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GEOCHEMICAL IDENTIFICATION OF THE SOURCE OF SALINITY IN GROUND WATERS EAST OF HILL CITY, GRAHAM COUNTY, KANSAS

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A report for the
Kansas Department of Health and Environment

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INTRODUCTION

The Kansas Department of Health and Environment (KDHE) has been investigating an area of saline ground water affecting several wells about one-half mile east of the city limits of Hill City, Graham County. The area of the contamination primarily comprises the SE 1/4 of the SE 1/4 of sec. 12, T.8S, R.23W, the S/2 of the SW 1/4 of sec. 7, T.8S, R.22W, and the N/2 of the NW 1/4 of sec. 18, T.8S, R.22W. The wells include domestic and garden wells and irrigation wells used for a small orchard. Ground water in the area of the contamination is obtained from sands in Pleistocene terrace deposits.

Movement of water in the terrace deposits is affected by the regional ground-water flow and the amount of pumping, especially when the irrigation wells are operating. Movement and the shape of the saline water plume will also be affected by the permeability of the terrace deposits, such as faster movement in the channel sands than in the fine sands, silts and and clays of the alluvium.

The suspected origin of the saltwater causing the contamination is from an industrial operation in the SE 1/4 of the SE 1/4 of sec. 12, T.8S, R.23W involving acids used in petroleum production. The KDHE reported that in 1982 a metal tank with an 8000 gallon capacity used to store hydrochloric acid (HCl) had leaked. Four, 750 gallon tanks containing a surfactant, corrosion inhibitor, acetic acid, and "mud acid" (hydrofluoric acid - HF) were also present. A pit located near the tanks has been used as an emergency overflow and for the neutralization and disposal of water from the washing of acid tank trucks. Another pit located west of the tanks was used by the companies who have operated at the site.

The KDHE requested that the source(s) of the contamination be geochemically identified. In addition to the saline water generated by the acid tank leak and acid truck washes, a question existed as to whether some oil-field brines might have been disposed in one of the pits in the past. The cause was not believed to be natural because saline waters are not known to occur naturally in the alluvial aquifers in the general area of contamination as indicated by recent and past analyses of ground water.

PROCEDURE

The source of salinity was identified by the mixing-curve methods of Whittemore (1984, 1988). Well-water samples were collected from both within and just outside of the contamination plume and sent to the Kansas Geological Survey (KGS) by the KDHE. Samples containing sediment were filtered through 0.45 um membrane filter paper before analysis. A sample of concentrated HCl used in the petroleum industry in Kansas was obtained from a petroleum service company in Hays. The HCl was diluted and then neutralized using reagent grade NaOH before analysis. Concentrations of chloride, bromide, and inorganic iodine were determined in the samples at the KGS by automated methods on a Technicon Auto-Analyzer. A modified version of the phenol red method of Basel et al. (1982) with oxone in place of chloramine-T was used for bromide. Inorganic iodine was measured by a catalytic method based on the reduction of ceric ion by arsenious acid and similar to that used by the U.S. Geological Survey (Fishman and Friedman, 1985). Splits of the samples were also analyzed at the KDHE laboratories for major and selected minor constituent concentrations.

RESULTS AND DISCUSSION

Analytical data from the KDHE and the KGS used in the salinity identification are listed in Tables 1 and 2. Table 3 lists 6 analyses of well waters from within a two-mile radius of the area surrounding the contamination plume and one (Hocker well) about 5 miles to the southeast. Three of the wells in Table 3 are in alluvial deposits, one is from the Niobrara Chalk, one from the Codell Sandstone Member of the Carlile Shale that underlies the Niobrara, and one from the upper part of the Dakota Formation. Two samples were from water-supply wells serving Hill City. All of the samples in and next to the contamination plume (Tables 1 and 2) are from alluvial terrace deposits.

The chemical types of the uncontaminated ground waters represented by the samples with chloride concentrations less than 100 mg/L in Tables 1 and 3 are Ca-HCO_3 to Ca-SO_4. The chloride and sulfate concentrations for all 21 samples in a report on the geology and ground-water resources for Graham County (Prescott, 1955) ranged from 5 to 75 mg/L and 3.7 to 335 mg/L, respectively. The highest concentrations were in ground waters from the Niobrara Chalk which often contains Ca-SO_4 type water and underlies the alluvium in the Hill City area. Water in the Niobrara Chalk is probably the source of the higher concentrations of sulfate in some of the alluvial waters, but is not expected as the source of the high chloride contents of the contamination plume based on the available data.

The high nitrate level in the water from the Niobrara Chalk listed in Table 3 is probably from local contamination from animal or human waste. The waste contamination could have contributed a small amount of chloride to the total 71 mg/L in the ground water at that site. Many of the well waters in

Table 1. Constituent Concentrations in Samples from Wells in Terrace Deposits in the Study Area. All constituent concentrations were determined by the Kansas Department of Health and Environment.

Well name	Well type	Location	Date collected	pH	Ca mg/L	Mg mg/L	Na mg/L	Total alk. mg/L $CaCO_3$	SO4 mg/L	Cl mg/L	NO_3 mg/L as N	F mg/L
Frank Ganzel	Garden	8S-23W-12DDDC	08-08-88		196	21.0	54	260	211	122	10.5	0.3
Royal Acid north	Monitor	8S-23W-12DDDC	01-26-87		160	14.1	29	268	98	71	7.80	0.3
"	"	"	04-29-87		162	13.5	42	261	90	97	10.5	0.2
Royal Acid south	Monitor	8S-23W-12DDD	04-29-87		206	17.8	44	288	147	120	10.0	0.2
Royal Acid KDHE	Monitor	8S-23W-12DDD	11-13-87[a]		312	27.8	108	242	141	506	1.67	3.0
"	"	"	01-15-88[b]		279	15.8	56	202	244	279	2.22	2.2
"	"	"	01-15-88[c]		284	14.0	56	245	228	269	3.09	2.1
"	"	"	07-07-88		174	10.0	24	242	160	64	5.50	2.5
Vanns MiniMart	Store supply	8S-23W-13AAA	08-08-88		106	9.0	13	256	30	28	3.46	0.3
Eugene Johnson	Domestic/house	8S-22W-07CCC	04-14-86		382	36.3	80	267	54	640	7.60	0.2
"	"	"	04-29-87	7.1	564	54.1	117			752		
"	"	"	01-15-88		599	57.7	140	346	42	1170	4.28	0.2
"	"	"	01-30-88		660	61.7	170	361	38	1340	4.25	0.2
"	"	"	07-07-88		357	34.0	126	279	84	642	6.50	0.2
E. Johnson east #2	Irrigation	8S-22W-07CCC	04-29-87	7.2	178	20.3	80			201		
"	"	"	07-07-88		368	50.7	141	298	74	726	4.73	0.3
E. Johnson windmill	Stock	8S-22W-07CCC	04-14-86		167	14.6	37	247	62	156	6.70	0.3
"	"	"	04-29-87		212	18.6	40			232		
E. Johnson test	Test	8S-22W-07CCC	04-29-87	7.0	212	20.9	96			700		
Lynn Van Loenen	Domestic	8S-22W-07CCD	01-26-88		154	17.5	84	266	125	143	12.4	0.3
"	"	"	07-07-88		201	23.4	110	245	114	298	8.95	0.3
Pennington	Domestic	8S-22W-18BBB	08-01-88		194	18.6	57	292	110	169	16.4	0.2
Stan Lovelady	Domestic	8S-22W-18BBB	01-26-88		200	17.9	55	304	101	170	15.1	0.3
"	"	"	08-11-88		162	14.4	49	279	80	126	13.6	0.3
Miller	Domestic/house	8S-22W-18BBA	01-26-88		240	23.6	66	279	48	328	3.58	0.2
"	"	"	07-07-88		240	23.3	64	275	58	342	4.59	0.2
Williams	Domestic	8S-22W-18BBA	01-26-88		182	16.5	52	295	99	150	13.0	0.3
Richard Ganzel	Domestic?	8S-22W-18BBA	08-08-88		166	15.9	53	296	66	142	11.0	0.3

[a] Sample bailed from top of water column
[b] Sampled after pumping 100 gallons
[c] Sampled after pumping 300 gallons

Table 2. Constituent Concentration Data for Geochemical Identification of Samples from the Study Area. All values were determined by the Kansas Geological Survey.

Well name	Well type	Location	Date collected	Cl mg/L	Br mg/L	I ug/L	Br/Cl x 10^4	I/Cl x 10^6
Frank Ganzel	Garden	8S-23W-12DDDC	08-08-88	123	0.41		33	
Royal Acid KDHE monitor	Monitor	8S-23W-12DDD	07-07-88	64	0.19	61	30	950
Vanns MiniMart	Store supply	8S-23W-13AAA	08-08-88	28	0.08		29	
Eugene Johnson	Domestic/house	8S-22W-07CCC	06-07-88	610	0.34		5.6	
"	"	"	07-07-88	643	0.33	15	5.1	23
Eugene Johnson west		8S-22W-07CCC	06-07-88	96	0.12		12.5	
Eugene Johnson east #2	Irrigation	8S-22W-07CCC	07-07-88	737	0.35	16	4.7	22
Lynn Van Loenen	Domestic	8S-22W-07CCD	07-07-88	304	0.21	15	6.9	48
Pennington	Domestic	8S-22W-18BBB	08-01-88	169	0.30		17.8	
Stan Lovelady	Domestic	8S-22W-18BBB	08-01-88	127	0.22		17.3	
Miller	Domestic/house	8S-22W-18BBA	07-07-88	331	0.26	30	7.9	90
Richard Ganzel	Domestic?	8S-22W-18BBA	08-08-88	142	0.21		14.8	
Concentrated HCl from Halliburton, supplied by Vulcan			07-08-88	400000	50	850	1.2	2.1

Table 3. Constituent Concentrations in Samples from Wells Surrounding the Study Area in Different Formations (from Prescott, 1955 and Kansas Geological Survey). The first four analyses are from Prescott (1955), the fifth from the U.S. Geological Survey (1982), and the last two from Macfarlane et al. (1988).

Well name	Well type	Location	Geologic source	Date collected	pH	Ca mg/L	Mg mg/L	Na mg/L	Total alk. mg/L $CaCO_3$	SO4 mg/L	Cl mg/L	NO_3 mg/L as N	F mg/L
L. and F. Zohner	Domestic	8S-22W-08BCC	Crete Mbr Sanborn Fm	05-29-52		85	9.8	16	231	30	14	1.31	0.4
C.E. Wainwright	Stock	8S-23W-02CDD	Niobrara Formation	11-24-52		155	18.0	74	268	91	71	44.0	0.4
C.E. McFadden	Stock	8S-23W-09CCC	Terrace deposits	11-24-52		126	21.0	27	236	191	16	0.25	0.6
City of Hill City	Public supply	8S-23W-13	Terrace deposits	04-16-52		112	19.0	22	242	123	21	1.31	0.6
"	"	"	"	08-06-81	7.2	180	28.0	56	230	340	77	0.20	0.6
C. Hocker	Domestic	8S-22W-34CCD	Codell Ss Mbr Carlile Shale	06-15-87	6.9	189	26.0	102	319	247	118	3.16	0.6
Hill City, U.D.	Observation	8S-23W-02DCB	Upper Dakota Fm	07-08-88	8.2	3.3	0.9	708	625	244	343	<1	7.9

the study area also have nitrate levels exceeding the drinking-water standard of 10 mg/L NO_3-N. However, the highest is 16.4 mg/L NO_3-N in comparison with the 44 mg/L for the Niobrara Chalk well. The maximum contribution of chloride from the animal or human waste source in the study area is probably less than a few tens of mg/L. The plume waters with higher chloride concentrations generally have lower nitrate contents, further ruling out an animal or human waste source as being an appreciable contribution to the total chloride.

The water from the Codell Sandstone Member is a Ca-HCO_3,SO_4 type, while the water from the upper Dakota Formation is a Na-HCO_3,Cl type. The chloride concentrations for the two samples are 118 and 343 mg/L for the Codell and the upper Dakota, respectively, values much lower than the highest chloride in the contamination plume.

The background chloride concentration in the terrace deposits appears to be under 100 mg/L. Waters with chloride contents of 100-200 mg/L around the edge of the contaminated area are generally of Ca-HCO_3 type, while all waters with chloride concentrations above 200 mg/L are of Ca-Cl chemical type. Chloride concentrations range up to 1340 mg/L, while sulfate contents vary from 38 to 147 mg/L in the contamination area and show no clear correlation with chloride levels. Moreover, some of the lowest sulfate values are for the highest chloride concentrations. The lower sulfate/chloride ratios of the more contaminated waters in contrast to the higher ratios for the bedrock waters indicates that the of upconing of natural mineralized waters from the underlying Niobrara Chalk or other bedrock as a possible origin for the high chloride is very unlikely.

The type of contamination source was geochemically identified using mixing curves of bromide/chloride and sodium/chloride weight ratios versus chloride concentration (Figures 1 and 2). The individual curves in Figure 1 were calculated using end points that bracket the range in composition of freshwaters and contaminated waters in the study area, and a sample of HCl used in the petroleum industry in Kansas. The area where points for typical oil-field brines from central to west-central Kansas would fall is also shown on Figure 1. The geochemical identification procedure involves the location of points for the contaminated waters of concern relative to different mixing zones.

The two outer boundaries in Figure 1 enclose all of the waters in the study area, forming a zone of mixing between freshwaters and an HCl source. The width of the zone about the HCl point represents an estimated total of possible variance in the composition of the acid and the analytical error. The dashed line in the center of the mixing zone represents the mixing between the points for the KDHE monitoring well water collected on July 7, 1988, and the HCl sample. Except for the F. Ganzel sample, all of the ground waters with >100 mg/L chloride fit the mixing of freshwater with HCl. The F. Ganzel well lies to the west in the upgradient direction of ground-water flow from the acid pit.

A graph of the I/Cl ratio versus chloride concentration for data in Table 2 would appear similar to Figure 1. The I/Cl ratio decreases with increasing chloride concentration in the contaminated waters within a mixing zone with the HCl as the saltwater end point. The I/Cl ratios of typical oil-field brines in Kansas are generally >40 times that of the HCl sample.

Although Figure 1 indicates that the contamination source is definitely not oil-field brine, it cannot be used to differentiate between the HCl and an anthropogenic source of salt contamination such as road salt. Figure 2 shows

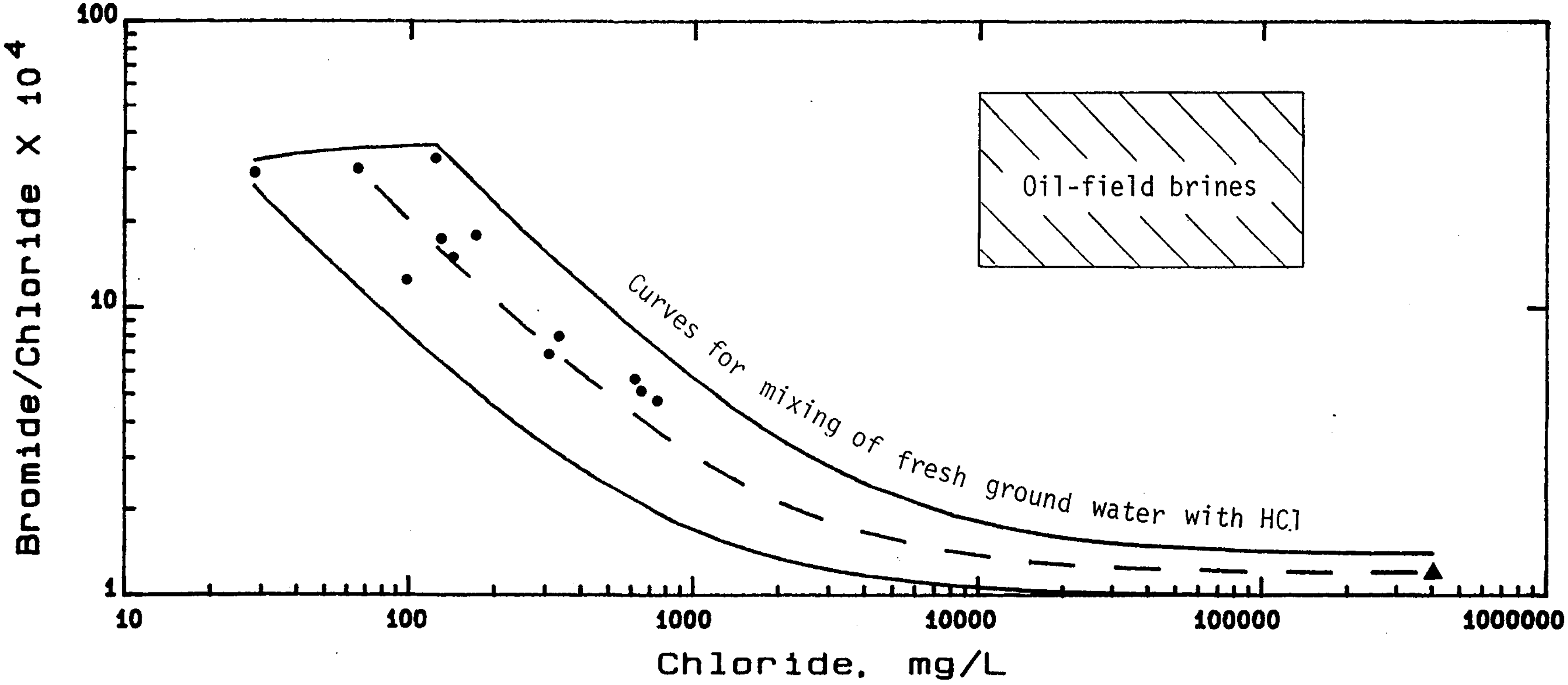

Figure 1. Mixing Curves for the Br/Cl Weight Ratio versus Chloride Concentration for Ground Waters in the Study Area (●) and Commercial Grade of Hydrochloric Acid (▲). See Table 2 for data. The hatched box labeled "Oil-field brines" represents the range in chemical character of most Kansas oil-field brines.

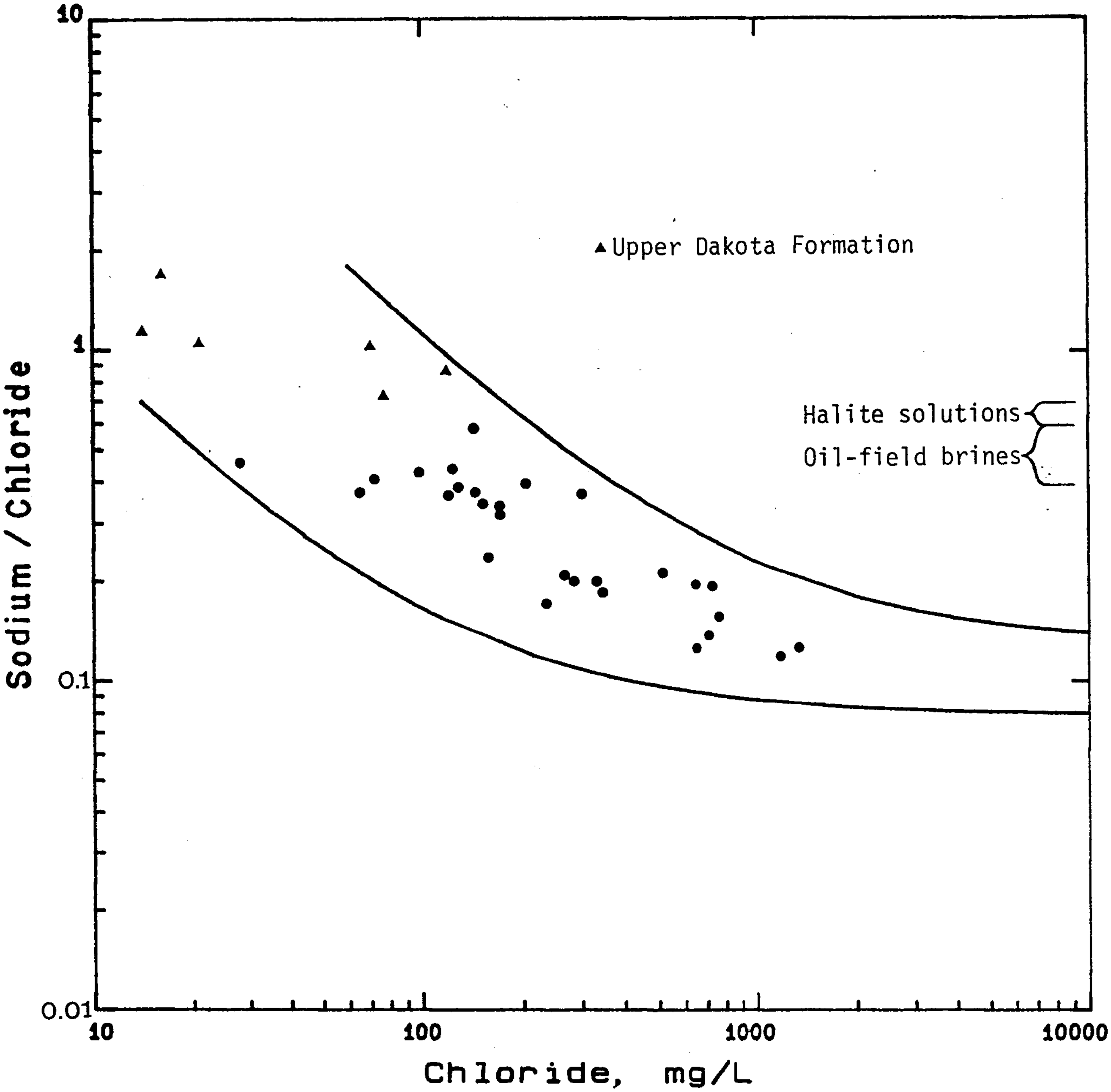

Figure 2. Mixing Curves for the Na/Cl Weight Ratio versus Chloride Concentration for Ground Waters within the Study Area (●), Table 1, and Surrounding the Study Area (▲), Table 3. The brackets on the right of the diagram represent the usual ranges in the Na/Cl ratio for halite-solution brines and oil-field brines in Kansas.

that the Na/Cl ratio of the waters of the study area decreases with increasing chloride concentration. The end points for computing the two curves were selected such that the resulting mixing zone enclosed all of the ground waters listed in Tables 1 and 3 except for the Dakota aquifer. The extrapolation of the mixing curves to higher chloride values suggests that the Na/Cl weight ratio of the contamination source is near 0.1. This value is much lower than the 0.65 obtained from the solution of halite (NaCl), the primary component of road salt. The value fits the leaching of calcium, magnesium, and sodium from soils and sediments by HCl, followed by the exchange of some of the calcium and magnesium for sodium on clays. If the salt origin were other than the hydrochloric acid, the source would have to have been primarily $CaCl_2$ in character. There is no evidence or record of a large amount of this chemical having been present in sufficient quantities at or near the site to have been able to cause the contamination.

The samples from the KDHE monitoring well have relatively high fluoride concentrations in comparison with values for the other ground waters in the contamination area. The accompanying calcium concentration is higher than could be present if the ground water were in equilibrium with fluorite. The results suggest that a small amount of HF has also infiltrated from the acid pits and produced a solution supersaturated with respect to fluorite. Alternatively, the HCl could have leached fluoride containing minerals in the soils and sediments. The concentrations are too low, however, to cause substantial increases in fluoride in ground waters at the distances of the contaminated water supplies from the acid pits.

The chemistry of the contaminated water is somewhat similar to ground water in a Pleistocene outwash aquifer in Kentucky polluted by HCl from a break in an industrial waste-discharge line. The polluted Kentucky water was of Ca,Mg-Cl chemical type, had low Na/Cl and SO_4/Cl ratios, and high fluoride concentrations (Grubb, 1970). The pH of the contaminated water was low (2.4-6.6) in comparison to the near neutral pH of the Hill City ground waters. Ratios of Ca/Mg are higher in the contaminated Hill City waters than in the polluted Kentucky waters. Solution of carbonate minerals in the soils and aquifer sediments in the Hill City area and lime (CaO) and/or limestone fragments placed in the acid pits apparently have neutralized the HCl that infiltrated to the ground water. The high Ca/Mg ratio supports the dissolution of mainly calcium compounds. Magnesium concentrations also directly correlate with chloride values, but reach levels only about an order of magnitude lower than the calcium. The total alkalinity, nearly all of which is present as bicarbonate, does not increase very much with increasing chloride concentration due to the control of carbonate equilibria (calcite solubility/precipitation relationships) in the system.

CONCLUSIONS

The source of the high chloride concentrations in the contaminated ground water in the alluvial aquifer to the east of the Royal Acid pits is most probably the infiltration of hydrochloric acid from the surface. The acid was neutralized by dissolving carbonate minerals in the soils and sediments and lime in the pits to produce a Ca-Cl type water with a low Na/Cl ratio. Mixing curves based on Br/Cl ratios fit the acid source and indicate that no significant amounts of oil-field brine are present in the contaminated waters. The mixing trend of decreasing Na/Cl ratios with increasing chloride contents points to a Na/Cl value that is much too low to be from common road salt composed primarily of halite (NaCl) as a source.

Natural mineralized waters in the alluvial sediments and in the bedrock from the Niobrara and Carlile formations in the area are of Ca-SO_4 type and have chloride concentrations <120 mg/L. Mineralized water in the upper Dakota Formation has too low a chloride content and Na/Cl and SO_4/Cl ratios too high to be the salinity source. The composition of the natural waters in comparison with the relatively low sulfate concentrations and Na/Cl ratios in the most contaminated portion of the plume indicate that a natural source of contamination is highly unlikely.

Although many of the well waters have nitrate levels exceeding the drinking water standard by a few mg/L, the ground waters with the higher chloride contents tend to have lower nitrate concentrations. Thus, animal or human waste does not appear to have contributed appreciably to the high chloride portions of the contamination plume.

ACKNOWLEDGMENTS

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