

GEOCHEMICAL IDENTIFICATION OF SALTWATER CONTAMINATION
AT THE SIEFKES SUBSIDENCE SITE

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INTRODUCTION

Ground water has been found to be saline at a site in northeast Stafford County where subsidence has occurred. The subsidence is in the area of a plugged well used in the past for oil-brine disposal in the NE1/4, NE1/4, NE1/4 of section 3, T. 22 S., R. 12 W. A new disposal well is located in the SW1/4, NE1/4, NE1/4 of section 3 to the southwest of the plugged well. Two monitoring wells were installed near the plugged disposal well in January, 1989. One of the well sites (No. 1) is to the southwest of the plugged well between the plugged well and the new disposal well. The other well (No. 2) is to the northeast of the plugged well. The wells are screened in the unconsolidated Quaternary sediments of the Great Bend Prairie aquifer and overlie Permian bedrock (Salt Plain Formation). The bottom of the screens are at the bottom of the sands and gravels of the aquifer.

The Kansas Corporation Commission requested that the Kansas Geological Survey determine the source of the salinity using the geochemical methods of Whittemore (1984, 1988). Two samples were bailed from each of the monitoring wells, one from the top of the screened interval and one from the bottom. A sample was also taken from the disposal tank containing oil brine from several oil wells in the area. The specific conductance, chloride, sulfate, and bromide concentrations of the samples sent to the Survey were measured and the salinity source identified based on mixing curve plots.

PROCEDURE

The samples sent to the Survey were filtered through 0.45 um membrane filter paper before analysis. Chloride, sulfate, and bromide, concentrations were determined using automated colorimetric methods on a Technicon AutoAnalyzer II. The estimated maximum error in the chloride determinations is 2% and ranges from about 10% for the low sulfate to 4% for the high sulfate values. The estimated maximum error for the bromide measurements >0.4 mg/L is approximately 5%, while the low values are accurate to ± 1 of the significant figure.

RESULTS AND DISCUSSION

The sample identification and results for the waters analyzed are listed in Table 1. The

waters from the top of the screened interval are fresh. The estimated total-dissolved solids (TDS) concentrations for the shallow waters are both below 500 mg/L, the recommended upper limit for drinking waters, based on the relationship that the TDS in mg/L equals approximately 0.65 times the specific conductance in umhos/cm. The waters collected from the aquifer base are saline with sulfate contents above the recommended drinking-water standard and chloride concentrations above both the recommended drinking standard and the freshwater classification limit. The higher of the two chloride values is also above the usable water classification limit.

Table 1. Sample Identification and Results. All samples were collected on June 14, 1989.

Description	Depth of sample, ft	Sp.C., umho/cm	Cl, mg/L	SO ₄ , mg/L	Br, mg/L
MW-1	85 (top)	640	72	13	0.08
MW-1	135 (bottom)	8,110	2,390	290	0.45
MW-2	80 (top)	445	18	12	0.03
MW-2	130 (bottom)	16,500	5,220	670	0.92
Siefkes disposal tank	Mixture of brines from 6 wells	51,400	19,490	1,490	71

The identification of the salinity source at the aquifer base was made 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 1) contains points for the data in Table 1 and data for waters from the 6 sites in the observation well network of Groundwater Management District No. 5 that are closest to the Siefkes subsidence location. Each observation-well site in the network has three wells, one screened in the middle to shallow part of the unconsolidated aquifer, one screened near the aquifer base, and one screened in the underlying Permian bedrock. The data are for observation well site numbers 1, 5, 16, 17, 18, and 22 which range from approximately 2 to 7 miles distant from the Siefkes location (Whittemore, et al., 1987). The ranges in natural chloride concentrations at these sites

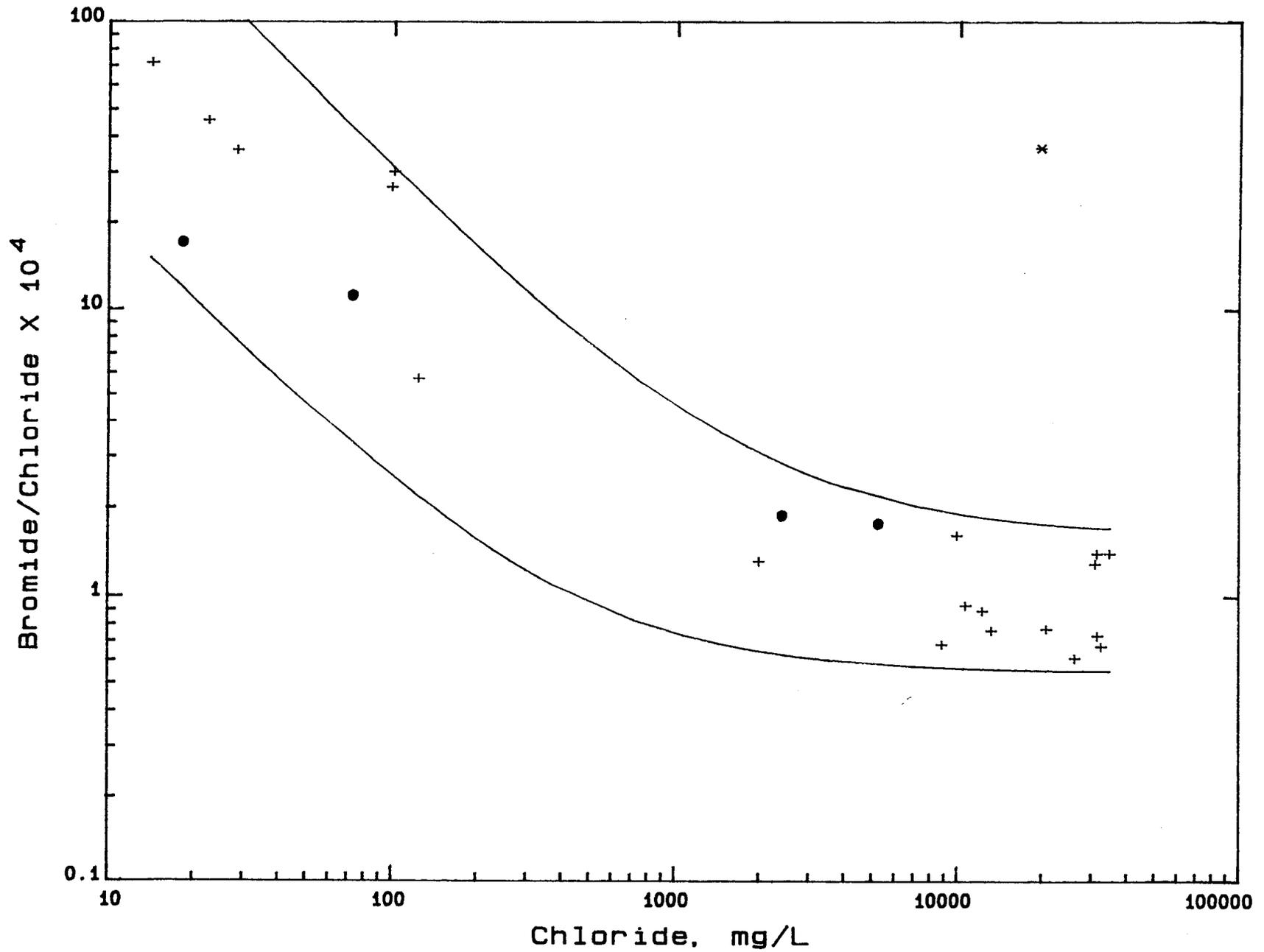


Figure 1. Bromide/Chloride Weight Ratio Versus Chloride Concentration. Symbols: * oil brine, ● monitoring wells at the site, + ground waters from observation wells in the Groundwater Management District network.

for ground waters from the shallow to middle aquifer, aquifer base, and Permian bedrock are 14-123 mg/L, 1,980-31,500 mg/L, and 9,880-34,800 mg/L, respectively.

Figure 1 also contains two mixing curves, each of which is calculated from the conservative mixing of two end-member waters. A freshwater end member was selected for the left end of each of the two mixing curves based on the range in the bromide/chloride ratios of the freshwaters on the plot. A saltwater end member was chosen for right end of each of the two mixing curves based on the range in the ratios for the GMD5 observation wells. The two mixing curves define a mixing zone between freshwaters and natural halite-solution brines. All of the points for the Siefkes monitoring wells fall within the mixing zone. The point for the oil-field brine lies well above the mixing zone. The bromide/chloride ratio for the oil brine is within the 0.002-0.006 range common for most oil brines in Kansas.

The salinity identification method based on the bromide/chloride to chloride plot is very sensitive to detecting a small amount of oil brine in the presence of mainly halite solution. No oil-field brine contamination appears to have affected the saline ground waters at the Siefkes site within the errors of the limit of detection of the method for these waters (approximately <1% contribution of oil brine to the total chloride of the saline ground water).

A graph of the sulfate/chloride weight ratio versus chloride concentration (Figure 2) with two mixing curves generated in a similar manner to those on Figure 1 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 sulfide. However, the sulfate/chloride ratio for the oil brine from the Siefkes site is higher than for many oil brines in Kansas. Thus, the separation between the ratios of the oil brine and the halite-solution brine is not nearly as great as for the bromide/chloride ratios. Sulfate/chloride ratios often range more widely than bromide/chloride ratios for the same waters as in the case of well waters from the GMD5 observation network. The points in Figure 2

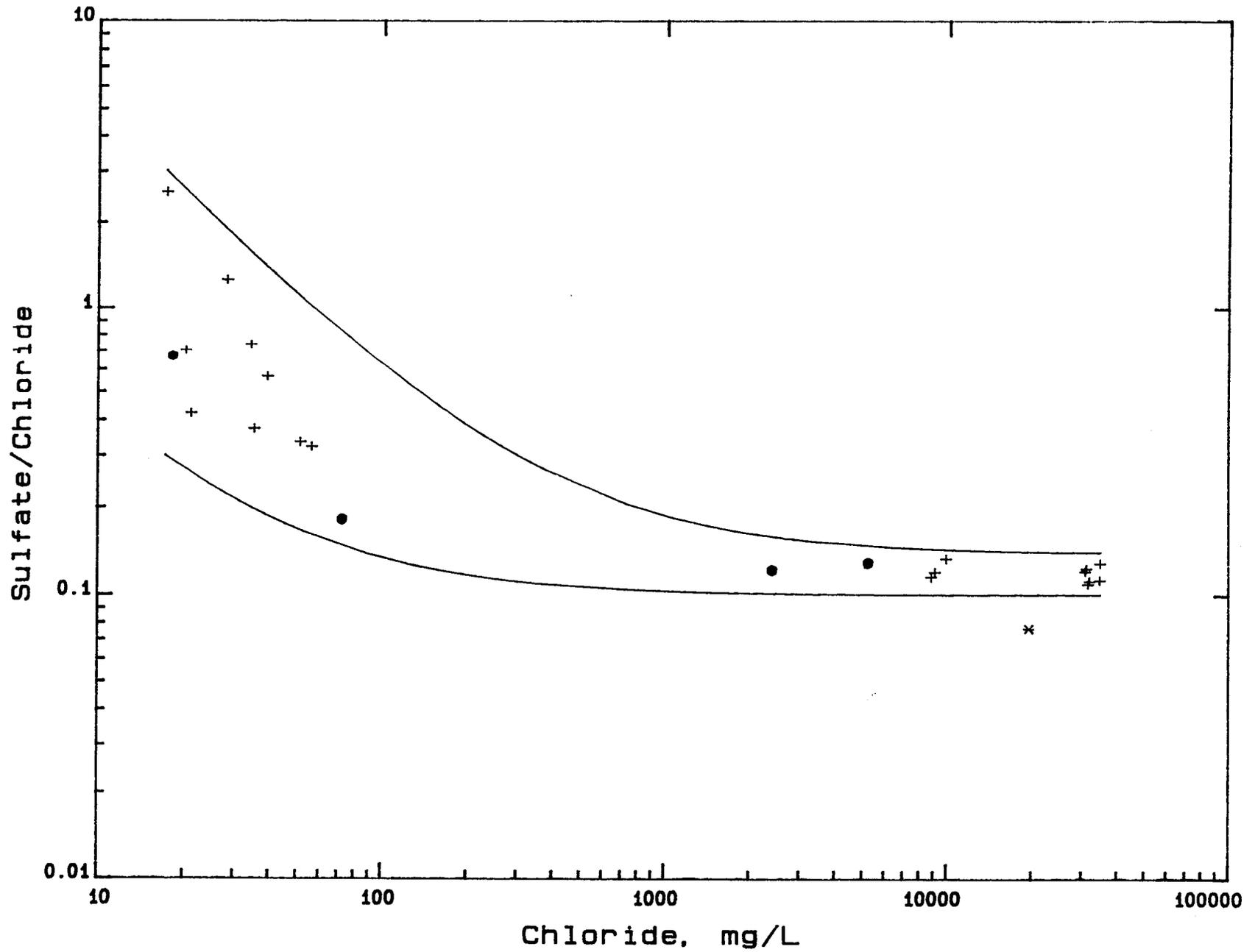


Figure 2. Sulfate/Chloride Weight Ratio Versus Chloride Concentration. Symbols: * oil brine, ● monitoring wells at the site, + ground waters from observation wells in the Groundwater Management District network.

shown for the GMD5 network are for the two closest sites, numbers 16 and 17, which are about 4 miles to the west and 2 miles to the east, respectively, of the Siefkes location.

The difference between the salinity of the water from the bottom of the aquifer at the two monitoring well locations could be due to mixing of water during sampling as well as a natural cause. If the sampling were mainly responsible for the difference, then the higher value is more representative of the actual bottom water.

CONCLUSIONS

The source of saline ground water at the base of the unconsolidated aquifer below the Siefkes subsidence site is halite-solution brine. The chemistry of the ground waters from the aquifer at this site is very similar to ground waters from the surrounding area. Thus, oil brine contamination has not occurred at the locations sampled by the Siefkes monitoring wells. The chloride concentration of the most saline water collected near the aquifer base is lower than that naturally found 4 miles to the west and 2 miles to the east based on the GMD5 observation well network. Therefore, subsidence activity does not appear to have increased the salinity of the water above what might be expected naturally in the area.

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