

**GEOCHEMICAL IDENTIFICATION OF SALTWATER CONTAMINATION
AT THE HARBAUGH CONTAMINATION SITE, BARBER COUNTY**

a report for the
Kansas Corporation Commission

by

Donald O. Whittemore
Kansas Geological Survey
Lawrence, Kansas

Kansas Geological Survey Open-File Report 93-15

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INTRODUCTION

Ground water has been found to be saline by the Kansas Corporation Commission (KCC) in eastern Barber County, south-southeast of Medicine Lodge, and just south of the Medicine Lodge River in sections 20 and 29, T. 33 S., R. 11 W. The location is known as the Harbaugh contamination site. Chloride concentrations in the ground-water contamination plume delineated by the KCC range to over 6,000 mg/L. The plume occurs primarily in the alluvial aquifer of the Medicine Lodge River. The plume is oriented in a southeasterly direction which is the general direction of the alluvial valley in the area. The Gerlane Quadrangle (USGS 7.5 minute series topographic map) shows that the Medicine Lodge River is split into two channels separated by about a half mile in the vicinity of the Harbaugh site. The south channel of the river flows just to the north of the site.

The bedrock underlying the alluvium and at the surface above the valley is the middle part of the Permian Nippewalla Group which comprises the Cedar Hills Sandstone and the Salt Plains Formation. The strata range from silty shale to sandstone and contain halite (rock salt) cement and gypsum in the deeper subsurface. The occurrence of the evaporite minerals has resulted in saltwater in the sediment pores. Fresh ground-water recharge from the surface flushes the saltwater from the units, thus the salinity of the water generally increases from the surface with depth in the Permian. Shaley units can confine saltwaters in parts of the Permian rocks. In the near surface, where the halite has been completely dissolved from the rocks, gypsum may remain because it is less soluble than the salt. Williams and Bayne (1946) indicate that near-surface Cedar Hills Sandstone in the vicinity of Medicine Lodge contains gypsum.

The Harbaugh site is also located in the area of the Rhodes Field of oil and gas production. Waterflooding has been used for secondary recovery operations within the oil field. A flow of saltwater to the surface, called the Wild Boys blowout, occurred during past drilling in the floodplain area in sec. 33, T. 33 S., R. 11 W., to the southeast of the Harbaugh site. Another blowout occurred in the northeast quarter of sec. 20, T. 33 S., R. 11 W. to the northeast of the Harbaugh site. The possible effect of the waterflooding and other oil and gas activities on the ground-water quality as well as the blowouts are of concern to the KCC and landowners in the area.

The KCC requested that the Kansas Geological Survey (KGS) determine the source(s) of the salinity using the geochemical methods of Whittemore (1984, 1988). Water samples collected from monitoring, observation, and stock wells and brine from the Wild Boys blowout and oil and gas wells were sent to the KGS for analysis. The monitoring, observation, and stock wells are completed at the base of the alluvium of the Medicine Lodge River at an average depth of 35 ft. A sample collected from the river less than a mile downstream of the Harbaugh plume area during moderate flow, and water obtained from the surface pipe of a well in an old

waterflood unit were also sent. The specific conductance, chloride, sulfate, and bromide concentrations of the samples were measured and the salinity source identified based on constituent ratios and mixing curve graphs.

PROCEDURE

The samples received by the KGS 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 errors in the chloride and sulfate determinations are 3% and 4%, respectively. The estimated maximum error for the bromide measurements is 5% for the values >0.2 mg/L, and 10% for the concentrations <0.2 mg/L.

RESULTS AND DISCUSSION

The sample identification and chemical results for the waters analyzed are listed in Table 1. The freshest water is from the Medicine Lodge River; the total-dissolved solids (TDS) concentration is approximately 600 mg/L based on the relationship that the TDS in mg/L equals approximately 0.60-0.65 times the specific conductance in uS/cm or umho/cm. The ground water from the background well in the alluvial aquifer is also fresh based on the classification of freshwaters as containing less than 1,000 mg/L TDS; the TDS content is about 900 mg/L as estimated from the conductance. The chloride concentration for both of the waters is less than the 250 mg/L recommended for supplies of public drinking water, while the sulfate exceeds the recommended drinking level of 250 mg/L for sulfate in the alluvial aquifer well. Both of these waters contain appreciably more sulfate than chloride, suggesting the relatively greater importance of gypsum solution than halite solution in shallow subsurface bedrock adjacent to and underlying the alluvial aquifer. The rest of the ground-water wells yield samples that are saline, with chloride concentrations appreciably greater than sulfate.

The salinity sources were identified using constituent ratios and mixing curves on plots of bromide/chloride and sulfate/chloride versus chloride concentration. The bromide/chloride plot (Figure 1) contains 7 mixing curves, each of which is calculated from the conservative mixing of two end-member waters. Conservative mixing refers to the simple mixing of waters without chemical reactions, such as mineral precipitation or adsorption, that could alter the concentrations of one or both of the constituents. The two solid lines in Figure 1 represent the mixing of freshwater with natural Permian saltwater. The saltwater end member for the two lines is water from the Salt Plains Formation that flowed to the surface during the Wild Boys blowout. The low bromide/chloride ratio for the water is typical of salt-solution brines in Kansas (Whittemore, 1988). In comparison, oil brines in Kansas have substantially higher

Table 1. Chemical Data for Water Samples from the Area of the Harbaugh Contamination Site, Barber County.

KGS Lab No.	Description	Legal location	Sp.C. uS/cm	Cl mg/L	SO ₄ mg/L	Br mg/L	Br/Cl x 10 ⁴	SO ₄ /Cl
920271	Monitoring well 4	SE SE SW 20-33S-11W	19420	6470	569	19.4	29.99	0.0880
920272	Monitoring well 8	SE SW SE 20-33S-11W	13210	4220	583	11.6	27.46	0.1380
920273	Monitoring well 10	NW NW NE 29-33S-11W	11200	3340	743	7.30	21.84	0.2223
920274	Contaminated stock well	NE NW NE 29-33S-11W	15280	5080	488	14.8	29.11	0.0960
920275	Alluvial aquifer background well	NW SW NE 20-33S-11W	1395	158	269	0.143	9.05	1.703
ω 920276	Medicine Lodge River	W2 NE NW 28-33S-11W	940	77.7	197	0.065	8.37	2.535
920277	Wild Boys blowout observation well	C NE SW 28-33S-11W	5180	1394	379	2.01	14.42	0.2719
920278	Oil brine from disposal tank, Mississippian	NE NE SW 20-33S-11W	192000	124100	185	550	44.32	0.00149
920279	Wild Boys blowout, Salt Plains Fm	C NE SW 28-33W-11S	I.S.	156800	4500	30.0	1.91	0.02870
920644	Epicerter observation well, next to old blowout hole	NE NE SE 20-33S-11W	16710	5320	637	1.60	3.01	0.1197
920645	Surface pipe of well # 8 in old waterflood unit	NW NE NE 20-33S-11W	176000	131400	4830	34.5	2.63	0.03676

I.S. = insufficient sample to determine specific conductance

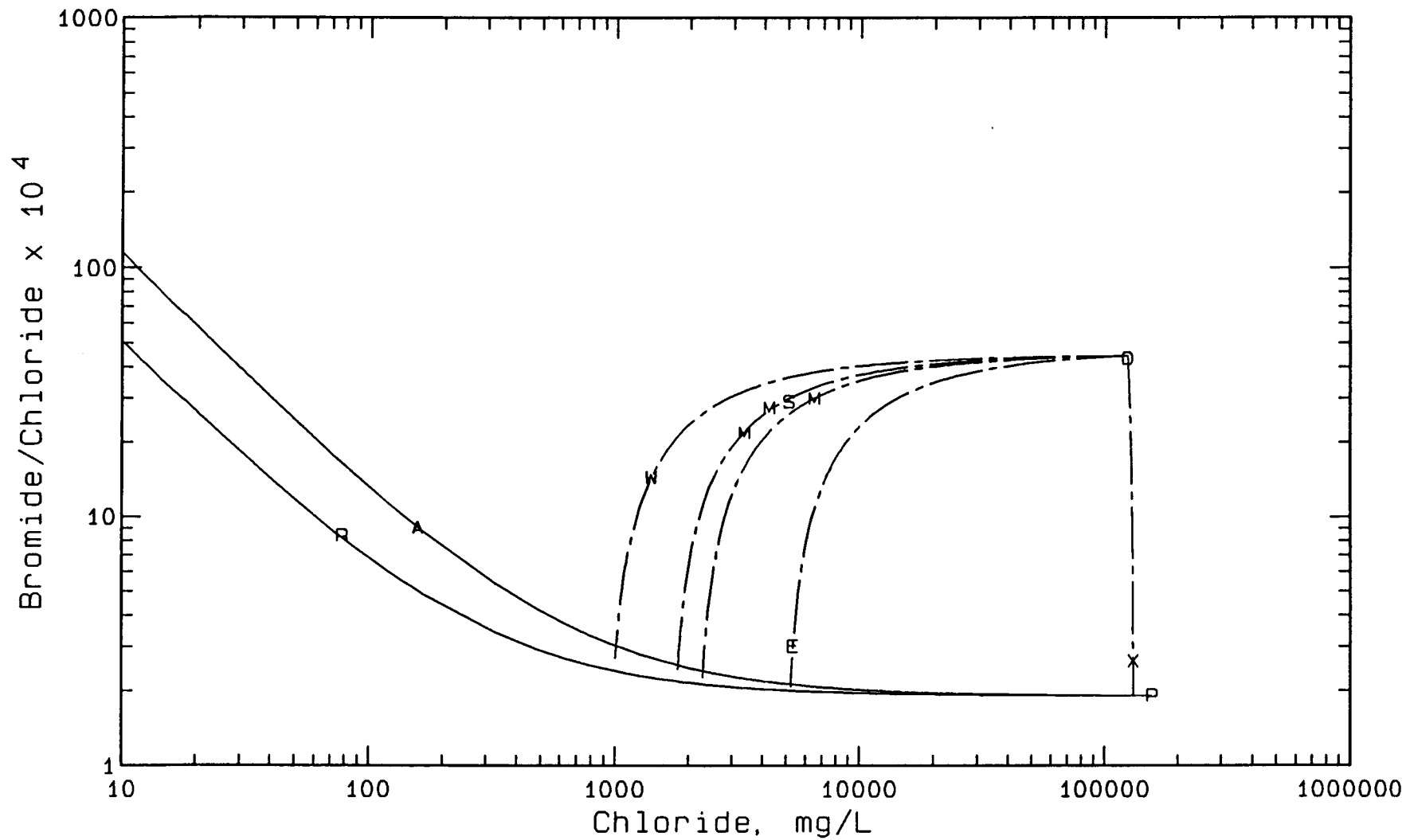


Figure 1. Bromide/Chloride Weight Ratio Versus Chloride Concentration for Samples in Table 1. Legend: A = alluvial background well; E = epicenter observation well; M = monitoring well; O = oil-field brine; P = Salt Plains Formation; R = Medicine Lodge River; S = stock well; W = Wild Boys blowout observation well; X = well #8 surface pipe.

bromide/chloride ratios, such as the brine sample from the Mississippian listed in Table 1. The bromide/chloride ratio at a given chloride is very sensitive to the presence of a small amount of oil brine mixed with halite-solution saltwater due to the much greater bromide concentration in oil brine than in halite-solution. Thus, if the Wild Boys blowout water contained a small amount of oil brine, the bromide/chloride ratio would be higher by a detectable value than observed. Based on chemical data for many samples from Permian strata in Stafford and Pratt counties to the north (Whittemore, 1993) the Wild Boys blowout water appears to contain less than 2% oil brine.

The two solid lines in Figure 1 were drawn from the Salt Plains Formation end point through the points for the alluvial background and Medicine Lodge River samples. Each of these lines was extrapolated, based on the mixing equation, to a chloride content of 10 mg/L. The resultant bromide/chloride ratios at 10 mg/L chloride are in the same range as the ratios for waters with about 10 mg/L chloride in the Great Bend Prairie aquifer and Permian strata underlying the unconsolidated aquifer in southern Pratt County (Whittemore, 1993). Likewise, the background well water and river sample in Figure 1 have bromide/chloride ratios in the same range as natural ground waters with similar chloride values as determined in the Whittemore (1993) study.

Saline ground waters with a source of salinity only from mixing with the natural Permian saltwater would plot along or very near to the solid mixing curves in Figure 1. The points for the monitoring, observation, and stock well waters lie at higher bromide/chloride ratios, indicating the presence of oil brine. The contribution of the oil brine to the chloride concentration of each water can be estimated assuming the oil brine composition to be that for the Mississippian brine sample in Table 1. The 5 dashed mixing curves in Figure 1 represent the mixing of the oil brine with saline water with a Permian chloride source. Each of these mixing curves starts at the oil brine, passes through a point for one or more of the saline ground waters, and stops at an end point midway between the two solid curves for the mixing of freshwaters and Permian saltwater. Thus, the lower chloride end point for the 5 dashed curves indicates the contribution of Permian saltwater (halite-solution) to the ground water.

The oil-brine contribution to the chloride concentration can be computed from the mixing equations, and is approximately equal to the difference between the total chloride content and the chloride from the Permian source. The resultant sources of chloride are listed in Table 2 along with the chloride mass percentage and volume percentage of oil brine in the mixture. The halite-solution source represents the chloride derived from waters in Permian strata.

In general, the higher the chloride concentration in the ground waters in the Harbaugh contamination plume (monitoring wells and stock well), the higher the percent contribution of the oil brine to the total chloride. The percent by volume of oil brine required to produce the

Table 2. Estimate of the Permian Saltwater and Oil-Brine Contributions to the Chloride Concentration of the Ground Water Samples from the Study Area. The oil brine percentage is computed as the oil brine chloride over the total chloride times 100. The estimated error in the oil brine percentage is calculated using the range in the freshwater bromide/chloride ratios and the combination of maximum analytical errors in the contaminated water, halite-solution end point, and oil brine that give the greatest error value.

Sample description	Chloride, mg/L			Oil brine Cl, %	Oil brine Cl, % error	Oil brine, % by volume
	Total	Halite Solution	Oil brine			
Alluvial background well	158	158	0	0		0
Monitoring well 4	6,470	2,200	4,270	66	12	3.44
Monitoring well 8	4,220	1,700	2,520	60	11	2.03
Monitoring well 10	3,340	1,790	1,550	46	8.9	1.25
Contaminated stock well	5,080	1,840	3,240	64	12	2.61
Wild Boys blowout obs. well	1,394	1,001	393	28	5.8	0.32
Epicenter observation well	5,320	5,200	120	2.2	1.2	0.10
Surface pipe, well #8	131,400	129,200	2,200	1.7	1.1	1.78

observed mixtures in the plume is small, only 1.25-3.44%. Thus, the main source of the water is natural while 46-64% of the chloride in the plume samples analyzed is from oil brine.

The Wild Boys blowout and epicenter observation wells are in the alluvium of the Medicine Lodge River valley, but at different locations outside of the Harbaugh plume. A relatively substantial amount of chloride is derived from oil brine in the sample from the Wild Boys observation well, although the volume percent is only 0.32%. The oil-brine contribution relative to halite dissolution is very small in the epicenter well water. The surface pipe sample from the well in the old waterflood well #8 has only a very small percentage of oil brine.

A graph of the sulfate/chloride weight ratio versus chloride concentration (Figure 2) for the water samples in the area can be used to indicate additional effects of oil brine contamination and to suggest a probable mechanism by which the Harbaugh plume originated. 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 Permian strata, while oil brines often have relatively much lower sulfate contents as a result of sulfate reduction to sulfide. The much greater sulfate concentration and sulfate/chloride ratio for the Salt Plains Formation than for the oil brine in Table 1 indicate this relationship. The water from the surface pipe of well #8 in the old waterflood unit is similar in composition, based on sulfate/chloride and bromide/chloride ratios, to that of the Wild Boys blowout water and probably is also from the Salt Plains Formation. Figure 2 includes points for all the waters in Table 1 along with 5 points for water samples from test wells in the Cedar Hills Sandstone underlying or adjacent to the alluvial valley of Elm Creek at Medicine Lodge.

The solid mixing line in Figure 2 was calculated using an end point with the same chloride as the Medicine Lodge River and a sulfate/chloride ratio that would produce a curve passing between the river and alluvial background well points when mixed with the Salt Plains Formation saltwater from the Wild Boys blowout. The curve with different length dashes is for conservative mixing of the same freshwater end point with the Mississippian oil brine. Figure 2 shows that the points for the saline ground waters in the Harbaugh plume area do not fall between the two curves but at higher sulfate/chloride ratios than either of the curves. The reason for this is saturation of the waters with respect to gypsum, i.e., the high sulfate (and calcium) concentrations in the saline waters is limited by the solubility of gypsum. The limited sulfate concentration relative to chloride in the high salinity waters derived from Permian evaporites results in a lower sulfate/chloride ratio than more dilute ground waters from Permian strata.

The shallow Cedar Hills ground waters at Medicine Lodge (points C on Figure 2, data from Williams and Bayne, 1946) help illustrate the gypsum solubility control. The curve with long equal-length dashes is a conservative mixing line between the freshwater end point and the 3 Cedar Hills waters with higher chloride. The extrapolation of this mixing curve to the chloride

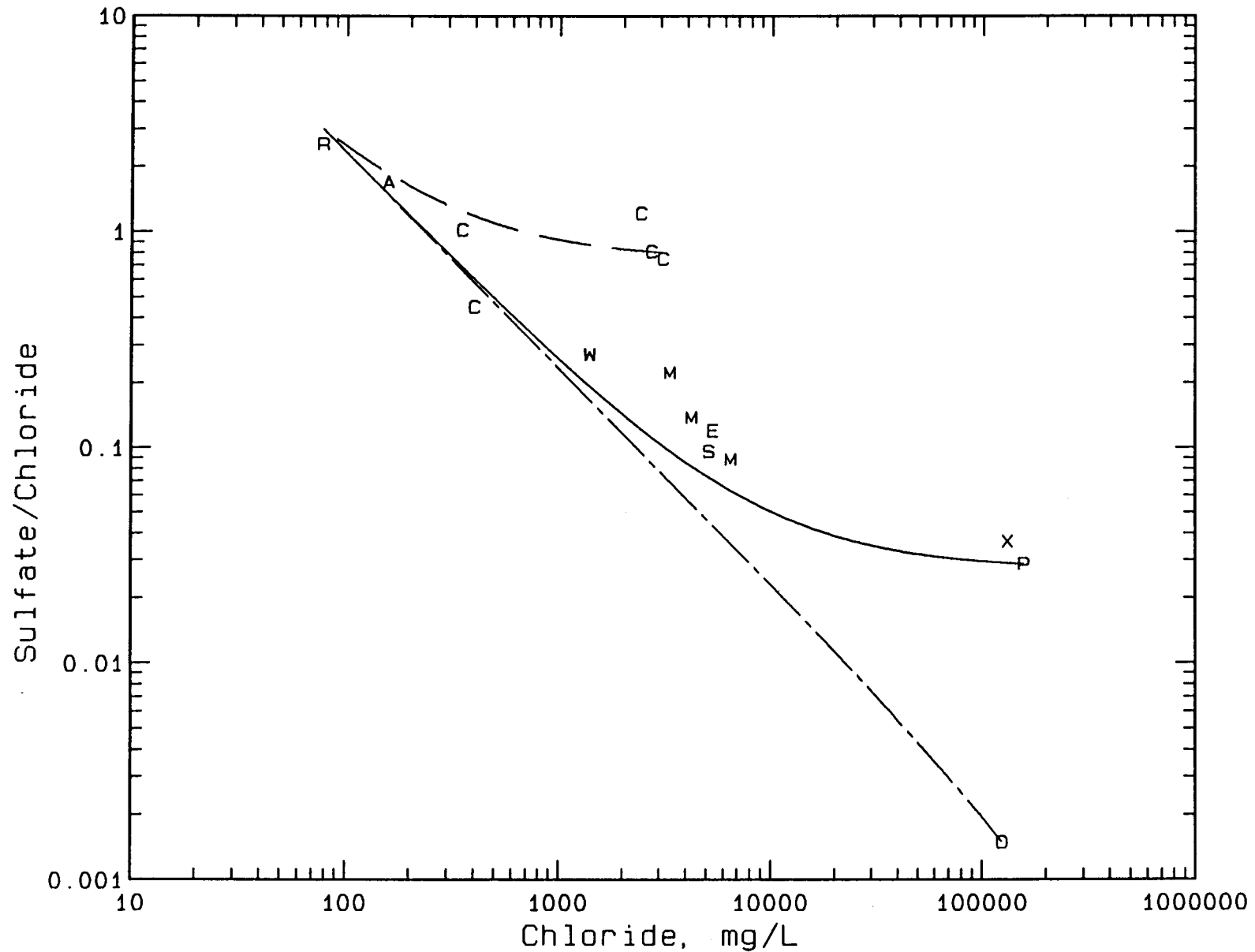


Figure 2. Sulfate/Chloride Weight Ratio Versus Chloride Concentration for Samples in Table 1 and from the Cedar Hills Sandstone of Elm Creek Valley at Medicine Lodge. Legend: A = alluvial background well; C = Cedar Hills Sandstone at Medicine Lodge; E = epicenter observation well; M = monitoring well; O = oil-field brine; P = Salt Plains Formation; R = Medicine Lodge River; S = stock well; W = Wild Boys blowout observation well; X = well #8 surface pipe.

of the Salt Plains Formation point would give a sulfate concentration of about 100,000 mg/L. However, the solubility of gypsum limits the amount of sulfate that can be present in solution in the saltwater to several thousand mg/L. The Salt Plains Formation water and the Cedar Hills samples with chloride above 2,000 mg/L plotted on Figure 2 are probably all saturated with respect to gypsum, even though the sulfate contents of the Cedar Hills waters are in the 2,200-2,950 mg/L range in comparison to the 4,500 mg/L in the Salt Plains water. As the concentration of the major dissolved constituents (except for calcium, which is also limited by gypsum solubility) in waters increases from low to high salinity, the amount of gypsum that can be dissolved generally increases, but at a much lower rate than the increase in the chloride.

Mixing of either the oil brine or the Salt Plains saltwater with less saline water (chloride less than 30,000 mg/L) that is saturated with respect to gypsum would result in a solution undersaturated with (a potential to dissolve more of) gypsum. If there were no gypsum present in the strata in which the mixing occurred, then the conservative mixing curves could be used. However, the presence of gypsum in the Permian in the area can result in the undersaturated mixtures dissolving more gypsum, thereby increasing sulfate contents. This could explain the sulfate/chloride ratios in the saline ground waters in the Harbaugh area that are higher than the conservative mixing curves with either the Salt Plains saltwater or oil brine. Alternatively, the sulfate concentrations in the alluvial aquifer at the observation, monitoring, and stock well depths could be naturally higher than in the alluvial background well.

If the water quality for the alluvial background well is assumed as natural for the alluvial aquifer in the area, then the greater chloride concentrations in the contamination plume derived from both the halite-solution and oil-brine sources could be expected to originate from past anthropogenic activities. For example, an artificial penetration in the subsurface could exist such as an old borehole or blowout hole. The presence of additional halite-solution water with additional sulfate than for conservative mixing suggests 3 possibilities for the entrance of Permian water: (1) saline water is entering from a level in the Permian that is shallower, and has a lower chloride and higher sulfate/chloride ratio, than for the Wild Boys blowout water, (2) saltwater is flowing upwards from about the same level as the Wild Boys blowout water and dissolving more gypsum in shallower Permian strata as it mixes with less saline water, (3) a combination of the two previous mechanisms, but without the requirement that the deeper Salt Plains water dissolve more gypsum during its upward flow. The presence of oil brine in the contamination plume could be derived either from the surface or the subsurface and fit the observed chemistry along with one of the 3 explanations for additional halite-solution chloride. Points for the monitoring, observation, and stock well waters on Figure 2 could fit a curve that would represent the mixing of slightly saline water with a composition along the uppermost dashed mixing curve with saltwater that is a mixture of the Salt Plains saltwater and oil brine.

The end point for the slightly saline water along the uppermost dashed curve would represent the mixture of alluvial water and shallow Permian water.

The assumption of water from the alluvial background well for background water quality is especially important to whether mechanisms 1) and 2) for Permian water entrance are viable. The even lower chloride in the Medicine Lodge River sample appears to support the alluvial background well water as appropriate for the background. If the chloride in the natural alluvial water were appreciably higher than observed, ground-water discharge to the river might be expected to produce a higher chloride in the river water than measured. However, the chloride and sulfate concentrations generally increase with depth in the alluvium of Elm Creek next to Medicine Lodge where the ground waters do not appear to be substantially affected by oil brine (Williams and Bayne, 1946). The maximum chloride and sulfate concentration in the alluvium of that area were 835 and 708 mg/L, respectively, based on their study. Therefore, the depth of the wells in the alluvium relative to the depth to bedrock in the alluvial channel of the Harbaugh area should be considered. If the sulfate values observed in the monitoring, observation, and stock well waters are natural for the alluvium, then the mechanisms requiring additional sulfate in upward flowing Permian waters would not be necessary. Higher natural chloride in the alluvial waters than in the background well water would also decrease the amount of Permian water required to flow upwards through an artificial penetration. However, the halite-solution contribution to the ground waters (Table 2) appears to be too large, based on existing information, to be naturally present in the alluvial aquifer.

CONCLUSIONS

The sources of saline ground water in the Harbaugh contamination plume and nearby observation wells in alluvium of the Medicine Lodge River are mixtures of halite-solution and oil brine. The chloride contribution from the halite-solution (Permian) source appears to be too high to be naturally present in the alluvial aquifer, suggesting that upward flow of saltwater from the underlying Permian bedrock may have entered through a borehole or blowout hole. Oil brine contributes approximately 390-4,190 mg/L chloride in the saline ground waters in the alluvium of the Harbaugh plume, representing approximately 28-64% of the total chloride concentration. The water from the epicenter observation well to the east-northeast of the plume contains only about 100 mg/L chloride from oil brine, representing two percent of the total chloride. The oil brine source in the Harbaugh area could either be derived from the surface or the subsurface and still be consistent with the chemistry observed for the saline waters.

ACKNOWLEDGMENTS

The report was conducted in cooperation with Case Morris of Conservation Division District 1 of the Kansas Corporation Commission in Dodge City. Lawrence Hathaway, Chief of the Analytical Services Section of the Kansas Geological Survey, determined the specific conductance, chloride, and sulfate concentrations in the water samples.

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Addendum to
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December, 1993

ADDENDUM

The original report found that the sources of saline ground water in the Harbaugh contamination plume and nearby observation wells in alluvium of the Medicine Lodge River are mixtures of halite-dissolution and oil brine. The chloride contribution from the halite-dissolution (Permian) source appears to be too high to be naturally present in the alluvial aquifer, suggesting that upward flow of saltwater from the underlying Permian bedrock may have entered through a borehole or blowout hole. Oil brine contributes approximately 390-4,200 mg/L chloride in the saline ground waters in the alluvium of the Harbaugh plume, representing 28-65% of the total chloride concentration.

During continued investigation of the saltwater plume, the Kansas Corporation Commission (KCC) discovered saline water with a chloride concentration of 10,000 mg/L in monitor well 18 to the northwest of the area where the saltwater plume appears to originate. The chloride concentration is the highest observed in the alluvial aquifer of the plume area. Monitor well 18 lies just to the south of the Medicine Lodge River and north of the plugged oil or gas well near monitor well 11. The KCC collected a water sample and sent it to the Kansas Geological Survey for geochemical identification of the saltwater source.

The results for the sample are added to Table 1 in the original report and included with this addendum. The chloride concentration determined by the KGS (9,980 mg/L) is the same (within analytical error) as that determined by the KCC. The bromide/chloride ratio is very low (0.000203) and is nearly the same as for the water sample collected from the Wild Boys blowout. The low bromide/chloride ratio at the high chloride content indicates that no detectable oil brine contributes to the salinity of the ground water at monitor well 18. In contrast, water from monitor well 4 about 300 ft to the south-southeast of monitor well 18 contained a total chloride concentration of 6,470 mg/L of which 65% was estimated to be from oil brine and 35% from a Permian halite-dissolution source. The substantial change in the salinity sources comprising water from monitor well 4 in comparison with that from well 18 suggests that the origin of the oil brine is to the south of well 18, to the northwest of well 4, and near monitor well 11.

The chloride concentration distribution in the vicinity of monitor well 18 suggests that a local source of Permian saltwater such as a flowing borehole is the primary origin of halite-dissolution salinity in the alluvium. The chloride concentration determined by the KCC for monitor well 21 to the west of monitor well 18 and about the same distance south of the Medicine Lodge River was 3,500 mg/L. Monitor wells 23 and 5 located to the north of monitor wells 21 and 18, respectively, and on the north side of the Medicine Lodge River both yielded water with a chloride concentration of 400 mg/L. If the source were primarily natural discharge of Permian saltwater to the Medicine Lodge River, the chloride values for waters from monitor wells 5, 18, 21, and 23 should be more similar than observed.

Table 1. Chemical Data for Water Samples from the Area of the Harbaugh Contamination Site, Barber County.

KGS Lab No.	Description	Legal location	Sp.C. uS/cm	Cl mg/L	SO ₄ mg/L	Br mg/L	Br/Cl x 10 ⁴	SO ₄ /Cl
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920645	Surface pipe of well # 8 in old waterflood unit	NW NE NE 20-33S-11W	176000	131400	4830	34.3	2.61	0.03676
930553	Monitor well 18	SE SE SW 20-33S-11W		9980	2630	2.03	2.03	0.2636

I.S. = insufficient sample to determine specific conductance