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GEOCHEMICAL CHARACTERIZATION OF SALTWATER CONTAMINATION IN THE MACKSVILLE SINK AND ADJACENT AQUIFER

A Report for the Kansas Corporation Commission

by

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ABSTRACT

A sink developed in 1988 around a plugged injection well formerly used for saltwater disposal in southcentral Kansas. Saltwater with a chloride concentration of 35,000-37,500 mg/L filled the sink. Observation wells drilled around the sink delineate a saltwater plume with a chloride content as high as 16,000 mg/L that originates near the sink and extends approximately 0.5 mile within the unconsolidated aquifer towards an irrigation well. The area of contaminated water with a chloride content of >150 mg/L is about 158 acres. The volume of contaminated water with a chloride concentration >1,000 mg/L at the base of the aquifer is estimated as 40 million gallons assuming an average thickness of 5 feet for the saline water layer. Mixing curves of Br/Cl and SO_4/Cl versus chloride concentration were used to identify the sources of the saltwater based on the chemistry of fresh and contaminated ground water and oil brines from producing wells in the plume area. Brine in the sink is derived from halite solution, is chemically similar to saltwater in underlying Permian strata, and contains less than 2% oil brine. Oil brine and halite solution contribute about 95-80% and 5-20% of the chloride in the saltwater plume, respectively, based on mixing calculations using bromide, sulfate, and chloride concentrations. The calculation accuracy is dependent on the relative proportions of different oil and gas brines that contaminated the aquifer and on sampling and analytical error. Deviations of contaminated ground-water chemistry from a conservative mixing curve of (Ca + Mg)/Na versus chloride concentration with endpoints of fresh groundwater and the average brine mixture indicate locations of increasing or decreasing dissolved-salt concentrations in the plume. The northeastern third of the plume is advancing, while the southwestern half is being diluted. The geochemical data suggest that the main contamination sources originated at and/or near the injection well.

INTRODUCTION

On July 21, 1988, a sinkhole catastrophically formed around a plugged injection well formerly used for saltwater disposal in southeast Pawnee County, about 5 miles northwest of the town of Macksville (Figure 1). The sink occurred in T. 23 S., R. 15 W., Sec. 30 CCC (SW1/4 of SW1/4 of SW1/4) in a pasture overlying the Great Bend Prairie aquifer within Groundwater Management District No. 5 (GMD 5). Water filling the bottom of the sinkhole was found to be salty. The saltwater contamination is of concern because the aquifer in the area is used for irrigation and stock purposes. One irrigation well is within a quarter mile of the main part of the saltwater plume, while two other irrigation wells are approximately a half-mile distant from the plume.

The development of the sink is believed to have resulted from the solution of salt beds at depth. Water causing the solution probably reached the salt beds via the saltwater injection well that was located within the sinkhole area. The injection well provided disposal of oil and gas well brines from many wells up to 1984, when the well was plugged. The location of the well and the present active and plugged wells used in the petroleum industry within the section in which the sink is located is shown in Figure 2.

Soon after the sinkhole formation, the Kansas Corporation Commission (KCC) installed four observation wells screened at the base of the aquifer around the sink. Ground water sampled from these wells was determined to be saline on the east and northeast sides of the sink, but fresh to the southwest. The KCC requested that the Kansas Geological Survey (KGS) determine the source of the saltwater in the sinkhole and the ground water using the mixing curve methods developed by Whittemore (1984, 1988), because

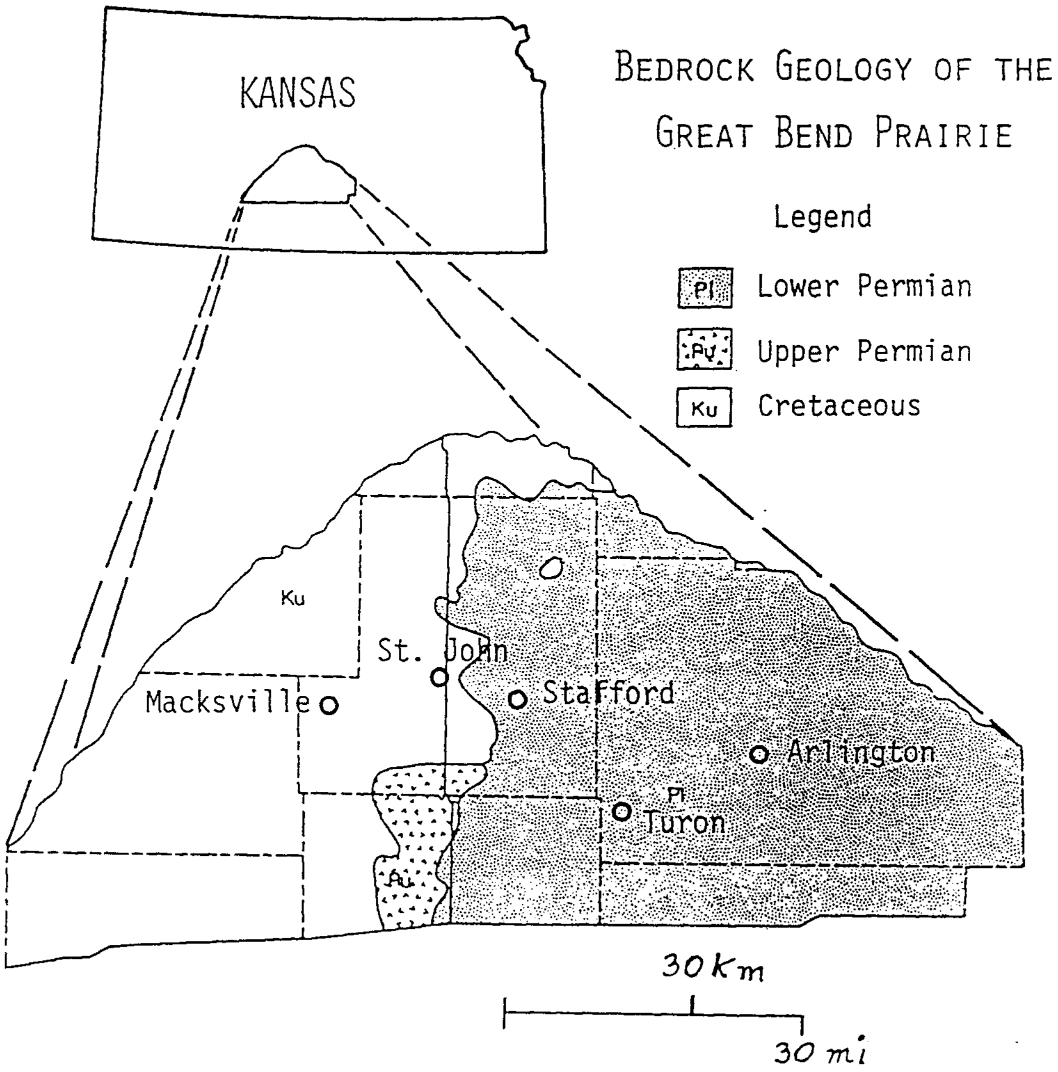

Figure 1. Bedrock Geology and Location of Macksville within the Great Bend Prairie.

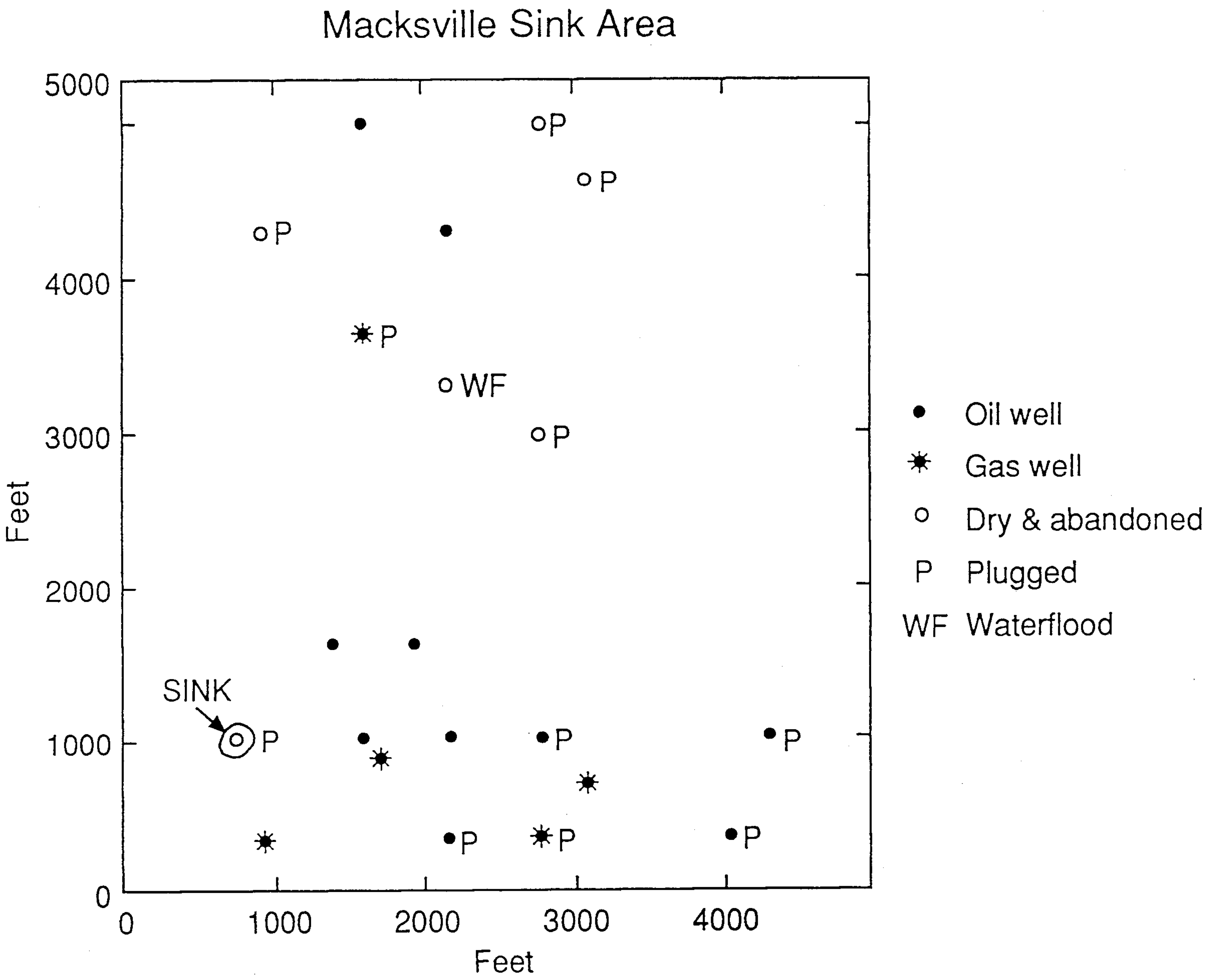

Figure 2. Location of Oil and Gas Wells and the Macksville Sink in Sec. 30, T. 23 S., R. 15 W. The source of information is the oil and gas records at the Kansas Geological Survey.

two possible types of saltwater sources existed: halite solution and oil-field brine.

Samples were collected by the KCC (with assistance from GMD 5) and sent to the KGS where an initial identification of source was made. After finding saltwater in the aquifer, the KCC drilled 27 additional observation wells by March, 1989, for further delineation and monitoring of the saline ground-water plume (Figure 3). Of the 31 total observation wells, 24 were screened at the base of the Quaternary aquifer and 7 in the Dakota drift below the aquifer. A well for withdrawal of the saltwater started pumping on March 10, 1989, for remediation of the aquifer. Water samples from all of these wells were also provided to the KGS for geochemical characterization. Later, another saltwater withdrawal well was installed. The saline water removed from the aquifer is disposed in a deep well completed in the Arbuckle Group.

HYDROGEOLOGIC AND HYDROCHEMICAL SETTING

The geology of the site comprises unconsolidated Quarternary sediments from the surface to a depth of about 120 feet. The sediments include clay, silt, and sand, with greater amounts of coarser grain sizes nearer the bottom of the deposit that forms the aquifer. Fine dune sands form the small hills in the area. A clay layer underlying the main aquifer sands overlies deeper Dakota drift. The drift rests on Cretaceous bedrock (Figure 1) consisting of interbedded shale, siltstone, and sandstone. The Permian Cedar Hills Sandstone underlies the Cretaceous rocks. The thickest bedded salt present at greater depths is the Hutchinson Member of the Wellington Formation, which is probably the origination point of the subsidence.

The depth to the water table is about 20-30 feet depending on the surface elevation of a location in the sink area. The regional ground-water flow direction in the Quaternary sediments is toward the east-northeast based

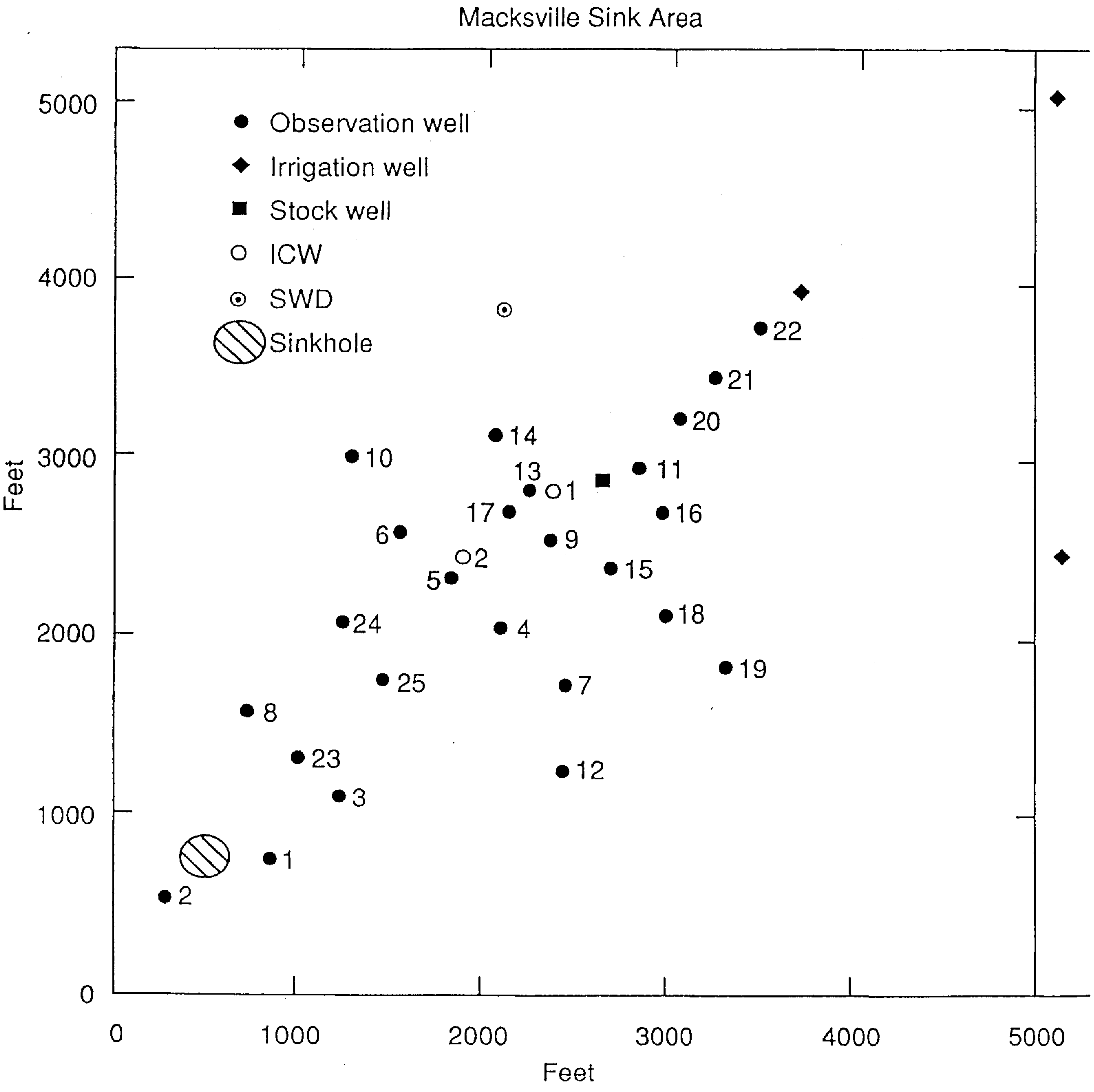

Figure 3. Location of Observation, Pumping (ICW), and Disposal Wells Associated with the Kansas Corporation Commission Remediation Project and Agricultural Water-Supply Wells in Sec. 30 and the Westernmost Part of Sec. 29, T. 23 S., R. 15 W.

on the potentiometric surface map of Fader and Stullken (1978). An irrigation well 0.8 mile to the northeast of the sinkhole has probably affected the local ground-water flow direction in the aquifer between the sink and the well (Figure 3).

The potentiometric surface of water in the Cedar Hills Sandstone in the general area is above that for the Quaternary aquifer based on fluid levels at an observation well site 11 miles to the east (GMD 5 water-level data for observation wells; and Macfarlane, personal communication). The potentiometric surface of fluid in the Arbuckle Group, in which the saltwater injection well that was located within the sinkhole was perforated, is below that of the Cedar Hills Sandstone. Therefore, any avenues for fluid movement along a borehole connecting all of the strata at the site would allow Cedar Hills water to move both upward and downward. Saltwater generated by solution of the bedded salt in the Wellington Formation would have had a higher density than any of the other waters in the system, and thus probably flowed to the Arbuckle disposal zone.

The quality of uncontaminated ground waters in the Quaternary aquifer in southeastern Pawnee County is fresh (Hathaway et. al., 1978). Total-dissolved solids, sulfate, and chloride concentrations are generally <500, <50, and <30 mg/L, respectively. Water in the Cedar Hills is expected to be saline, with chloride concentrations >30,000 mg/L based on observation wells screened in the Cedar Hills to the east (Whittemore et al., in preparation).

PROCEDURE

Water samples were collected from observation, remediation, stock, and irrigation wells by KCC and GMD 5 staff. Oil-field brines were collected from oil wells and a gas brine from a brine tank by KCC staff. Three sets of samples provided to the KGS were collected in September, 1988, and January and

March, 1989. The samples were filtered at the Kansas Geological Survey through 0.45 um membrane filter paper before analysis. Chloride, sulfate, bromide, and iodide concentrations were determined with a Technicon AutoAnalyzer II, while calcium, magnesium, and sodium concentrations were measured using a Jarrell-Ash inductively-coupled, argon plasma spectrophotometer, Model 975.

RESULTS AND DISCUSSION

Distribution of Chloride

The chloride content of water ponded in the sinkhole ranged from 35,000 mg/L soon after the sinkhole formation to 37,500 mg/L two-thirds of a year later. The small increase in the chloride content could be accounted for by evaporative concentration. There does not appear to be any significant difference in the distribution of chloride in the sink pond; the three values in Table 1 for the January 9, 1989, collection date are within analytical error. Field specific conductance measurements on April 14, 1989, for waters on the southwest and northeast edges of the pond were also the same within analytical error. Measurements of the KCC during the summer, 1989, after much rain had fallen show dilution of the pond water. Thus, the pond waters are well mixed (probably by wind), fresh ground water does not appear to be appreciably diluting the pond, and there is no apparent substantial addition of more saline water from below.

Uncontaminated water at the base of the Quaternary aquifer is represented best by observation wells 2 and 10 (Table 1) which yield waters with chloride concentrations of 27 and 30 mg/L, respectively, and sulfate contents of 30-33 mg/L. Chloride just above the aquifer base where irrigation wells are screened is as low as 18 mg/L as indicated by the well in the

Table 1. Concentrations of Dissolved Constituents in Waters from the Macksville Sink and Aquifer Plume.

Sample name*	Sample location#	Sample date	Cl mg/L	SO_4 mg/L	Br mg/L	Ca mg/L	Mg mg/L	Na mg/L	Br/Cl x 10^4	SO_4/Cl
Sinkhole	south	9-13-88	35000	3620	6.9	2080	513	21400	1.97	0.1034
Sinkhole	SW	1-09-89	37400	3890	7.3				1.95	0.1040
Sinkhole	center	1-09-89	37500	3890	7.3	2300	565	23080	1.95	0.1037
Sinkhole	NE	1-09-89	37000	3930	7.3				1.97	0.1062
OBSW 1		9-13-88	4500	64	14.2				31.6	0.0142
OBSW 1		1-19-89	3770	61	12.6				33.4	0.0161
OBSW 1		3-23-89	4440	64	14.3	243	54.0	2700	32.2	0.0144
OBSW 2		9-13-88	27	33	0.07				26	1.22
OBSW 2		3-23-89	27	30	0.06	63	6.5	36	22	1.11
OBSW 3		9-13-88	5450	89	16.0				29.4	0.0163
OBSW 3		3-24-89	4130	71	11.8	273	41.0	2444	28.6	0.0172
OBSW 4		9-13-89	12990	75	35.0				27.0	0.00577
OBSW 4		3-24-89	12100	94	33.4	2172	217.0	4691	27.6	0.00777
OBSW 5		1-19-89	10920	36	32.5				29.8	0.00329
OBSW 5		3-24-89	11750	106	36.0	1676	189.0	5059	30.6	0.00902
OBSW 6		1-19-89	12160	26	34.6				28.5	0.00214
OBSW 6		3-24-89	13570	73	38.4	3366	326.0	4616	28.3	0.00538
OBSW 7		1-19-89	8510	45	26.5				31.1	0.00528
OBSW 7		3-24-89	10590	90	32.4	1797	216.0	4555	30.6	0.00850
OBSW 8		1-19-89	465	32	1.53				32.9	0.069
OBSW 8		3-24-89	361	30	1.21	75	9.8	257	33.5	0.083
OBSW 8D		3-23-89	58	33	0.05	56	9.9	76	8.6	0.569
OBSW 9		1-19-89	10220	16	31.6				30.9	0.00156
OBSW 9		3-22-89	13070	72	39.4	2687	281.0	4558	30.1	0.00551
OBSW 9D		3-22-89	79	34	0.07	48	11.0	87	8.9	0.430
OBSW 10		3-22-89	30	31	0.09	64	7.9	37	30	1.03
OBSW 11		1-19-89	3260	21	10.3				31.6	0.0064
OBSW 11		3-22-89	4480	31	13.9	1803	182.0	580	31.0	0.0069
OBSW 12		1-19-89	361	31	1.20				33.2	0.086
OBSW 12		3-24-89	311	33	1.03	62	9.3	246	33.1	0.106
OBSW 13		3-22-89	2940	32	9.75	765	74.0	1075	33.2	0.109
OBSW 13D		3-22-89	1164	36	3.59	292	37.0	454	30.8	0.0309
OBSW 14		3-22-89	911	25	2.87	408	38.0	118	31.5	0.0274
OBSW 14D		3-22-89	206	34	0.43	105	17.0	95	20.9	0.165

Table 1. Concentrations of Dissolved Constituents in Waters from the Macksville Sink and Aquifer Plume.

Sample name	Sample location	Sample date	Cl mg/L	SO4 mg/L	Br mg/L	Ca mg/L	Mg mg/L	Na mg/L	Br/Cl x 10^4	SO_4/Cl
OBSW 15		3-22-89	8540	56	27.5	2289	223.0	2840	32.2	0.00655
OBSW 15D		3-22-89	494	26	1.69	218	33.0	87	34.2	0.0526
OBSW 16		3-22-89	3000	31	10.3	1134	107.0	554	34.3	0.0103
OBSW 16D		3-22-89	60	31	0.06	46	11.0	69	10	0.517
OBSW 17D		3-22-89	89	39	0.07	59	10.0	98	7.9	0.438
OBSW 18		3-22-89	7790	54	23.5	1931	194.0	2374	30.2	0.0069
OBSW 19		3-22-89	493	29	1.40	135	14.0	222	28.4	0.059
OBSW 20		3-22-89	173	37	0.58	92	11.0	62	33.5	0.214
OBSW 21		3-22-89	151	30	0.47	93	10.0	58	31.1	0.199
OBSW 22		3-22-89	240	37	0.68	117	14.0	74	28.3	0.154
OBSW 23		3-22-89	12340	115	41.5	854	182.0	7123	33.6	0.00932
OBSW 24		3-22-89	12160	116	36.8	1629	197.0	5897	30.3	0.00954
OBSW 25		3-22-89	15130	153	46.7	1500	246.0	8314	30.9	0.01011
ICW 1-4		3-10-89	6000	38	19.5	1599	157.0	1888	32.5	0.0063
ICW 1-1097.5		3-22-89	2890	32	9.58	796	77.0	930	33.1	0.0111
ICW 1-1137		3-22-89	2910	31	9.58	794	78.0	950	32.9	0.0107
ICW 1-1296		3-23-89	2830	31	9.23	776	74.0	886	32.6	0.0110
ICW 1-1451		3-24-89	2750	31	8.98	762	73.0	890	32.7	0.0113
ICW 1-2771.8		3-29-89	2420	30	7.90	689	66.0	771	32.6	0.0124
Stock well	30 ACCC	9-13-88	150	20	0.51				34.0	0.133
Stock well	29 CDDD	3-10-89	79	26	0.22				27.8	0.329
Irr. well	30 A	1-19-89	198	32	0.60				30.3	0.162
Irr. well	29 BBBB	3-29-89	18	14	0.04	53	4.7	18	22	0.78
Irr. well	29 CBBB	3-29-89	100	24	0.27	60	5.8	92	27.0	0.240
OB Riley	30 C	9-13-88	93000	189	332				35.7	0.00203
OB Riley 1B	30 C	3-23-89	91000	572	327	6000	1690	50300	35.9	0.00628
OB Riley 2B	30 C	3-23-89	86400	390	322	5990	1690	47400	37.3	0.00452
OB Benson 4	30 B	3-23-89	91800	255	358	6370	2020	50800	39.0	0.00278
GB Open tank	29 DC	3-23-89	172000	667	920	16450	4600	87800	53.5	0.00388

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*OBSW = observation well; D following OBSW number indicates well screened in Dakota drift, all other OBSW wells are screened at the base of the main aquifer sands; ICW = interceptor (saltwater withdrawal) well, number following the dash after the well number indicates amount of water pumped in thousands of gallons; Irr. = irrigation; OB = oil brine; GB = gas brine.

#Section and letters for quarter sections in order of largest to smallest quarter section in T. 23S, R. 15W.

northwest corner of section 30.

Data for the complete set of observation well samples collected during March 22-24, 1989, from the aquifer base were used to generate a contour map of chloride contents in the ground water (Figure 4). Chloride values exceed 15,000 mg/L in well 25 northeast of the sink. The contaminant plume extends in a northeasterly direction towards the irrigation well in the northeast quarter of the section. The chloride concentration changes slowly with depth below the water table until several feet above the aquifer base as determined from specific conductivity measurements of the KCC. The stock well between observation wells 11 and 13 is probably not completed to the base of the aquifer and, thus, does not contain water with high salinity even though within the areal extent of the saltwater plume.

The distribution of saline water in the aquifer and shape of the plume are controlled by several factors. The higher density of the saltwater than the freshwater caused the contamination to occur above a clay at the aquifer base. The entrance of fresh recharge through the sandy soils at the surface also has helped to keep the dissolved-solids contents low in the upper portion of the aquifer. Undulations on the surface of the clay underlying the aquifer sands have probably affected the direction of denser fluid flow and the variations in the thickness of the saline water layer. Although the regional ground-water gradient is to the east-northeast, the plume direction is to the northeast. Either this reflects a small local difference in the natural ground-water flow direction or indicates an appreciable influence on the local flow by the irrigation well in the northeast quarter of the section. The irrigation well in the northwest corner of the section to the east may have also contributed to the northeast flow direction. The asymmetric shape of the plume in the east-northeast direction may be related to the effect of the

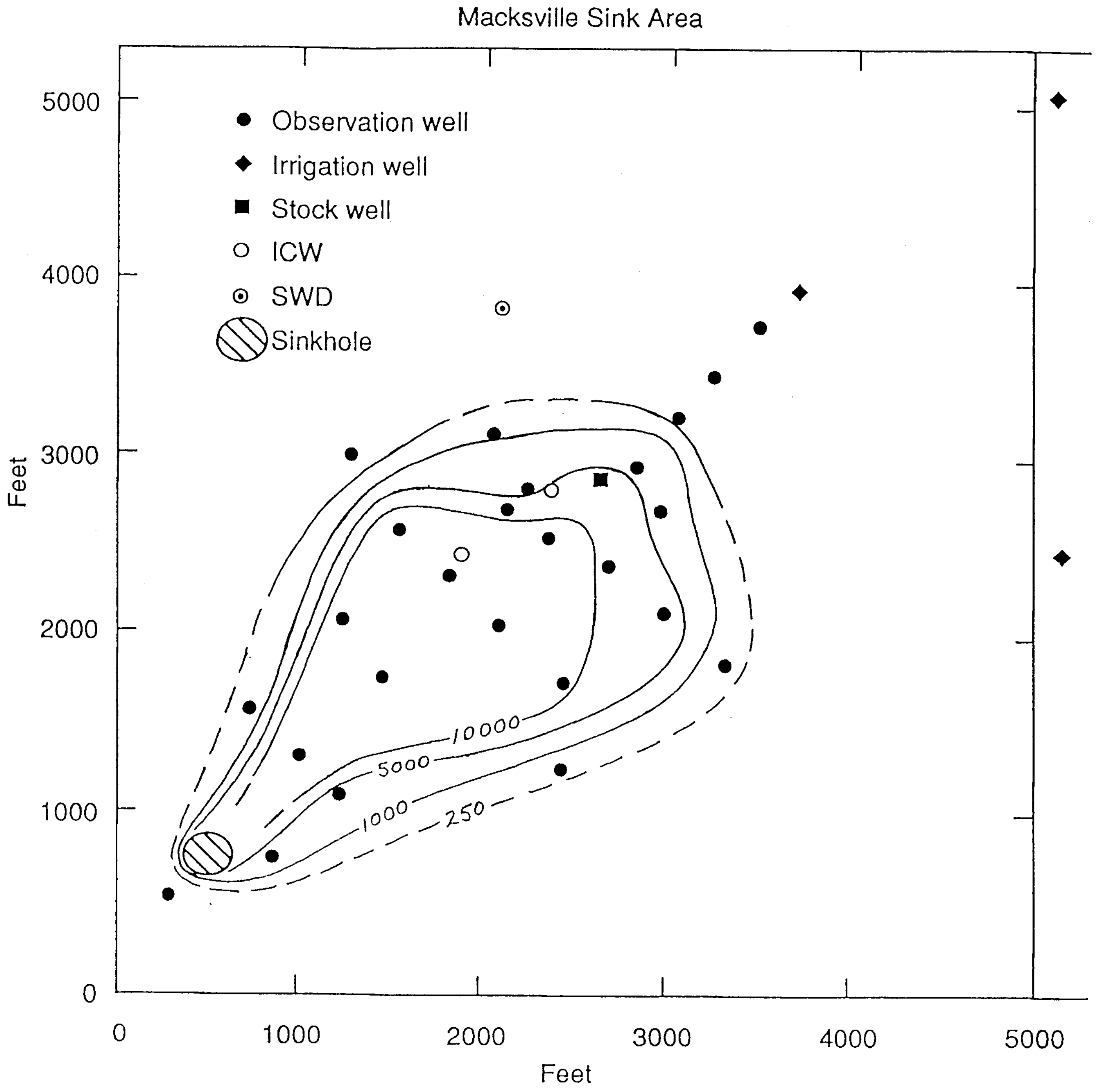

Figure 4. Chloride Contours for the Saltwater Plume at the Base of the Quaternary Aquifer in Sec. 30, T. 23 S., R. 15 W. Values are in mg/L.

irrigation well to the east of the plume and/or a regional ground-water flow direction indicated by Fader and Stullken (1978).

Identification of Salinity Sources

The sources of salinity in water ponded in the sinkhole and in ground water in the adjacent aquifer were identified using sample data and mixing curves on a plot of bromide/chloride versus chloride concentration, and confirmed with a similar graph of sulfate/chloride versus chloride. The bromide/chloride plot (Figure 5) contains two mixing zones. Each mixing zone is bounded by mixing curves, each of which is calculated from the conservative mixing of two end-point waters. Two freshwater end points were selected for the left end of the mixing curves on Figure 5 based on the chemistry of the two samples from observation well 2 (Table 1). The range in the bromide/chloride ratio at the chloride concentration of 27 mg/L for the two points represents the possible variation in the ratio in ground waters at that chloride in the area plus analytical and sampling error.

The zone of mixing between freshwater and halite-solution brine on Figure 5 is based on the two freshwater end points described above and two halite-brine end points for waters from Permian bedrock in Stafford and Pratt counties. The data for Permian waters are based on samples from the wells in the GMD 5 network studied by the KGS (Whittemore et al., in preparation). The freshwater and halite-solution mixing zone in Figure 5 is essentially the same as that for the GMD 5 network to the east. Bromide/chloride ratios for halite brines from the Wellington Formation in Saline and Sumner counties plot either within the mixing zone as drawn or within an extrapolation of the zone to higher chloride concentrations (Whittemore et al., 1981; Whittemore, 1982).

The zone of mixing between freshwater and oil-field brine on Figure 5 was drawn using the two freshwater end points and two brine end points that

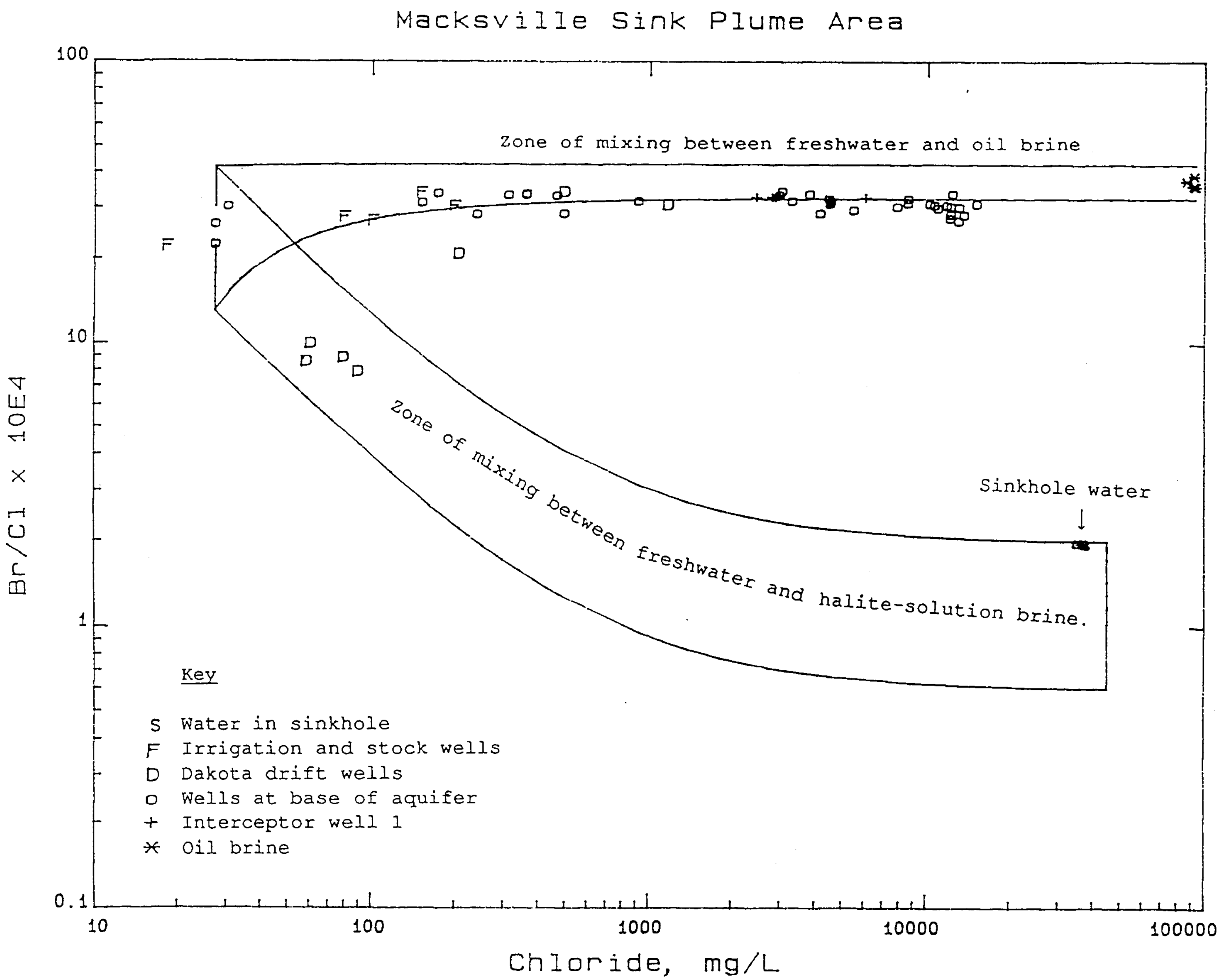

Figure 5. Bromide/Chloride Weight Ratio Versus Chloride Concentration and Mixing Curves for Sink Water, Ground Waters, and Oil Brines.

represent the combined actual range and sampling and analytical error in the values for 4 oil brines collected in the section with the sink (Table 1). The bromide/chloride value for the gas brine collected is not believed to be a true representation of the actual gas brine and was not used to select the brine end points. The gas brine was from an open tank that had allowed evaporation to concentrate the brine to the point where substantial precipitation of halite and other minerals, such as gypsum and/or anhydrite and calcite, had occurred. This was indicated by the appreciable quantity of soluble minerals included with the water sample.

Water from the sinkhole pond had a halite-solution source as indicated by the location of the points near the top of the freshwater and halite-solution mixing zone in Figure 5. The range in the bromide/chloride ratios for the four sink samples is very small, indicating both good consistency in the data and a constancy in the chemical character of the water. The amount of oil brine necessary to increase the bromide/chloride ratio from the center of the mixing zone to the location of the sink pond points on Figure 5 is <2%. The relative bromide concentration in the sink waters is low (7.1 +0.2 mg/L) compared to that of the oil brines (340 +20 mg/L), thus, the method is very sensitive to detecting a small amount of oil brine in the presence of mainly halite solution.

Points on Figure 5 for all samples from observation wells screened at the base of the main aquifer sands form a band extending from the values for wells 2 and 10 to those with the highest chloride concentrations. This band lies close to, but only partially within the mixing zone between freshwater and oil-field brine. The main source of salinity for the contaminated waters at the aquifer base is identified as oil-field brine. However, the difference between mixing lines that would describe the center of the sample data band

and the center of the freshwater and oil-brine mixing zone is significant.

The amount of halite-solution that would be necessary to decrease the bromide/chloride ratio of each saline water from a mixing line in the center of the freshwater and oil-brine mixing zone was calculated. The results indicate that the data can be explained by a salinity source in which oil brine accounts for 95-75% and halite solution for 5-25% of the chloride content. The average values for contribution of oil brine and halite solution to the source mixture are about 83% and 17%, respectively, assuming an average bromide/chloride ratio of 0.0037 for the oil-brine mixture. The location of the band of points on Figure 5 appears only a small vertical distance below the freshwater and oil-brine mixing zone because the method is not as sensitive to an addition of halite solution to oil brine as an addition of oil brine to halite solution. The effect of the addition of halite solution to the oil brine in terms of Figure 5 is primarily dilution of the bromide concentration.

The calculation of the saltwater sources in a saline water mixture can be expressed as volume percent of end member waters in addition to percent contribution to total chloride as described in the above paragraph. A graphic display of the volume percent lines for mixtures of the three end members, average freshwater (point A), oil brine (point B), and halite-solution brine (point C), is drawn in Figure 6. Points for waters from observation wells screened at the aquifer base and sampled during March, 1989, are plotted on the graph. The figure illustrates, just does Figure 5, that the main source of contamination of the aquifer waters is oil brine. The volume percent of both of the saltwater sources increases with increasing chloride concentration. A curve passing through the average trend of the points representing the aquifer samples indicates that the volume percentages of oil

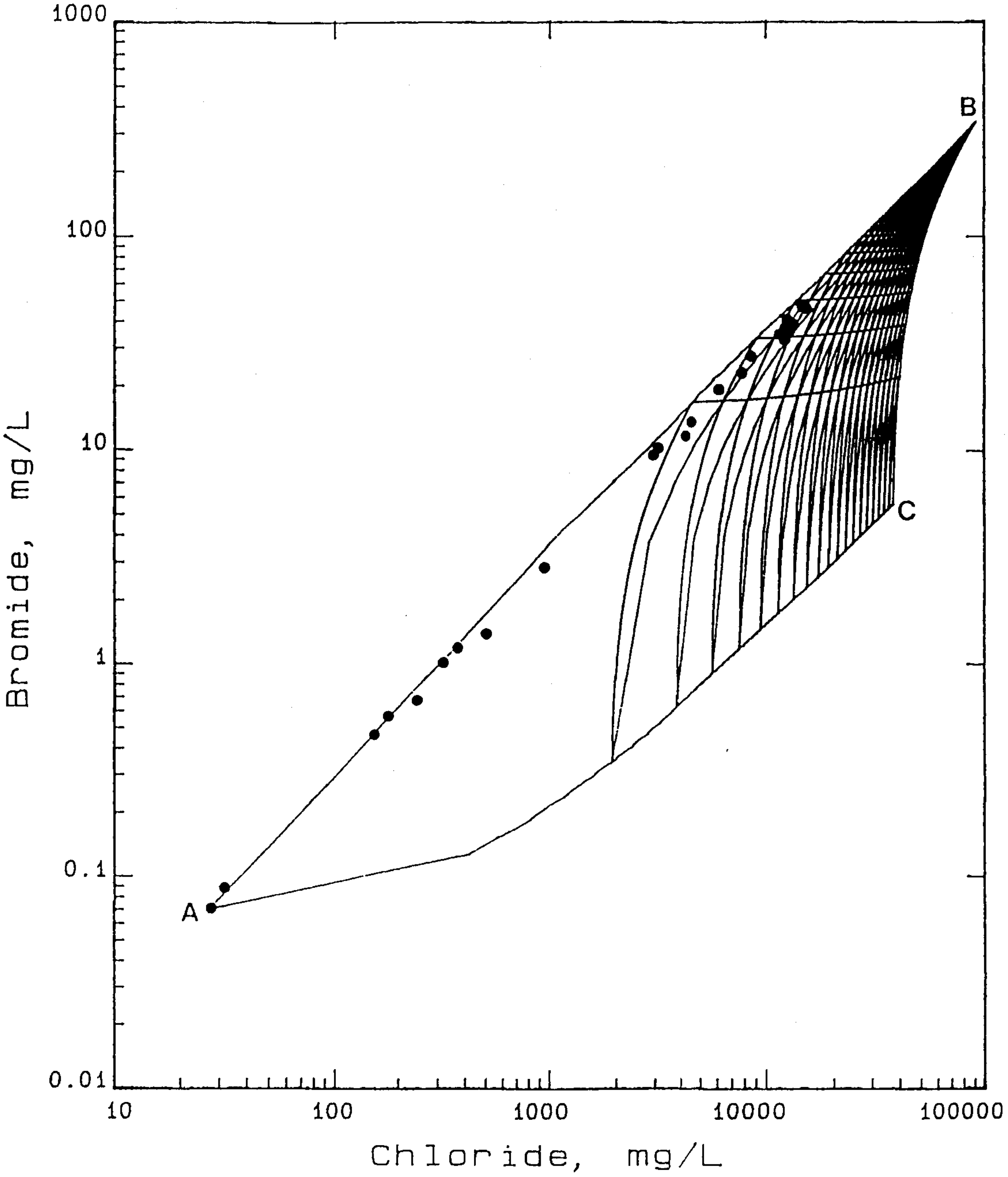

Figure 6. Volume Percent Lines for Mixtures of the Three End Member Waters, Average Freshwater (A), Oil Brine (B), and Halite-Solution Brine (C). Lines are drawn for every 5% volume interval. Points are for waters from observation wells screened at the aquifer base.

brine and halite-solution brine in saline mixtures with >10,000 mg/L chloride are 10-15% and approximately 6%, respectively.

The accuracy in the source mixture calculation is dependent on the relative proportions of different oil and gas brines that contaminated the aquifer and on sampling and analytical error. At this time, a good value for a gas well brine is not available. The assumption was made that the amount of oil brine would have been appreciably larger than that of the gas brines that had been disposed in the past, because some of the present gas wells produce smaller amounts of brine than the oil wells. Thus, the main effect on the source bromide/chloride ratio would have been the oil brines.

There is no apparent pattern to the different bromide/chloride ratios for the waters from the aquifer base when plotted on a figure of well locations. Analytical error can account for about half of the range of bromide/chloride values. The remaining ratio range can be explained by variations in the relative amounts of halite solution and oil and gas brine in the contaminant source mixture as well as variations in the particular oil and gas brine mixtures. Waters from observation wells 1 and 23 did not have bromide/chloride ratios lower than the general range of values for the other wells and there was no decreasing trend with time in the ratios for the three samples from well 1. The ratio for samples from well 3 are in the lower part of the range for the other wells, but the chloride content decreased from September, 1988, to March, 1989. Thus, if water with a composition similar to that in the sinkhole is now moving within the aquifer, it has not reached the closest wells in the expected flow direction.

The chloride concentration range for waters sampled from the observation wells screened in the Dakota drift is 58-1,164 mg/L. Points for all 4 of the wells yielding water with chloride contents <100 mg/L plotted within the mixing zone between freshwater and halite solution (Figure 5). The chloride content of natural waters in the Dakota drift appears to be 73 +16 mg/L, with the approximately 50 mg/L over the concentration for the freshest waters in the main aquifer sands being derived from saline Permian waters at greater depths.

Points for the two Dakota drift wells with ground waters having chloride values of 493 and 1,164 mg/L fall within the band of points for saline waters from the base of the main aquifer sands. The point for well 14D (206 mg/L chloride) lies between the two mixing zones on Figure 5, and on a mixing curve (not shown) that would connect the point for water from the Dakota drift in well 17D (89 mg/L chloride) with the water from the aquifer base in well 14 (911 mg/L chloride). The source of the chloride concentrations >100 mg/L in the Dakota drift is the overlying saline water at the base of the aquifer. The presence of ground water with a chloride content of 89 mg/L (well 17D) and 79 mg/L (well 9D) approximately 150 feet to the southwest and 300 feet to the south-southeast, respectively, from water with a chloride of 1,164 mg/L (well 13D) suggests that some saline water may have been introduced into the Dakota drift during drilling or along the outside of the well casing during or after well completion at well sites 13D, 14D, and 15D.

The source of chloride in excess of 30 mg/L in waters from two stock wells and two irrigation wells in Sec. 29 and 30 (Table 1) is mainly oil-field brine based on Figure 5. The point for the water from the irrigation well just to the northeast of the plume front falls within the general band of points for the saline waters from the observation well waters, suggesting that the main source of chloride is related to the contamination plume.

A graph of sulfate/chloride weight ratio versus chloride concentration (Figure 7) with two mixing curves generated in a similar manner to those on

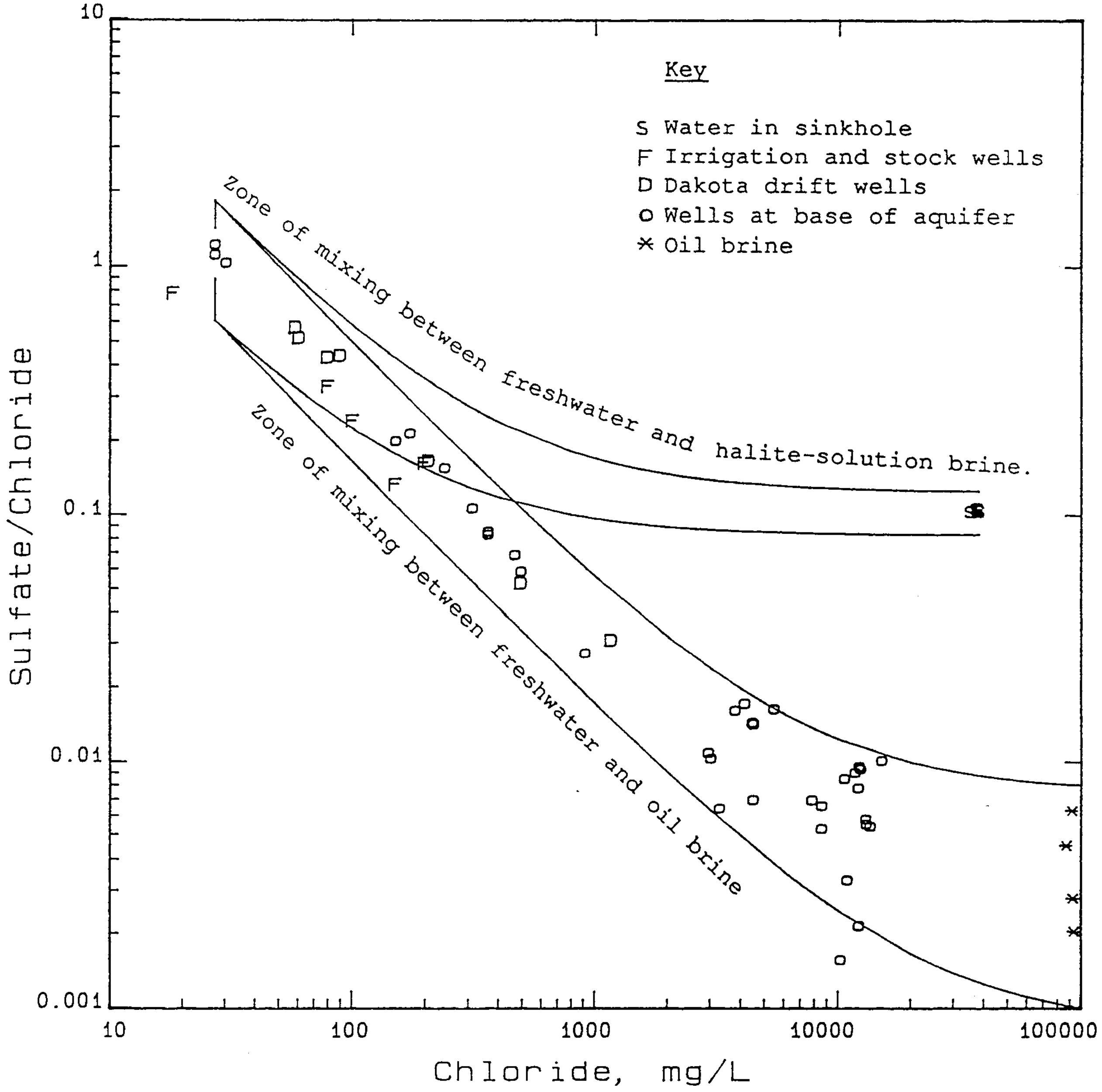

Figure 7. Sulfate/Chloride Weight Ratio Versus Chloride Concentration and Mixing Curves for Sink Water, Ground Waters, and Oil Brines.

Figure 5 supports the geochemical identification based on the bromide and chloride data. The relative sulfate/chloride ratios of halite-solution and oil-field brines are reversed in comparison with bromide/chloride ratios; halite brines have high sulfate concentrations due to solution of anhydrite and gypsum in the evaporite strata, while oil brines often have relatively much lower sulfate contents as a result of sulfate reduction to sulfides. The sulfate/chloride ratio for the water in the sinkhole is similar to that for waters from observation wells screened in the Cedar Hills Sandstone to the east in west-central Stafford County.

The separation of the two mixing zones for the sulfate/chloride figure is not as great as for the bromide/chloride graph. Thus, it is more difficult to clearly identify the main source of salinity for waters with chloride concentrations <450 mg/L because the two zones do not completely separate until above this chloride value. Another difficulty is accurately determining the sulfate content of highly saline waters with a low sulfate/chloride ratio because the high concentrations of other constituents interfere somewhat in the analyses if the samples are not diluted enough. When the samples are diluted to remove interferences, the sulfate concentration is low and in the range where the analytical error is greater. The greater error explains much of the greater range in sulfate/chloride ratios at the higher chloride concentrations in Figure 7.

The special value of Figure 7 is that it can be used to assist in calculating the limits of the amount of halite solution in the saltwater source mixture that contaminated the aquifer. The reason is that it is easier to detect a small amount of halite brine in the presence of oil brine than vice verse due to the high concentration of sulfate in the halite brine. The use of sulfate for source mixture calculations assumes that sulfate behaves in a conservative manner as chloride and bromide in the aquifer. However, sulfate can be adsorbed slightly during transport in aquifers containing fine-grained sediments and can be converted to sulfide in a reducing environment.

Sulfate concentrations have been included next to each of the sites with a well screened at the aquifer base on a figure with chloride contours (Figure 8). The sulfate values appear to be greater in the southwestern and central part of the contaminant plume than in the northeastern portion. This may indicate the slight effect of retardation of sulfate by adsorption. The sulfate values are much lower than would be necessary for saturation with respect to gypsum, therefore, precipitation of calcium sulfate does not control the sulfate in the system.

Nearly all of the saline samples with more than a few thousand mg/L chloride produced ferric oxyhydroxide precipitate upon standing, indicating that the ground water in the contaminated zone contains dissolved ferrous iron. In general, the greater the chloride concentration, the greater the amount of precipitate. The chemical environment needed to dissolve more ferrous iron is reducing, and could have been generated through oxidation of the dissolved organics in the oil-field brines contaminating the aquifer. The oxidation potential required to reduce sulfate to sulfide is lower at the pH of the ground water than that for the reduction of ferric to ferrous iron. No prominent hydrogen sulfide odor has been observed by GMD 5 staff during sampling of the wells. Thus, it is possible that no appreciable sulfate reduction has occurred.

If both the adsorption and reduction effects on sulfate are assumed to have been small, the greatest amount of halite solution similar to that in the sinkhole that could be mixed in with the oil brine would contribute only up to 10% of the total chloride concentration. This compares with the range of 5-

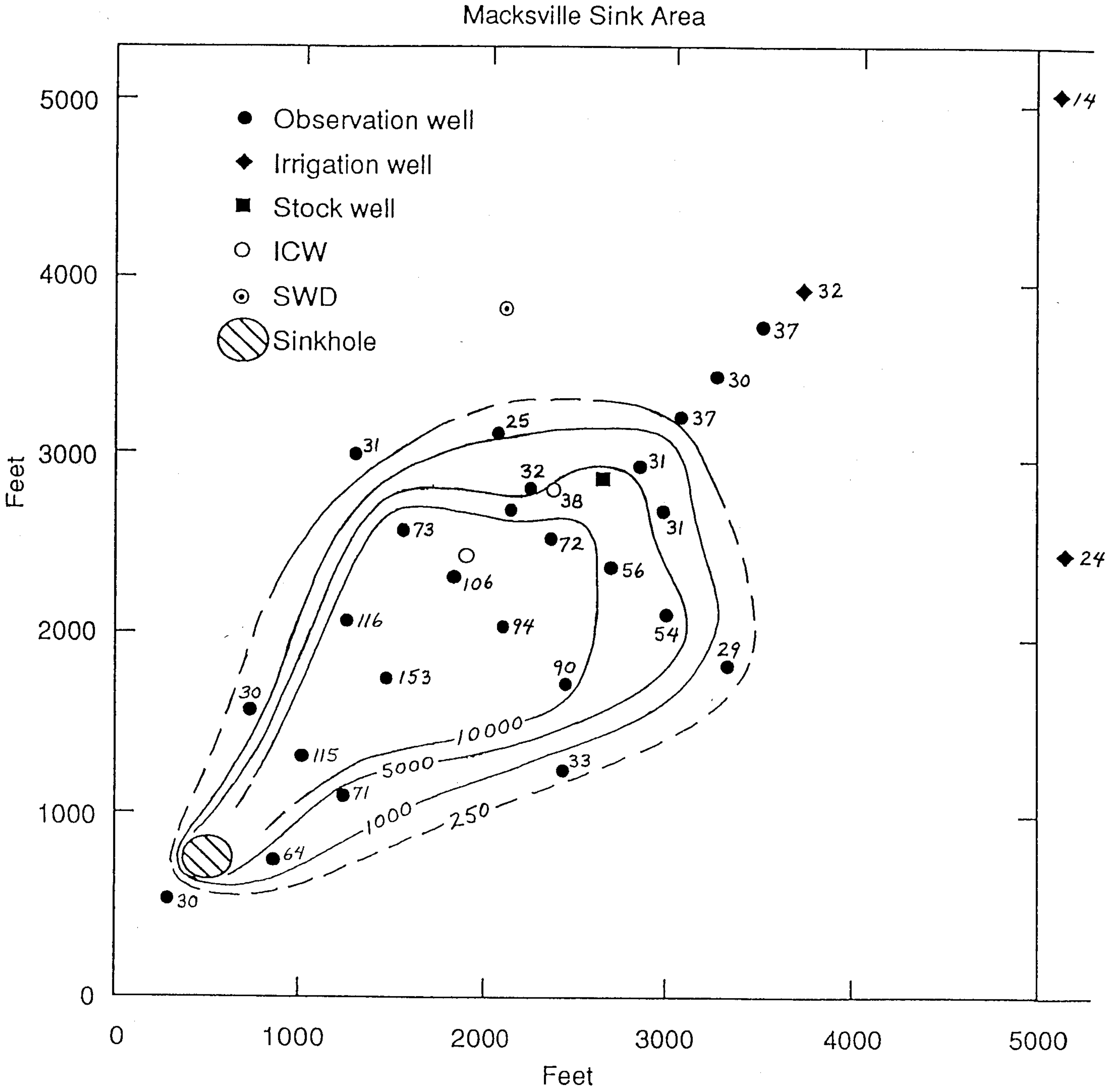

Figure 8. Sulfate Concentrations for Observation Wells Screened at the Aquifer Base and Irrigation Wells on a Contour Map of Chloride Concentrations. Sulfate values written beside the well locations and chloride contour intervals are in mg/L.

25% and average of about 17% based on the bromide and chloride data. Either sulfate contents of the ground water have been decreased by adsorption and/or reduction or the actual oil and gas brine mixture that polluted the aquifer had a slightly lower bromide/chloride ratio.

Geochemical Characterization of Plume Dynamics

Cation exchange will alter the chemistry of a saline water with a (Ca + Mg)/Na ratio substantially different from that of the native water present in sediments containing clays. The (Ca + Mg)/Na ratio for both oil and gas brines and halite solutions is much lower than that of the freshwaters in the Quaternary aquifer at the sink site. Sodium concentrations in the saltwater contaminant mixture were decreased during transport through the aquifer sediments, which contain clays in addition to silts and sands, as a result of adsorption on the clays and exchange for calcium and magnesium ions. The effect decreases the sodium/chloride ratio below that calculated for conservative mixing of freshwater and the saltwater source, as shown in Figure 9. The graph illustrates well why the sodium/chloride ratio is often a poor method for distinguishing oil brine from halite brine contamination of water resources.

The mixing curves in Figure 9 were generated in a similar manner to those in Figures 5 and 7. Several of the points for saline ground waters from observation wells at the aquifer base lie above or at the top of the mixing zone between freshwater and oil brine in Figure 9. These points are for observation wells that generally lie closer to the sink than those with sodium/chloride ratios below the mixing zone between freshwater and oil brine. A graph of the (Ca + Mg)/Na ratio, for which the values were calculated using cation concentrations converted to meq/L, versus chloride content (Figure 10) shows the effect of cation adsorption/exchange better.

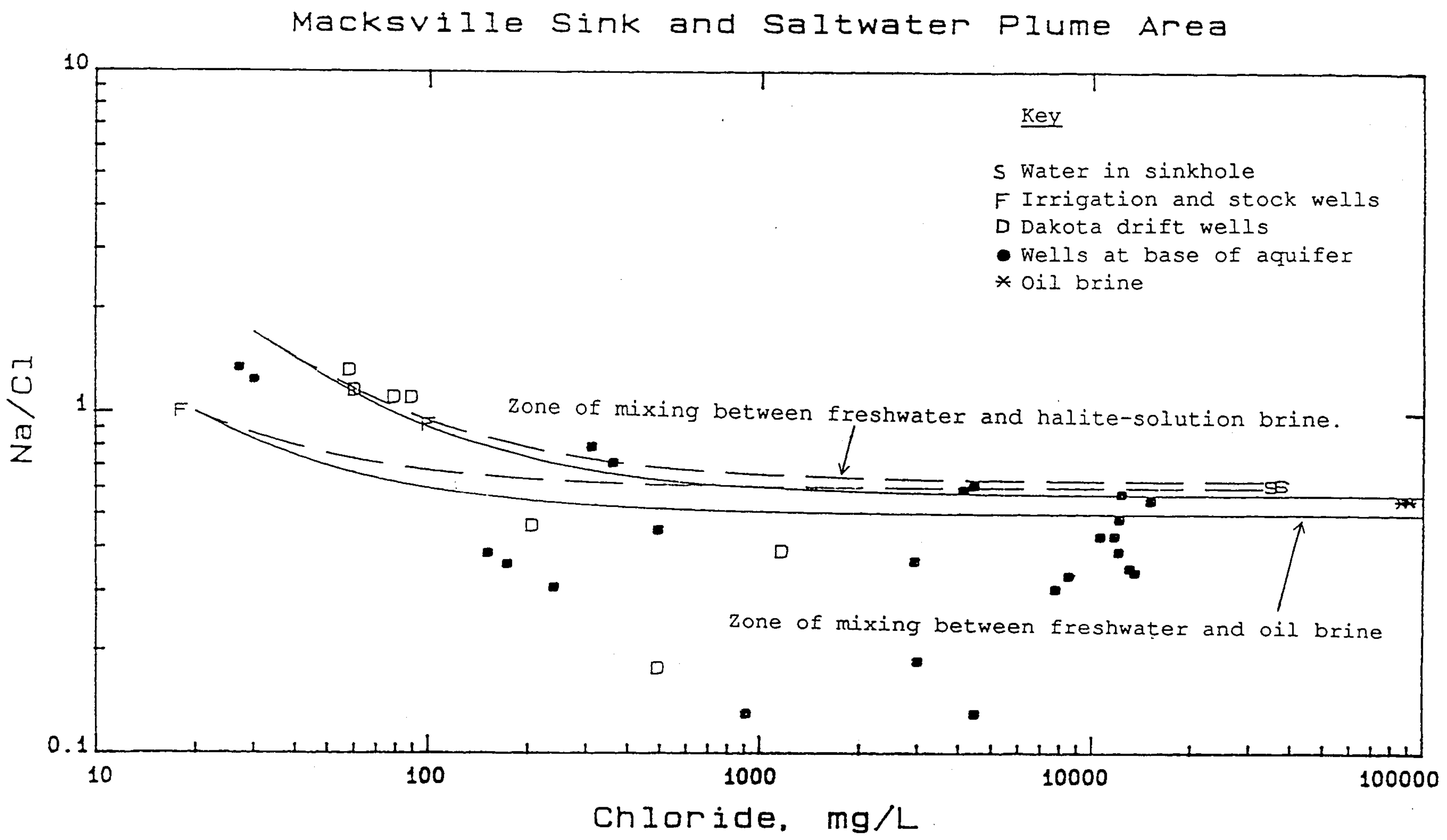

Figure 9. Sodium/Chloride Weight Ratio Versus Chloride Concentration and Mixing Curves for Sink Water, Ground Waters, and Oil Brines.

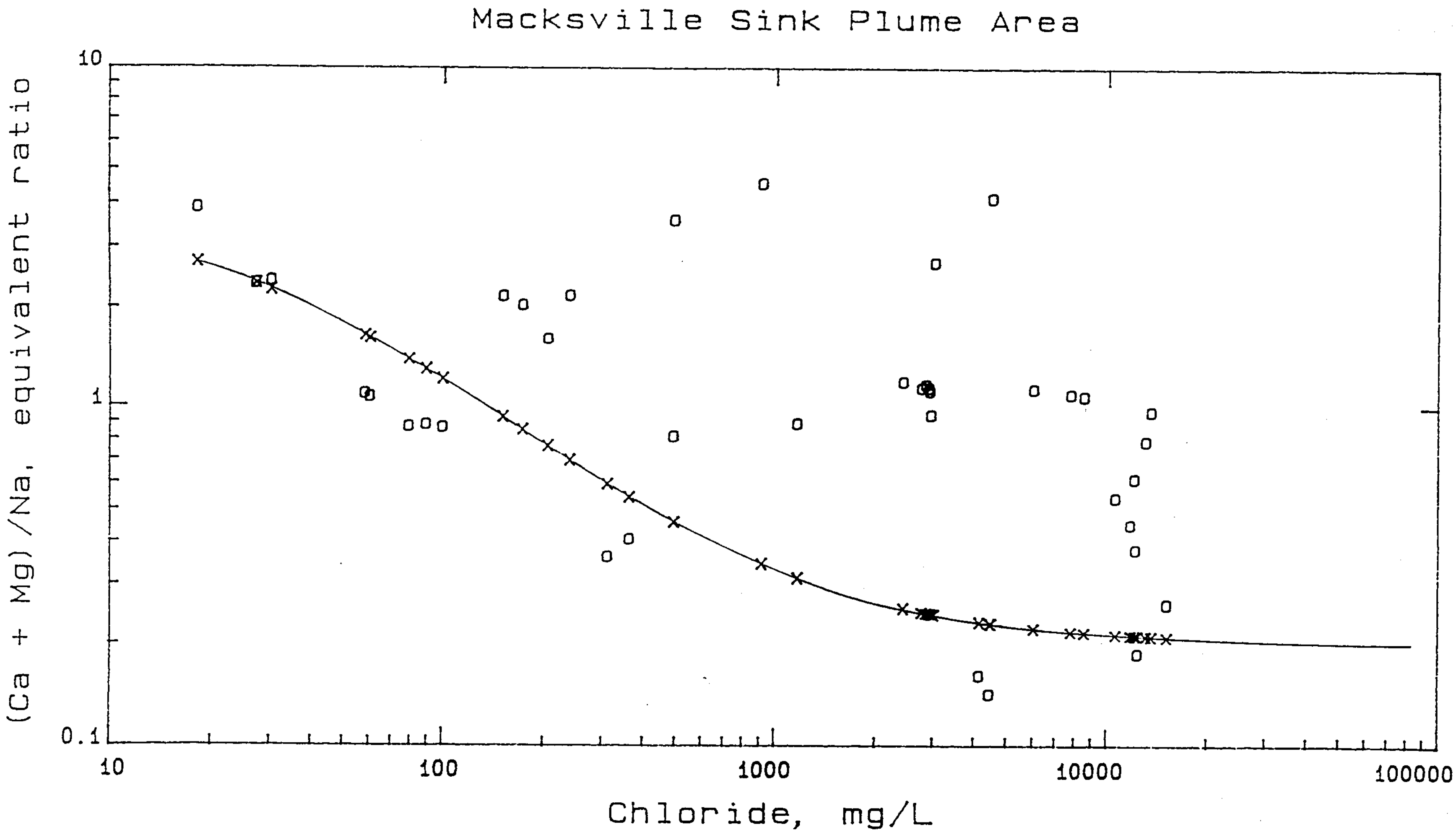

Figure 10. (Ca + Mg)/Na Equivalent Ratio Versus Chloride Concentration for Ground Waters. The 'x' symbols indicate the calculated ratio for each water assuming conservative mixing without cation adsorption/exchange between freshwater and the average saltwater source mixture.

Values for the (Ca + Mg)/Na equivalent ratio were calculated for each ground water assuming conservative mixing without cation adsorption/exchange between freshwater at observation well 2 and the average saltwater source mixture. A mixing curve was drawn through the computed points on Figure 10. Positive deviations in the ratio from the conservative mixing curve are much greater than negative deviations. The maximum positive deviations first increase, then decrease with increasing chloride concentration. The reason is that as the salinity of the contaminant water increases, the cation adsorption/exchange will increasingly alter the (Ca + Mg)/Na ratio until the source water becomes so saline that the amount of adsorption/exchange relative to the total-dissolved cation concentration becomes smaller.

The negative deviations in the (Ca + Mg)/Na ratio from the conservative mixing curve can be explained by dilution of the saline water in the aquifer. When the dissolved cation contents of the contaminated water decrease, the adsorbed cation concentrations on the clays become out of equilibrium with the water. The adsorbed (Ca + Mg)/Na ratio is then lower than before the entrance of the saline water, thus, the ratio in the water becomes lower than that predicted by conservative mixing as cations desorb.

Values for the actual minus the predicted (conservative mixing) (Ca + Mg)/Na ratio for waters from observation wells screened at the aquifer base are plotted and contoured on a graph of chloride contours for the same waters in Figure 11 as in Figure 10. The most positive deviations (>1.0) are located at the northeastern extent of the plume. This represents the area where the plume is advancing, i.e., where the dissolved-solids concentrations of the waters are increasing most. The area with (Ca + Mg)/Na ratio differences of 0.5-1.0 probably indicates where dissolved-solids contents have stabilized. Negative ratio differences represent where the plume is actively

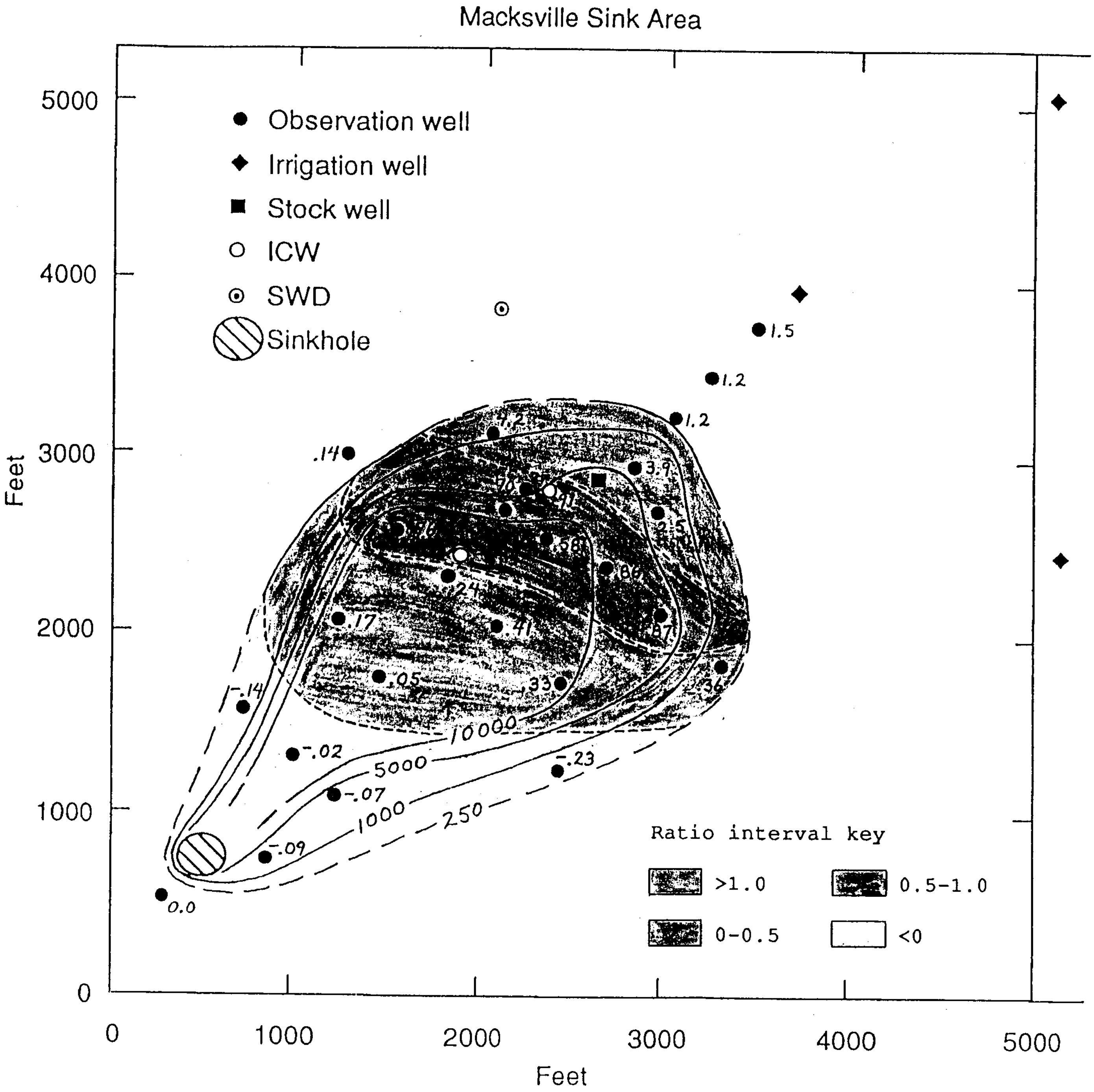

Figure 11. Values and Contours for Actual Minus Predicted (Conservative Mixing) Equivalent Ratio of (Ca + Mg)/Na for Waters at Aquifer Base Plotted on a Graph of Chloride Contours for the Same Waters. Ratio intervals are shaded. Chloride intervals are in mg/L.

being diluted the most, while positive differences of 0-0.5 probably indicate areas where dilution is occurring but at a slower rate. Variations in chloride concentrations in waters collected from the wells as determined by the KCC generally fit the interpretation of the pattern in Figure 11. Increases in chloride values are greatest in the areas of the most positive ratio differences and decreases are greatest in the area of negative ratio differences.

Hydrochemistry of Interceptor Well Waters

Six samples of water pumped at different times from interceptor well 1 used for aquifer remediation were analyzed (Table 1). The chloride concentration decreased from 6,000 mg/L soon after the initial pumping (4,000 gal) to 2,890 mg/L after about 1.1 million gal had been pumped, and to 2,420 mg/L at 2.8 million gal. The decrease in chloride content is probably caused by the pumping of less saline water from higher in the aquifer above the several feet of the saline water layer at the aquifer base. Assuming chloride concentrations of 100 mg/L for the water overlying the saline layer and 6,000 mg/L for the saline water, the volume proportions of saline and overlying water layers in the mixture pumped at 2.8 million gal would be 39% and 61%, respectively. The bromide/chloride ratio did not change (within analytical error) during the pumping, indicating that the saline water being pumped was from the same general aquifer zone throughout the sampling period.

Estimate of Contaminant Source Volumes

The volumes of oil brine and Permian halite brine necessary to contaminate the aquifer were estimated using the graph of chloride contours, an aquifer porosity of 25%, and an average depth of the saline water layer of 5 ft. The contoured areas of 250-1,000, 1,000-5,000, 5,000-10,000, and >10,000 mg/L chloride concentration on Figure 4 were represented by 625, 3,000, 7,500, and 12,000 mg/L chloride, respectively. The area for each of the contour intervals was determined by the number of grid cells occupied when superimposing the figure on coordinate graph paper. An area of 150 mg/L chloride content equivalent to the area of the 250-1,000 mg/L interval was assumed to surround the plume. The areas and volumes of water in each of the intervals are listed in Table 2.

The amount of oil and halite brine in the contaminated water were computed for a pollutant source mixture in which oil brine contributed 87% and halite brine 13% to the total chloride concentration. The estimated average composition reflects both the bromide/chloride and sulfate/chloride data. The total volume of oil brine was estimated as 3.3 million gallons (78,000 bbls), and the total volume of halite brine as 1.2 million gallons. The longitudinal dimension of the plume was approximately 3,500 feet in March, 1989 (Figure 4). If the source was located at the injection well, the distance that the plume could have traveled at a regional flow rate of one foot/day since the well was plugged in 1984 (5 years) would be 1,825 feet. The plume would have required 4.6 year to travel the remaining distance of 1,675 feet for the same flow rate. The flow rates of the contaminant sources estimated for a 4.6 year period are 1.35 gal/min and 0.50 gal/min for oil brine and halite-solution brine, respectively. These flow rates total 1.85 gal/min and do not appear to be unrealistic.

Table 2. Estimated Volumes of Water in Saline Water Layer at Aquifer Base for Areas of Plume Contour Intervals. An average saline layer of 5 ft and a porosity of 25% were assumed.

Plume interval, mg/L chloride	Average chloride for interval, mg/L	Interval area, million sq. ft (acres)	Total water volume, million gal
<250	150	1.30 (30)	12.2
250-1,000	625	1.30 (30)	12.2
1,000-5,000	3,000	1.25 (29)	11.7
5,000-10,000	7,500	1.07 (24)	10.0
>10,000	12,000	1.98 (45)	18.5
	Totals	6.90 (158)	64.5

CONCLUSIONS

The source of saltwater ponded in the Macksville sinkhole is halite-solution brine similar in chemical composition to that in the Cedar Hills Sandstone. Oil-field brine contributes <2% of the chloride content of the sink brine. The saltwater in the sink appears to be relatively stagnant and changes in dissolved-solids content mainly due to concentration by evaporation and dilution by atmospheric precipitation. The saltwater most likely entered the bottom of the sinkhole due to displacement of Permian saltwater below the sink by Quarternary sediment that fell into the collapse column.

Saline water in the plume at the base of the main aquifer sands in the Quaternary sediments is derived mainly from oil and gas brines produced in the past in the area, but also includes some halite-solution saltwater. Calculations based on bromide and chloride values indicate that oil and gas brines could have contributed from 95% to 75% and halite brine from 5 to 25% of the total chloride concentration in the saline waters from the different observation wells. Calculations based on sulfate and chloride concentrations assuming conservative behavior of sulfate suggest that the contribution of oil brine is >90% and of halite brine is <10%. However, there is some evidence of slight retardation of sulfate during plume transport and, although the amount of chemical reduction of sulfate to sulfide in the aquifer is believed to be small, the actual amount is unknown. Thus, the estimates for halite solution contribution to chloride based on sulfate values may be low. The estimate for the halite-solution amount considering both methods is a range of 5-20% and an average of 10-15%. The missing data most important to improving the calculation are an analysis of gas brine representative of the actual gas brine disposed in the past with the oil brines in the area, and an estimate of the volume ratio of gas brine to oil brine for saltwaters disposed in the former injection well at the sinkhole site.

There is no apparent areal pattern to the bromide/chloride ratios in saline waters at the base of the main aquifer sands. Thus, the oil-brine and halite-brine mixture causing the aquifer plume contamination remained relatively constant. No substantial amount of water similar to that in the sinkhole had reached the closest observation wells in the expected ground-water flow direction by March, 1989, since rapid sink formation.

The chloride concentration of uncontaminated waters in the main aquifer sands of the Quaternary sediments is <30 mg/L in the Macksville sink area. Natural waters in Dakota drift beneath a clay layer underlying the main aquifer sands contain 58-89 mg/L chloride. The additional chloride in the uncontaminated Dakota drift waters is derived from dispersion of halite-solution waters in the Permian rocks underlying the Cretaceous bedrock at the site. Slightly saline waters collected from some of the observation wells in the Dakota drift have the same chemical character as saline waters at the base of the contaminated aquifer. They are probably derived from entrance of some of the overlying saline water during well drilling and installation or afterwards along the well annulus.

Cation adsorption and ion exchange have appreciably altered the (Ca + Mg)/Na ratio of the saline waters in the aquifer from that of the saltwater sources. Contours of the difference between the actual (Ca + Mg)/Na ratio and the ratio calculated assuming conservative mixing show where changes in the contaminant plume are occurring. The most northeastern portion of the plume area with chloride contents >250 mg/L should have the most rapid increases in dissolved-solids concentrations, while the southwest half of the plume is probably being actively diluted.

A comprehensive interpretation of the hydrochemical results suggests that the main source of the saltwater mixture contaminating the aquifer emanated from near and/or at the former injection well within the sink site. Oil and gas brines comprising most of the contaminant mixture could have leaked from the well or disposal lines near the well and mixed with a small amount of Permian salt water that moved upward along the injection well. This mixture continued for a period of at least a few years based on the size of the plume and a regional flow rate of ground water in the aquifer of about a foot/day. Brine line leaks and spills in other areas overlying the plume might have added to the plume to a small extent, but do not appear to have appreciably affected the plume chemistry. When the injection well was plugged, the main contaminant source probably stopped. Since then, the northeastern front of the plume has continued to migrate to the northeast, while the southwestern half of the plume has been diluted.

The areal extent of the contaminant plume (chloride concentration $\geq$150 mg/L) is approximately 158 acres. The total amount of contaminated water, assuming a 5 foot depth of the saline layer at the aquifer base, is estimated as 64 million gallons, of which about 40 million gallons has a chloride content >1,000 mg/L. The flow rates of the contaminant sources estimated for a 4.6 year period of an active source are 1.35 gal/min and 0.50 gal/min for oil brine and halite-solution brine, respectively.

The best area for locating interceptor wells for removing very saline water from the aquifer base is within the zone of (Ca + Mg)/Na ratio deviations >0.5 that are within the 5,000 mg/L chloride contours as shown on Figure 11. This area represents both high concentrations of dissolved salts at the aquifer base as well as the portions of the plume in which dissolved solids are relatively constant or increasing. Both of the present interceptor wells are currently in this area. The proposed location of a third interceptor well between observation wells 11 and 15 also fits the criteria. The appreciable decrease in chloride concentration during pumping of interceptor well 1 suggests that pumping rate should be slower and the length of the well screen shorter to be completely within the saline water layer at the aquifer base.

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