell within the zone of mixing of freshwater with halite brine (Figure 1). The elevated iodide/chloride ratio in this sample could be derived from as little as 0.03 percent by volume of oilfield brine from the Mississippian System and Morrowan Stage of the Lower Pennsylvanian Series. The higher iodide/chloride could not be derived from a much larger volume of pollution from brines produced from the Kansas City Group because the bromide/chloride ratio in the sample would also be above the halite-brine mixing zone.

Salt waters from two observation wells in the Upper Permian bedrock, and saline water from an observation well in the middle of the overlying Tertiary (Ogallala) sediments in Seward County have low sulfate/chloride ratios and lower sodium/chloride ratios than for unaltered halite solutions (Tables 1 and 2). Both of these ratios decrease with increasing chloride concentrations in the groundwaters. The sum of the dissolved calcium and magnesium exceed the sulfate concentration (in mg/L), a composition unusual for most Permian saltwaters or saline groundwaters affected by Permian brine. The Permian well water with the high chloride content is from the Big Basin Formation, and the other is possibly from the Whitehorse Formation. Both of these formations consist of fine-grained silty sandstone, siltstone, and shale in southwest Kansas (Gutentag et al., 1981).

The Day Creek Dolomite, which lies between the Big Basin and Whitehorse Formations, contains dolomitic anhydrite and gypsum with interbedded shale. The Dog Creek Formation of the Lower Permian Series underlies the Whitehorse Formation and contains shale, siltstone, very fine-grained sandstone, and thin dolomite and gypsum layers. Immediately below the Dog Creek rocks is the Blaine Formation, consisting of interbedded gypsum, anhydrite, and shale, and bedded halite (Gutentag et al., 1981). The composition of the four formations above the Blaine suggests that, if initially fresh waters circulated through them, the ion exchange sites on the clays would probably be saturated mainly with calcium and magnesium.

The Blaine halite is probably the source of the salt water contaminating groundwaters in the unconsolidated aquifer. Salt waters generated within the Blaine Formation would probably be similar to waters in the Cedar Hills Sandstone and Salt Plain Formation underlying the aquifer of the Great Bend Prairie, which have sodium/chloride ratios of 0.65 ± 0.05 and contain sulfate concentrations greater than the sum of calcium and magnesium. If the salt waters then flowed upwards through the overlying Lower and Upper Permian strata, some sodium could be exchanged for calcium and magnesium ions, thereby increasing the concentrations of the latter two constituents and decreasing the sodium/chloride ratio in the migrating waters.

The comparison of dissolved calcium and magnesium with sulfate in the waters from the unconsolidated aquifer is more diagnostic for Permian sources of dissolved solids if the concentrations related to carbonate solution are subtracted. Thus, ratios of non-carbonate hardness/sulfate were calculated (Table 2). Nearly all groundwaters from water-supply wells in the study area that contain greater than 150 mg/L chloride have non-carbonate hardness/sulfate values greater than 1.0. This ratio is less than 1.0 for essentially all waters from supply wells in the rest of Seward County. The non-carbonate hardness/sulfate ratio is very high in the underlying Upper Permian rocks and in more saline portions of the Ogallala Formation (Table 2). The sodium/chloride ratio increases and the non-carbonate hardness/sulfate decreases with decreasing chloride concentration in the samples from the three observation wells, trends also generally true for the overlying saline and fresh waters in the study area. These observations help verify that the source of higher chloride concentrations in the unconsolidated aquifer is salt water from the Permian bedrock.

CONCLUSION

The source of saline water in the unconsolidated aquifer in southeastern Seward County is natural salt water from the underlying Permian bedrock and is not oilfield brine pollution. The salt water probably originates from the Blaine Formation and is altered in composition by ion exchange as it migrates upwards through overlying sandstones, siltstones, and shales containing gypsum, anhydrite, and dolomite before it disperses into the Ogallala Formation.

RECOMMENDATIONS

1. The change in sulfate and chloride concentrations and specific conductance with increasing depth should be documented for groundwaters from water-supply wells in the study area. The depth information should be the screened interval and not just the total depth of a well. Contour maps of chemistry at various depth ranges and cross-sections showing chemistry and screened interval should be

prepared to illustrate the current distribution and stratification of saline water in the aquifer.

2. A few wells should be selected for short- and long-term monitoring. Wells for short-term monitoring should be irrigation wells sampled on a monthly schedule before, during, and after a growing season to determine whether drawdown can induce upconing of more saline water. Wells for long-term monitoring should be sampled annually and could include different types of water-supply wells. Data from these observations could be used to determine whether regional water-table decline might appreciably increase upward migration of deeper saline and salt waters.

3. Detailed cross-sections of the stratigraphy in the Quarternary and Tertiary sediments should be prepared to determine the distribution of less permeable zones which could retard the vertical flow of saline water. This data would also be necessary for the development of hydrogeological models for the area.

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