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A Regional Study of Ground-Water Quality in Barry County, Michigan

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A REGIONAL STUDY OF GROUND-WATER QUALITY IN BARRY COUNTY, MICHIGAN

by

Margene K. Brewer

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A REGIONAL STUDY OF GROUND-WATER QUALITY IN BARRY COUNTY, MICHIGAN

Margene K. Brewer, M.S.

Western Michigan University, 1991

A regional study of ground-water quality in Barry County, Michigan was conducted using a computerized database from the Science for Citizens Center at Western Michigan University in Kalamazoo, Michigan. The database, initiated by the Michigan Groundwater Survey, consists of residential well logs and chemical analyses of samples collected from residential wells by the Barry County Health Department. Qualitative and statistical analyses of the data indicate that the glacial drift aquifer is recharging the bedrock aquifer throughout most of the county. Ground-water quality appears to be controlled mainly by the open-system dissolution of carbonate minerals. The water chemistry is also influenced by physical factors such as flow path and landform. Elevated levels of chloride and nitrate in samples collected from approximately 25% of the glacial drift wells suggest that the drift aquifer is being degraded, possibly as a result of land use and waste management practices.

ACKNOWLEDGEMENTS

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Margene K. Brewer

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INTRODUCTION

Growing awareness of human impact on ground-water quality and increasing demand for ground-water resources in the 1980s has resulted in a need for background studies of aquifers in Michigan on a county by county basis. To meet this need, the Southwest Michigan Ground Water Survey and Monitoring Program was initiated for Barry County in 1985 (Simms, 1988). The objective of the Survey was to determine the state of the ground water in the member counties through mapping aquifers and developing a background water quality database (Simms, 1988). The well logs and chemical analyses collected by the Survey and Barry County Health Department personnel, were used as the database for a regional study of ground-water quality in the county's aquifers.

Since Barry County is largely a rural and agricultural area, study of its ground-water flow systems and ground-water chemistry is needed to provide information on the existing and potential impacts of farming and waste management practices on the potable water supply in the drift and bedrock aquifers. This background information can then be used in developing productive and protective land and waste management practices in Barry County.

This paper presents the results of a regional ground-water quality study of the aquifers in Barry County, Michigan. The three objectives for the study were: (a) to determine the flow relationships between the aquifers, (b) to define the present state of ground-water quality, and (c) to examine possible controls on the ground-water chemistry.

Physiography

Barry County is located in the southwestern portion of the southern peninsula of Michigan and covers an area of 576 square miles (Figure 1). About 3.5% of this area is covered by a total of 167 lakes and wetlands. The county's most obvious topographic feature is the Thornapple River valley which trends east to west and turns north in the northwest corner of the county (Figure 2). The Thornapple River is the trunk drainage for most smaller streams in Barry County. The Thornapple, Little Thornapple, and Coldwater rivers and their associated streams are part of the Grand River basin. Gun Lake and the minor creeks in the four southern townships are part of the Kalamazoo River basin (Figure 2).

The remainder of the county's topography can be described as alternating ridges and plains. Two well-defined ridges, trending northeast/southwest are located in the western portion of the county. These two ridges are separated by a narrow gravel plain. Though little relief

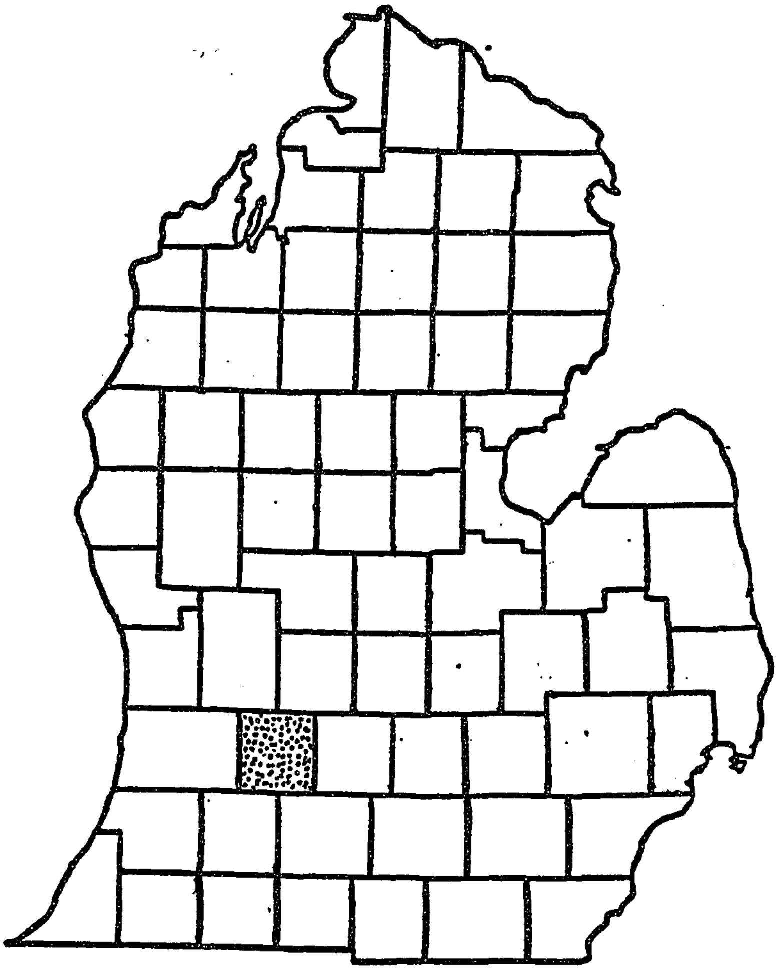


Figure 1. Location of Barry County in Michigan.

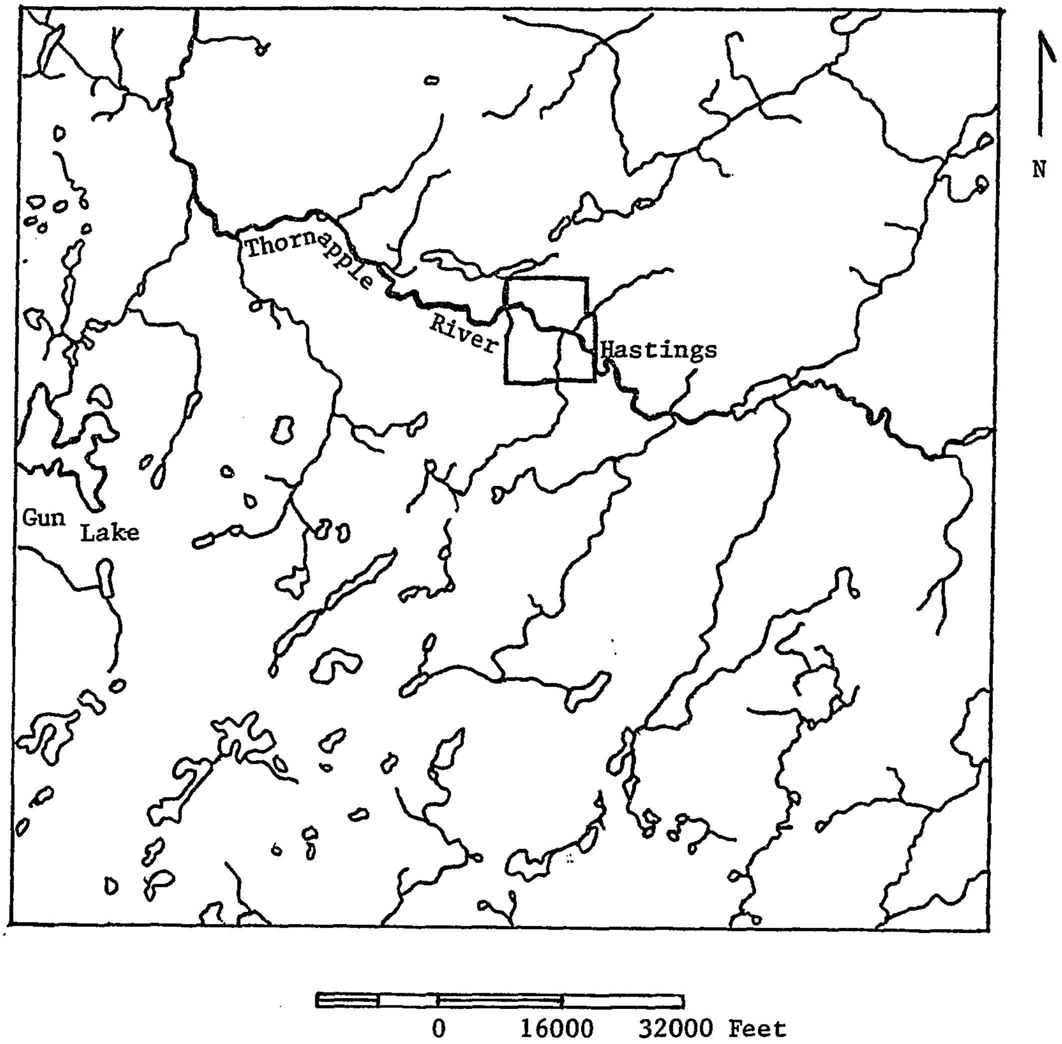


Figure 2. Drainage Features in Barry County, Michigan.

exists between the narrow plain and the ridges, over 200 feet of relief is found between the western ridge and the Gun Plain to the west. Boulder belts commonly follow the trends of these ridges. Two broad, more subtle ridges trend southeast to northwest across the center and northern portions of the county. These ridges are cut by small transverse stream valleys. Broad low lying plains occur in the south-central and west and northwest townships. Hummocky topography with poorly integrated drainage dominates the ridges.

Surficial Geology

All of the topographic features in Barry County can be attributed to the glacial processes that shaped lower Michigan's landscape. Total drift thicknesses range from 150 to 400 feet (Lilienthal, 1974). Figure 3 is a composite map of the glacial landforms in Barry County. During late Wisconsinan time, about 14,000 years ago, two lobes of the Laurentide ice sheet converged in what is now Barry County. The two well-defined ridges in the west and southwest part of the county are end moraines produced during the westward retreat of the Lake Michigan Lobe of the ice sheet. The broader ridges trending southeast-northwest are end moraines of the Saginaw Lobe, produced during its northeasterly retreat. Areas of low relief underlain by till and mapped as till plains were also left

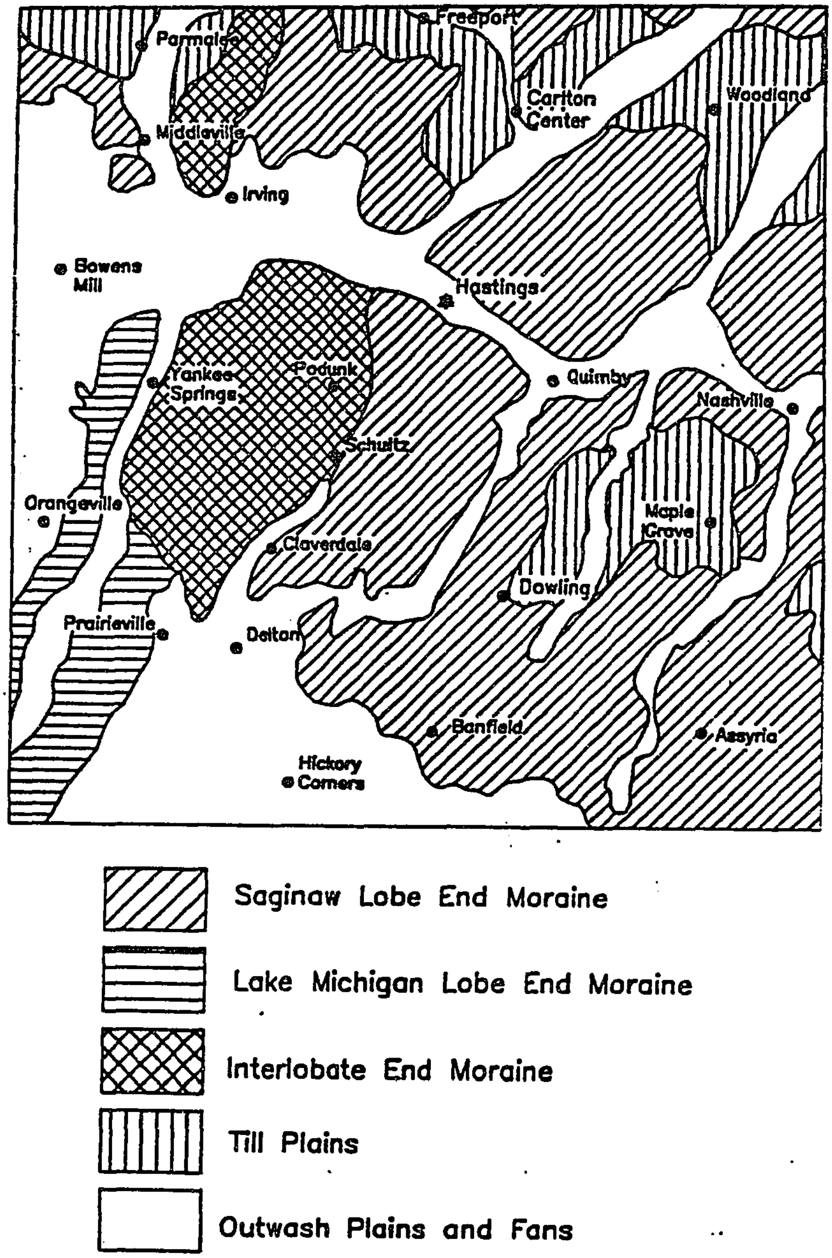


Figure 3. Surficial Geologic Landforms of Barry County, Michigan

by the retreating Saginaw Lobe.

The county contains several glacial outwash features. The Thornapple River follows the course of a large meltwater channel that lies between the two end moraines of the Saginaw lobe. The smaller transverse stream valleys which intersect the end moraines are a result of subglacial meltwater flow (Simms, 1988). Remnants of eskers, indicating the most recent direction of glacier movement (Selby, 1985), occur in these valleys. The low lying plains adjacent to the moraines are outwash aprons generated by meltwater deposition from both lobes.

The numerous lakes and wetlands that occur in the valleys were most likely formed by stagnant ice collapse and slump. Blocks of ice embedded in glaciolacustrine or outwash deposits were buried in the material and remained frozen long after the glacier retreated. Later melting of the ice blocks resulted in depressions on the land surface, now occupied by ponds or wetlands (Selby, 1985).

These glacial processes have resulted in a grain-size distribution ranging from large boulders to lacustrine clay. In the interlobate moraines, materials are predominantly coarse sands and gravels, with occurrences of bouldery, loamy till. The end moraines of the Lake Michigan Lobe also are made up of coarse sands and gravels with interbedded stony, bouldery till. The Saginaw Lobe moraines contain coarse materials, with the variability and coarseness decreasing toward the till plains (Simms, 1988). Most of the morainal material is unstratified and poorly sorted, typical of this type of deposit. The till plains are underlain by loamy, clayey till.

Materials in the outwash channels generally are coarse and gravelly. Grain sizes in the outwash aprons range from cobbles several inches in diameter near the moraines to fine sands at the distal margins of the deposits. Lenses of lacustrine clay are scattered throughout. The reworking action of meltwater produces well-sorted sands and gravels in these deposits.

Minerals in the glacial drift originate from sedimentary, igneous, and metamorphic lithologies. The sedimentary fraction consists of sandstone, shale, and carbonate clasts. Clays in the moraine systems of Barry County have been analyzed by Monaghan and others (1986). Their results show that chlorite, illite, kaolinite, and vermiculite, but not smectite, are present in the glacial drift.

Bedrock Geology

The bedrock units underlying the Pleistocene glacial drift occur within the Michigan basin, a relatively shallow, intracratonic structure formed during the Paleozoic era (Figure 4). Four of the five formations subcropping in Barry County are Mississippian in age. One is Pennsylvanian. All units except the Pennsylvanian Saginaw Formation are marine deposits and all units dip gently to the northeast. The subcrop pattern of the formations is shown in Figure 5. The oldest formation, the Coldwater Shale, occurs in the southwest corner of Barry County. The Coldwater Shale is early Mississippian in age and was deposited as an offshore marine mud (Dorr and Eschman, 1977). It is composed of slightly calcareous grey shale with some beds of highly calcareous shale, silty shale, and thin sandstone. The formation ranges in total thickness from 900-1000 feet (Lilienthal, 1974).

The Marshall Sandstone, also early Mississippian in age, overlies the Coldwater Shale to the north and east. The Marshall Sandstone was deposited as nearshore sands and silts (Dorr and Eschman, 1977). It consists of sandstone with some thin interbeds of sandy shale and shale, especially at the Marshall-Coldwater contact. In Barry County, the Marshall Sandstone ranges in thickness from 350-400 feet (Lilienthal, 1974). The Marshall Sandstone is an important aquifer for many southwestern Michigan counties. Its mineralogy will be discussed later.

Middle Mississippian rocks are absent in this part of Michigan, indicating that the inland seas in which the previous units were deposited must have withdrawn (Dorr and Eschman, 1977). The next unit to be deposited was the late Mississippian Michigan Formation. The Michigan Formation

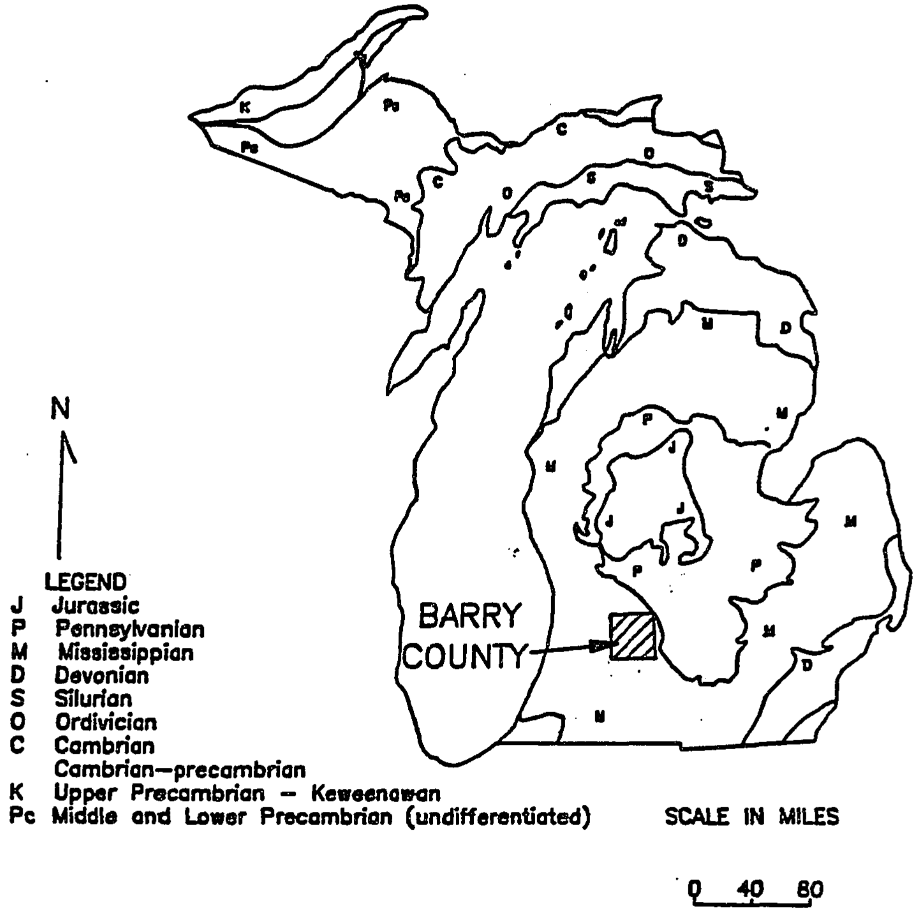


Figure 4. Location of Barry County in the Michigan Bedrock Basin.

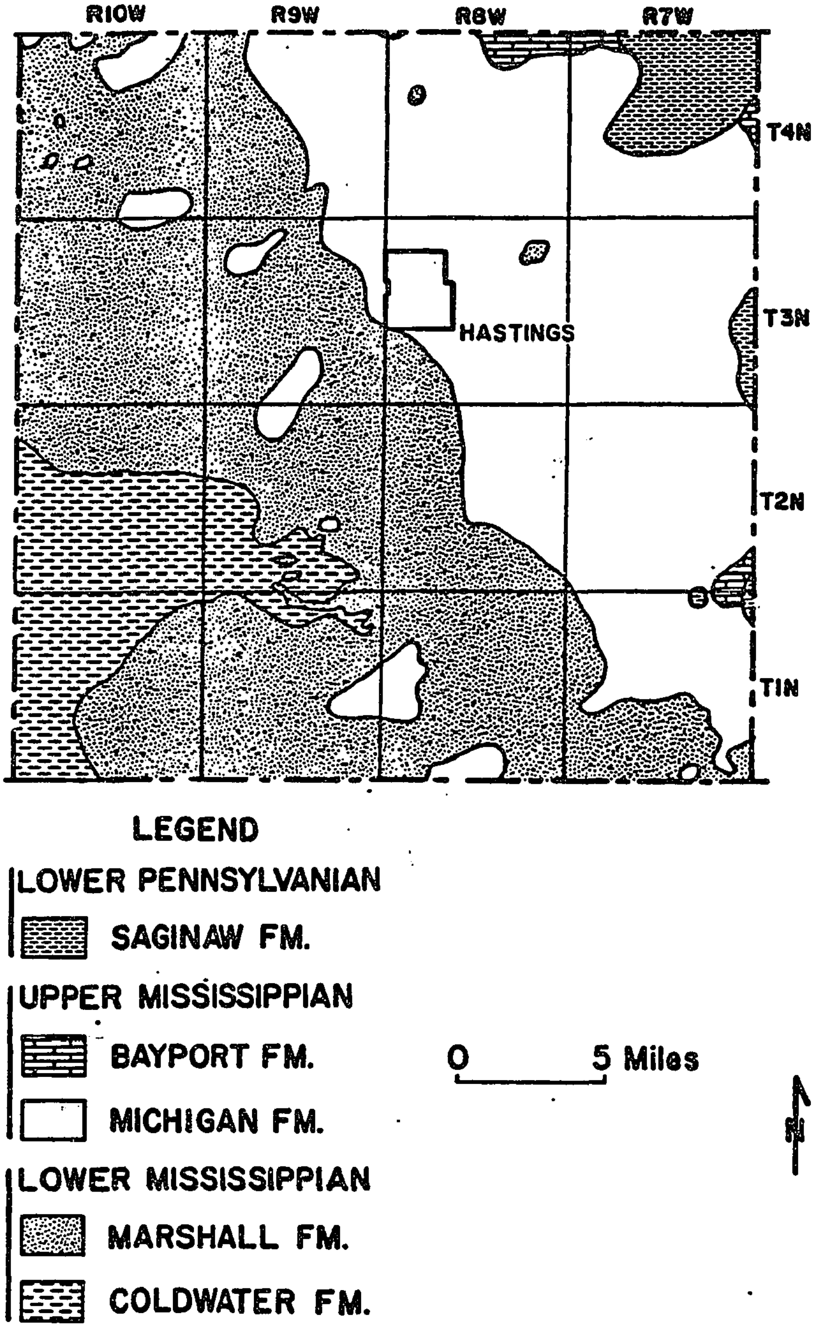


Figure 5. Bedrock Formations Underlying the Glacial Drift in Barry County, Michigan

Source: Lilienthal, Richard T., 1974, Subsurface Geology of Barry County, Michigan: MDNR Report of Inv. 15 p. 5

overlies the Marshall Sandstone to the north and east. This unit was deposited at a time when the basin was semi-isolated. Alternate periods of drying and flooding resulted in the formation of gypsum interbedded with shale, limestone, and dolomite. The Michigan Formation is 150-200 feet thick in Barry County (Lilienthal, 1974).

The late Mississippian Bayport Limestone overlies the Michigan Formation. This limestone was deposited after the semi-isolated basin had again become open sea (Dorr and Eschman, 1977). It is generally clean with some beds of dolomite and sandy limestone. Uplift of the basin toward the close of Mississippian time, resulted in erosion of the Bayport Limestone. The unit occurs as isolated remnants, 50 feet thick or less (Lilienthal, 1974) in the extreme northeast and east parts of the county.

The youngest unit subcropping beneath the drift is the early Pennsylvanian Saginaw Formation. It overlies the Bayport Limestone in the extreme northeast and east parts of the county. The Saginaw Formation was deposited in a fluctuating coastal swamp environment and contains a variety of sedimentary facies including stream channel, floodplain, tidal swamp, and shallow marine deposits (Dorr and Eschman, 1977). The formation consists of sandstone, siltstone, shale, limestone and coal. In Barry County, the formation is predominantly sandstone with interbeds of shaley sand, sandy shale, and shale. The thickness of the

Saginaw Formation in this area is about 50 feet (Lilienthal, 1974). The stratigraphic relationship of the bedrock units in Barry County to other formations in Michigan is shown in Figure 6.

Since the Marshall Sandstone is the bedrock aquifer used in Barry County, its mineralogy is important in analyzing the ground-water quality of this aquifer. A study of Marshall outcrops in Calhoun County, just southeast of Barry County (Monnett, 1948) lists quartz and chert as the major components of the sandstone. Other minerals present in significant amounts are biotite, muscovite, and feldspars. Minor constituents include ilmenite, chlorite, apatite, tourmaline, and calcite. Some outcrops also contain minor amounts of rutile and zircon.

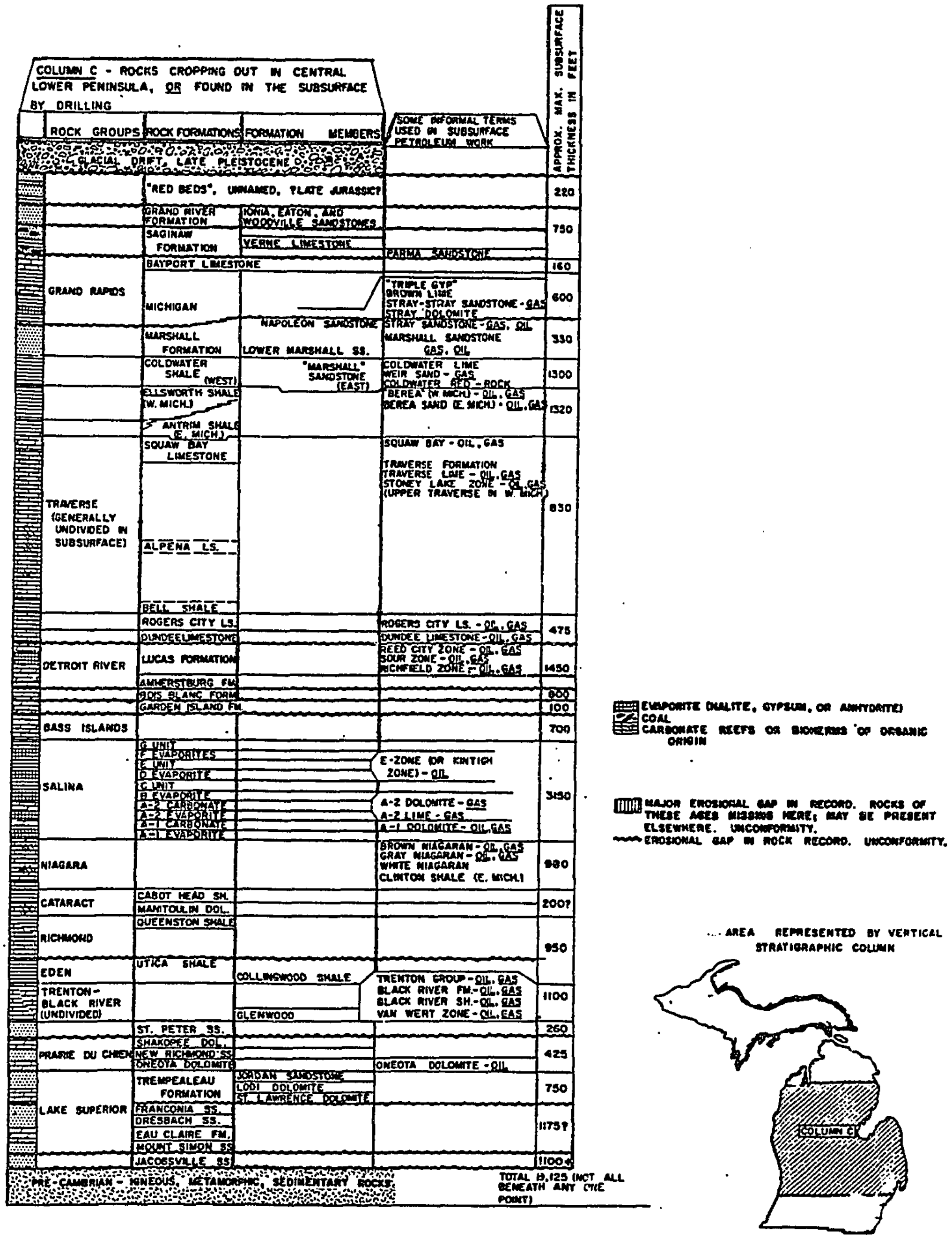


Figure 6. Michigan Stratigraphic Column.

Source: Dorr, J.A., and Eschman, D.F., 1977, Geology of Michigan, Ann Arbor, Michigan, University of Michigan Press, inside back cover.

METHODOLOGY

Hydrogeology

Flow systems were investigated using topographic and potentiometric surface patterns. Potentiometric surface patterns were created from the 1654 domestic well logs available in the database. More than 1400 of these wells are screened in the drift. Data taken from well logs include Michigan cartesian coordinates and static water level elevations measured at time of well construction. The SURFER (Golden Software, Inc., 1988) software package was used to generate potentiometric surface contour maps for the bedrock and glacial drift aquifers. Each map was then examined separately for flow patterns and recharge and discharge areas. Hydraulic head values on the two maps were compared to determine the relationship between the two aquifers.

Ground-water Quality

For the purposes of this study, the chemical data were divided into two groups, the glacial drift well data and the bedrock well data. Chemical analyses were initially examined for questionable records. Analyses showing zero concentrations for calcium, magnesium, bicarbonate, or hardness were not used. The occurrence of these ions is so prevalent in the ground water of southern lower Michigan, especially in the drift aquifers, that an absence most likely indicates an unreliable analysis. Wells showing evidence of being sampled through a water softener also were not included.

Because a noticeable percentage of the glacial drift wells appeared to have elevated levels of chloride, nitrate, and ammonium, data from the glacial drift wells were divided further using the following criteria:

chloride	>10 mg/L
nitrate	>5 mg/L
ammonium	>.5 mg/L

Ground water samples meeting the criteria above were considered degraded. Samples below these criteria were considered to represent "background" water quality for the glacial drift. These criteria were selected arbitrarily. Ground-water samples from glacial drift aquifers in southwest Michigan typically contain concentrations of chloride, nitrate, and ammonium at 11 mg/L, 1 mg/L, and .1 mg/L respectively (Cummings, 1980). Background water quality was not established for the bedrock because not enough data were available to select reasonable screening criteria.

Statistical analysis was performed on the data collected from the background wells, bedrock wells, chloride-degraded drift wells, nitrate-degraded drift wells, and ammonium-degraded drift wells using the STATGRAPHICS (Statistical Graphics Corp., 1987) statistical software package. Initially summary statistics were generated for the five data sets. Each parameter in each data set was examined for normal distribution using frequency histograms and normal probability plots. Examples of normal probability plots for the background drift wells are shown in Appendix A. The straight line plotted on each graph is a representation of a normally distributed plot calculated for that parameter. Points plotted on each graph represent the actual observed data, and show how skewed actual data is from normal distribution. Very few of the parameters have a normal distribution. The type of distribution of the data dictates what type of statistical test should be used for analyzing and comparing data sets.

Analytical data from the bedrock, the background glacial drift, and the degraded glacial drift were visually compared using box-and-whisker plots. The box-and-whisker plots are graphical representations of summary statistics as illustrated for calcium in Figure 7. The center box covers the middle 50% of the data. The "whiskers" extend out to a maximum length of 1.5 times the width of the inter-quartiles. Outliers beyond the whiskers are plotted as single points. The center line represents the median of

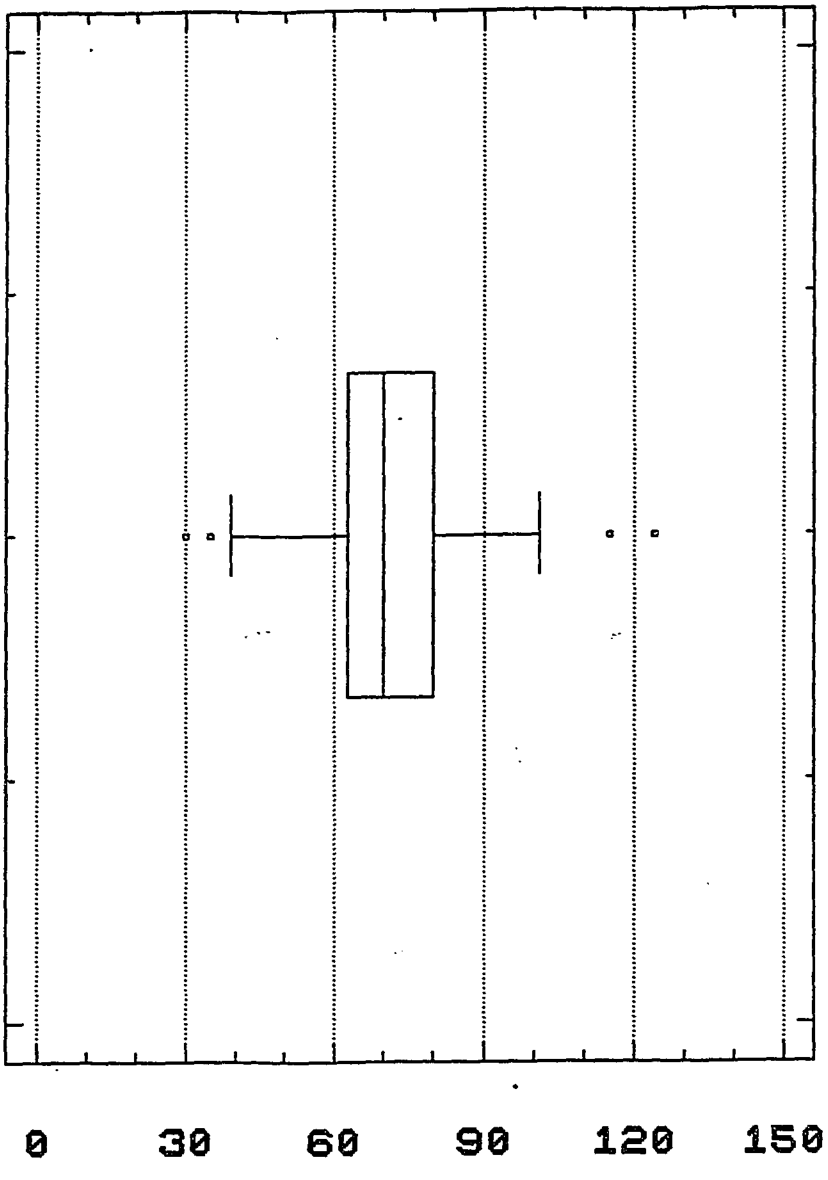


Figure 7. A Box-and-Whisker Representation of Summary Statistics.

the data.

Differences and similarities observed on the box-and-whisker plots were then tested statistically. The test chosen for each parameter was determined using the flow chart shown in Figure 8. A 95% confidence interval test compared the ratio of the variances for the two data sets being examined. If the variances were statistically equal, a non-parametric test was chosen. If the variances were statistically unequal, a parametric test was used to compare the data sets.

Non-parametric tests are preferred for data that are not normally distributed since calculations are not influenced by outliers in the data. The non-parametric Mann-Whitney-Wilcoxin test in the STATGRAPHICS package combines the data sets, ranks each value, separates the data again, and performs summary statistics on the rank classifications. The test then compares the rank medians of the data sets and produces a level of significance for the hypothesis of equal medians. Depending on the level of significance required by the scope of the study, this hypothesis is either accepted or rejected. A 5% level of significance was chosen as for this study. If the level of significance calculated by the test was 5% or greater, the hypothesis of equal medians was accepted. The median or mean (for parametric tests) is considered a representation of "typical" ground-water quality for a sample set. The

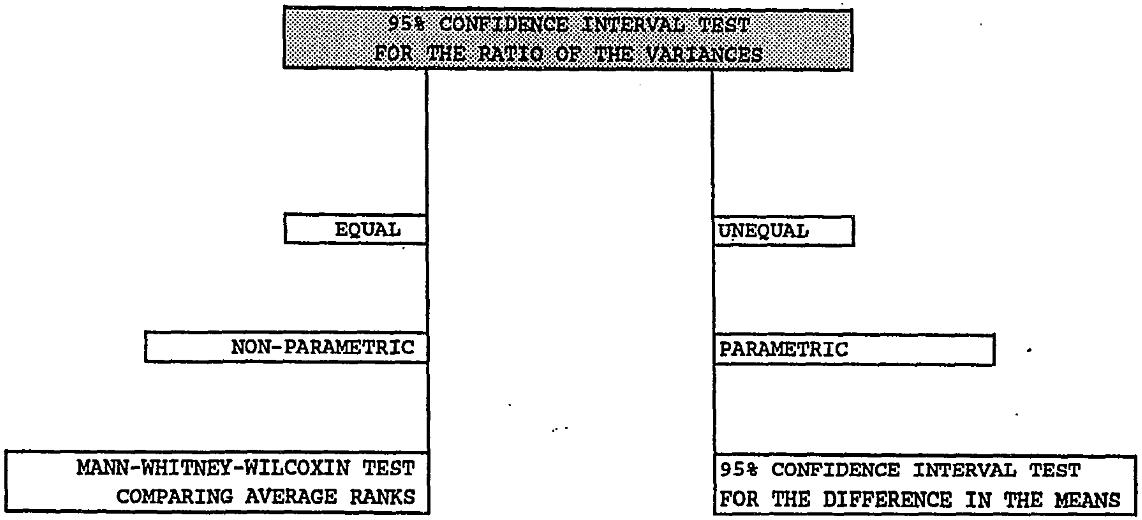


Figure 8. Statistical Procedures Used on Barry County Data.

Mann-Whitney-Wilcoxin test is analogous to the *t*-test for parametric data and is also called the Mann-Whitney U test (Siegel, 1956).

To the author's knowledge, no non-parametric tests exist for data sets having unequal variances. Therefore, a parametric test was used to compare these data. The test chosen was the 95% confidence interval for the difference in the means of two samples. If two means are equal their difference equals zero. The hypothesis of equal means was accepted if zero was within the 95% confidence interval calculated for the data sets. It should be noted that in this test actual data values are compared while in the non-parametric test rank classification numbers are compared.

In addition, all sample sets: the background drift, degraded drift, and bedrock, were compared on trilinear diagrams generated from the CHEM software package. In this package the dissolved ion concentrations (mg/L) of calcium, magnesium, sodium, potassium, bicarbonate, carbonate, sulfate, and chloride are converted to percentage reacting values (milliequivalents per liter) and plotted as such. Values for sodium and potassium are added together on the trilinear diagram, as are values for bicarbonate and carbonate.

Chemical Changes Along Flow Paths

Initially, chemical changes along flow paths were examined by plotting values for each chemical parameter in the background glacial drift data set on base maps of the county and comparing these maps to the potentiometric surface maps. When individual concentrations of each parameter were plotted on base maps of Barry County, the data in all cases were too variable to be contoured. No distinct spatial patterns or correlations between the concentrations of the parameters and the potentiometric surface contours were found for any of the parameters. The most reasonable explanation for this lack of association is the nature of ground-water flow in the glacial terrain. Hummocky topography, typical of interlobate areas, results in an abundance of local and intermediate flow systems, superimposed on the regional flow system (Figure 9). These local systems are evident by the number of lakes, ponds and wetlands in the county. The glacial drift wells chosen for sampling might be screened in short to moderate local flow paths where the ground water has short residence time, while the wells used in the flow maps are reflecting the regional flow patterns.

Next, recharge/discharge relationships were examined. As part of the Michigan Groundwater Survey, each well sampled was classified as representing ground water from a recharge, transition, or discharge zone. County health department personnel designated these zones based on topography, vegetation, and proximity to areas of suspected

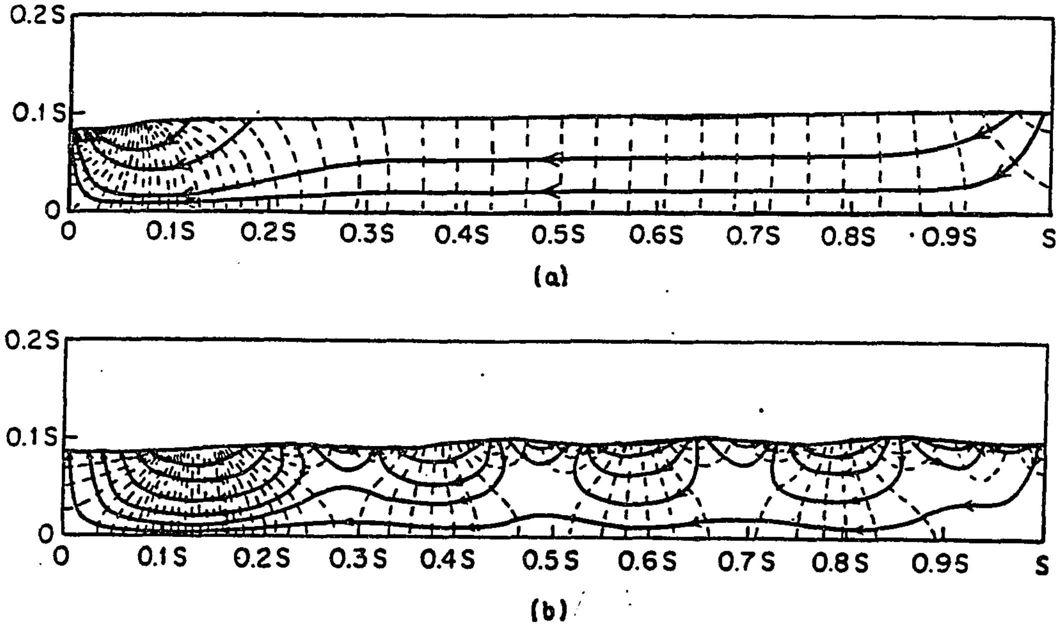


Figure 9. The Influence of Topography on Regional Ground-water Systems. (a) represents the water table configuration one might find with a gently and uniformly inclined lacustrine plain and (b) represents the water table configuration one might find in hummocky glacial terrain.

Source: Freeze, R. Allan, and Cherry, John A., 1979, Groundwater, Englewood Cliffs, New Jersey, Prentice-Hall, p.196.

ground-water discharge (lakes and perennial streams). Due to well spacing, individual flow paths could not be analyzed. Therefore, samples collected from wells in the recharge, transition, and discharge zones were each considered as a data set. The background drift wells from each zone were compared statistically for the entire county using the box-and-whisker plots and two-sample tests described earlier.

Influence of Landforms

The influence of physical factors such as landforms on the natural background water quality of the drift aquifer was examined by separating the background drift wells into those screened in moraine materials and those screened in outwash material. These two data sets were then compared using the box-and-whisker plots and two-sample test described in the ground-water quality methodology.

HYDROGEOLOGY

Glacial Drift Aquifers

The glacial drift in Barry County has been previously divided into nine aquifer units, which are found at different elevations throughout the glacial deposits (Simms, 1988). Though Simms studied each aquifer unit separately, he stated in his report that the individual units are hydraulically connected through the permeable and impermeable materials and should not be considered as discrete aquifers with well-defined physical and hydraulic boundaries. For this reason, and because the Barry County project is a regional study, the glacial drift is classified in this study as a single aquifer. The upper boundary of the aquifer is the land surface; the lower boundary is the bedrock surface.

The computer-drawn potentiometric surface map for the glacial drift wells is shown in Figure 10. The potentiometric surface largely reflects the topography of the county. The ground-water divide trending east-northeast in the southern part of the county coincides with the topographically high end moraine of the Saginaw Lobe and its associated outwash apron. The steep gradient along the southwestern border of Barry County, and the water

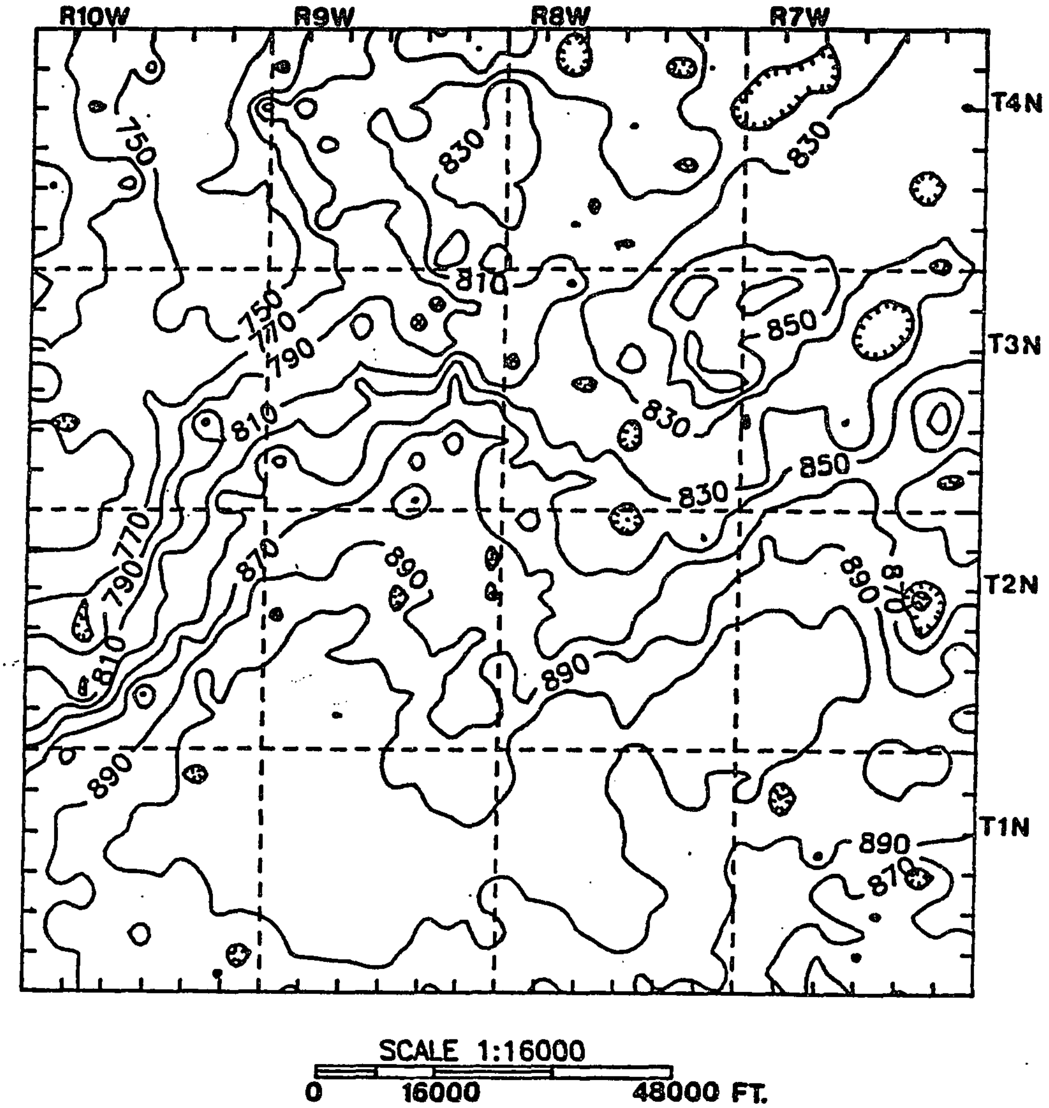


Figure 10. Potentiometric Surface for the Glacial Drift Aquifer in Barry County, Michigan.

table low around Gun Lake correspond to the sharp drop in elevation from a narrow end moraine to the Gun Plain. Also apparent is a narrow trough along the course of the Thornapple River. The glacial drift aquifer is recharged directly from precipitation onto the land surface. Regional discharge occurs into Gun Lake and the Thornapple River. Although the influence of local flow systems is not apparent on Figure 10, the abundance of small lakes and wetlands suggests that many local flow paths are superimposed on the regional system. The small closed potentiometric high and low areas probably represent individual wells with lower ground-water elevations rather than actual depressions or mounds in the potentiometric surface.

Bedrock Aquifer

Most of the wells screened in bedrock in Barry County are in the Marshall Sandstone; a few are in the Michigan Formation. The upper boundary of this aquifer is the bedrock surface. Simms (1988) noted that the Marshall Sandstone appears to have an upper flushed zone and a lower stagnant, briny zone. He considered this hydrochemical division to be the lower boundary of the aquifer.

Figure 11 is the computer drawn potentiometric surface map for the Marshall sandstone. The interpreted ground-water flow pattern is roughly similar to that of the

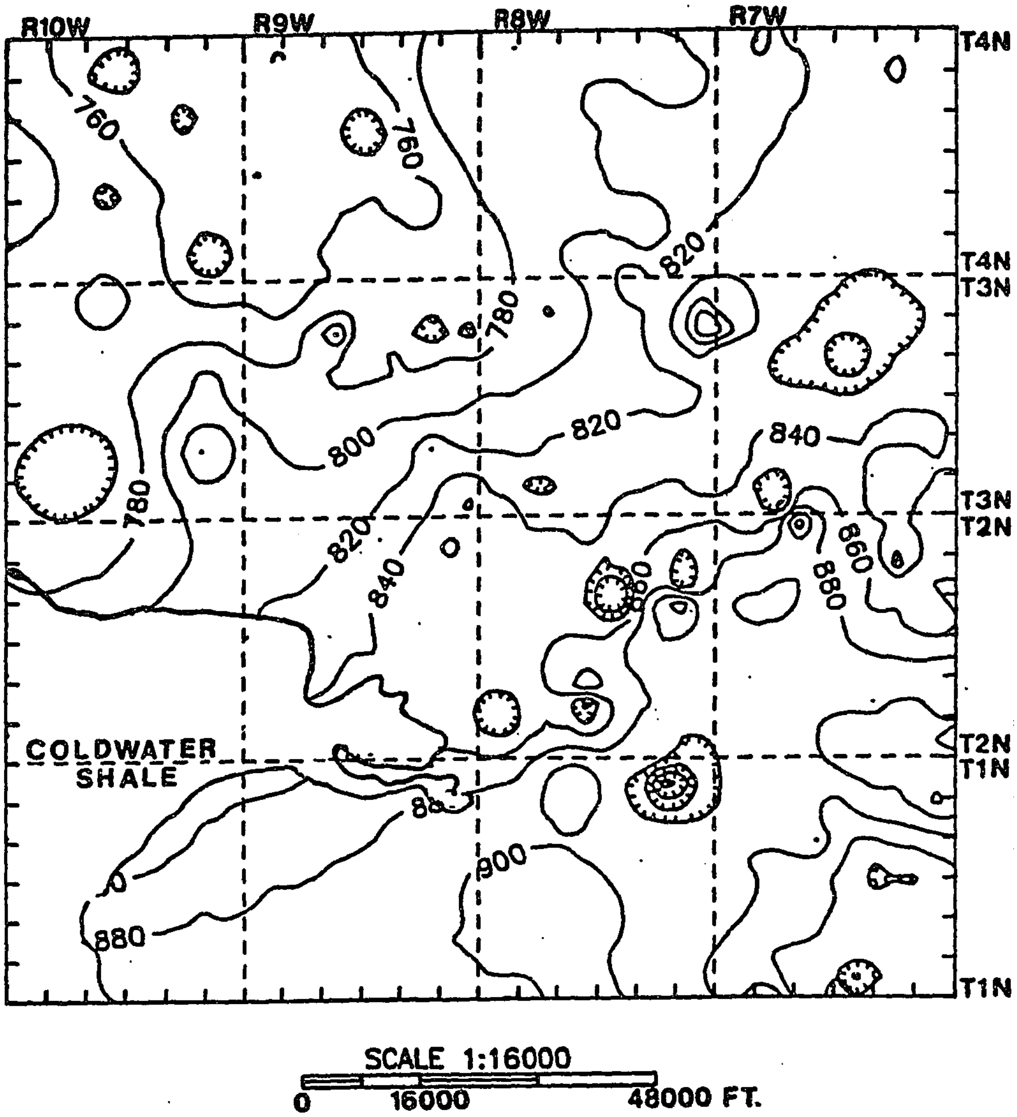


Figure 11. Potentiometric Surface for the Marshall Sandstone Aquifer.

glacial drift. Regional flow is to the northwest. The divide in the southeast corner corresponds with the large divide in the drift. A potentiometric depression surrounds Gun Lake. The effect of the Thornapple River can be faintly seen in the contour patterns of the northern townships. Approximately 200 data points were used for the bedrock potentiometric surface map. Because so few points are representing such a large area, the computer drawn contours are not as reliable as those generated for the glacial drift map.

Discussion

The potentiometric surface patterns suggest the two aquifer systems are hydraulically connected. Potentiometric head differences between the two aquifer systems indicate that water from the glacial drift is the principle source of recharge for the bedrock aquifer throughout most of the county. The apparent ground-water divide in the Marshall Sandstone in the southeast corner of Barry County and the absence of the formation in the southwest part of the county eliminates the possibility of lateral inflow to the Marshall from south of the study area. The Marshall Sandstone, as the glacial drift, appears to discharge into Gun Lake and the Thornapple River. Deeper flow paths in the Marshall Sandstone eventually discharge into Lake Michigan.

GROUND-WATER QUALITY

The majority of the wells in Barry County, and all the wells sampled in this study, are used for domestic purposes. Therefore water quality is significant for both health and aesthetic reasons. The chemical data collected by county health department personnel for the Michigan Groundwater Survey consist of 288 samples from residential wells. Approximately 18 samples were collected from each township. Of the total, 242 were collected from wells screened in the glacial drift, and 46 from wells screened in the bedrock aquifer. Wells selected for sampling were not located near known sources of contamination. The groundwater samples were analyzed for 33 inorganic parameters by several state and private laboratories. In this study, the concentrations of eight cations and four anions, together with silica, hardness, and conductivity parameters were examined. Field pH, Eh, and temperature measurements were not obtained for the Barry County wells.

Background Drift Wells

Summary statistics for the non-degraded drift wells are given in Table 1. Of the parameters included in this study, calcium, magnesium, bicarbonate, and sulfate have the highest chemical concentrations in ground-water samples

Table 1

Summary Statistics for Background Drift Wells

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Total alkalinity	mg/l-CaCO3	160	241	239	53	96	432	336	212	280	0.15
Ammonium	mg/l	126	0.10	0.06	0.09	0.00	0.40	0.4	0.04	0.11	1.80
Barium	mg/l	156	0.10	0.08	0.08	0.01	0.50	0.49	0.04	0.11	2.40
Calcium	mg/l	160	71	70	15	30	124	94	63	80	0.12
Chloride	mg/l	28	3.8	3.5	2.0	1.0	8.0	7	2.0	5.0	0.4
Spec. Conductance	umhos/cm	160	413	401	93	177	748	571	359.5	469.5	0.46
Total hardness	mg/l-CaCO3	160	273	270	57	115	477	362	243.5	302.5	0.26
Iron	mg/l	119	1.13	0.80	1.21	0.01	5.89	5.88	0.20	1.60	1.80
Magnesium	mg/l	158	23	23	6	0.02	48	47.9	20	26	0.05
Manganese	mg/l	138	0.08	0.04	0.12	0.01	1.19	1.18	0.03	0.07	6.40
Nitrate	mg/l	159	0.3	0.0	0.8	0.0	4.9	4.9	0.0	0.2	3.5
Potassium	mg/l	158	2.0	1.5	1.3	0.5	6.7	6.2	1.1	2.5	1.4
Silica	mg/l	160	8	6	7	2	48	46	5	7.65	3.5

Table 1--Continued

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Sodium	mg/l	5.0	17.5	4.9	25.4	1.1	61.0	59.9	1.4	1.9	1.8
Sulfate	mg/l	160	29.5	26	20	0	123	123	17	38	1.6

collected from the background drift wells. Potassium, barium, silica, iron, manganese, sodium, chloride, nitrate, and ammonium are detected in small concentrations. Calcium, magnesium, and bicarbonate ions are produced by the dissolution of carbonate minerals in the drift. Regression analyses of calcium and magnesium on alkalinity done at the 95% confidence level are illustrated in Figures 12 and 13. The graphs show highly significant correlation between these three parameters. Minor amounts of calcium may originate from the alteration of plagioclase to kaolinite. However, this contribution is probably modest compared to that of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). The dissolution of calcite occurs by the following reaction:

$$CaCO_3 + H_2CO_3 \text{ ---> } Ca^{2+} + 2HCO_3^-$$

Calcium also shows a strong correlation on the scatter plot with sulfate (data not shown). This could be due to the combined effect of oxidation of sulfide minerals and the dissolution of calcite caused by an increase in acidity, or the dissolution of calcium sulfate compounds (gypsum and anhydrite) in the glacial drift. Calcium values range from 30 mg/L to 124 mg/L in the non-degraded drift wells, with a mean value of 71 mg/L.

Magnesium could be derived from the carbonates magnesite ($MgCO_3$) and dolomite. In addition, a scatter plot of magnesium and silica (Figure 14) suggests that some

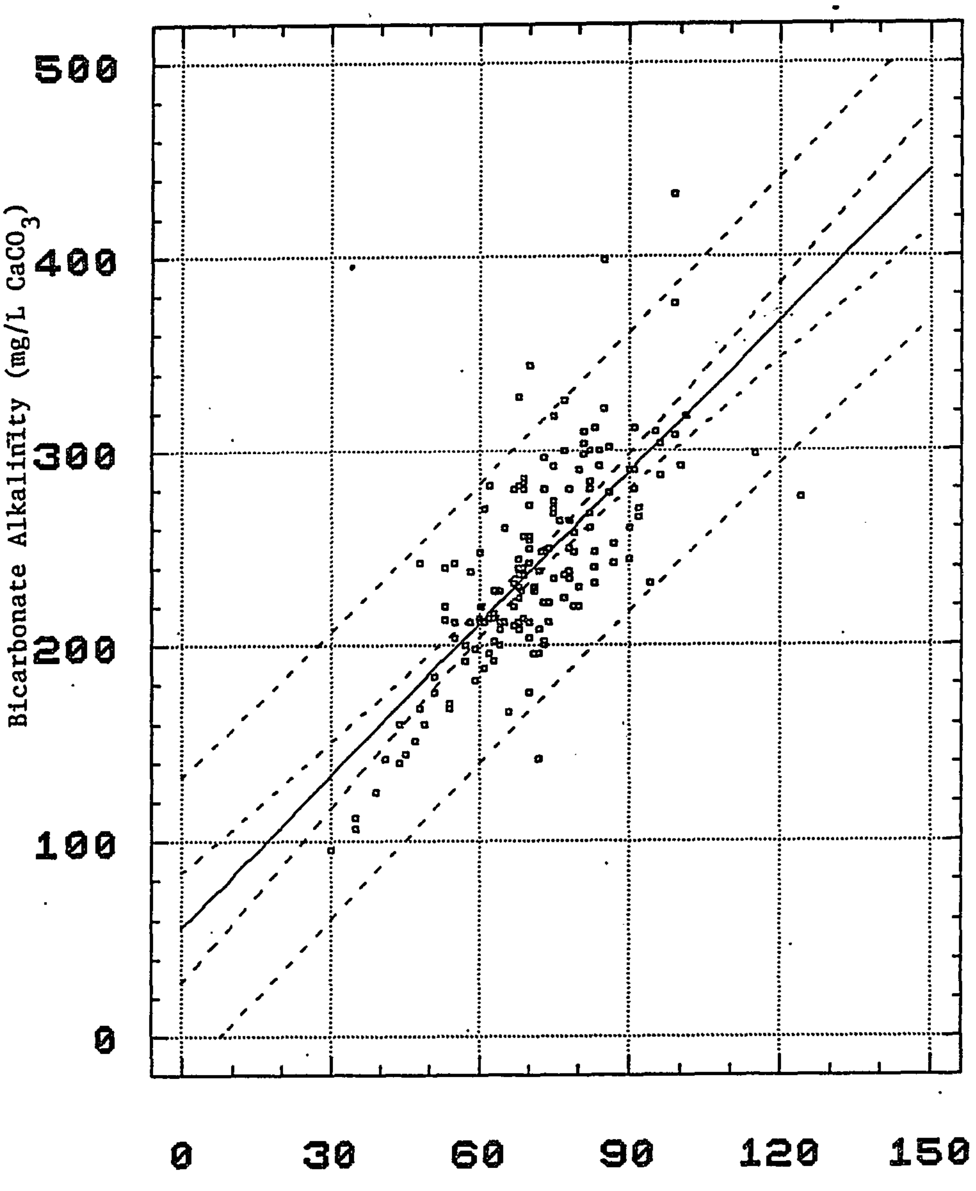


Figure 12. Regression Analysis of Bicarbonate Alkalinity and Calcium for the Glacial Drift Aquifer.

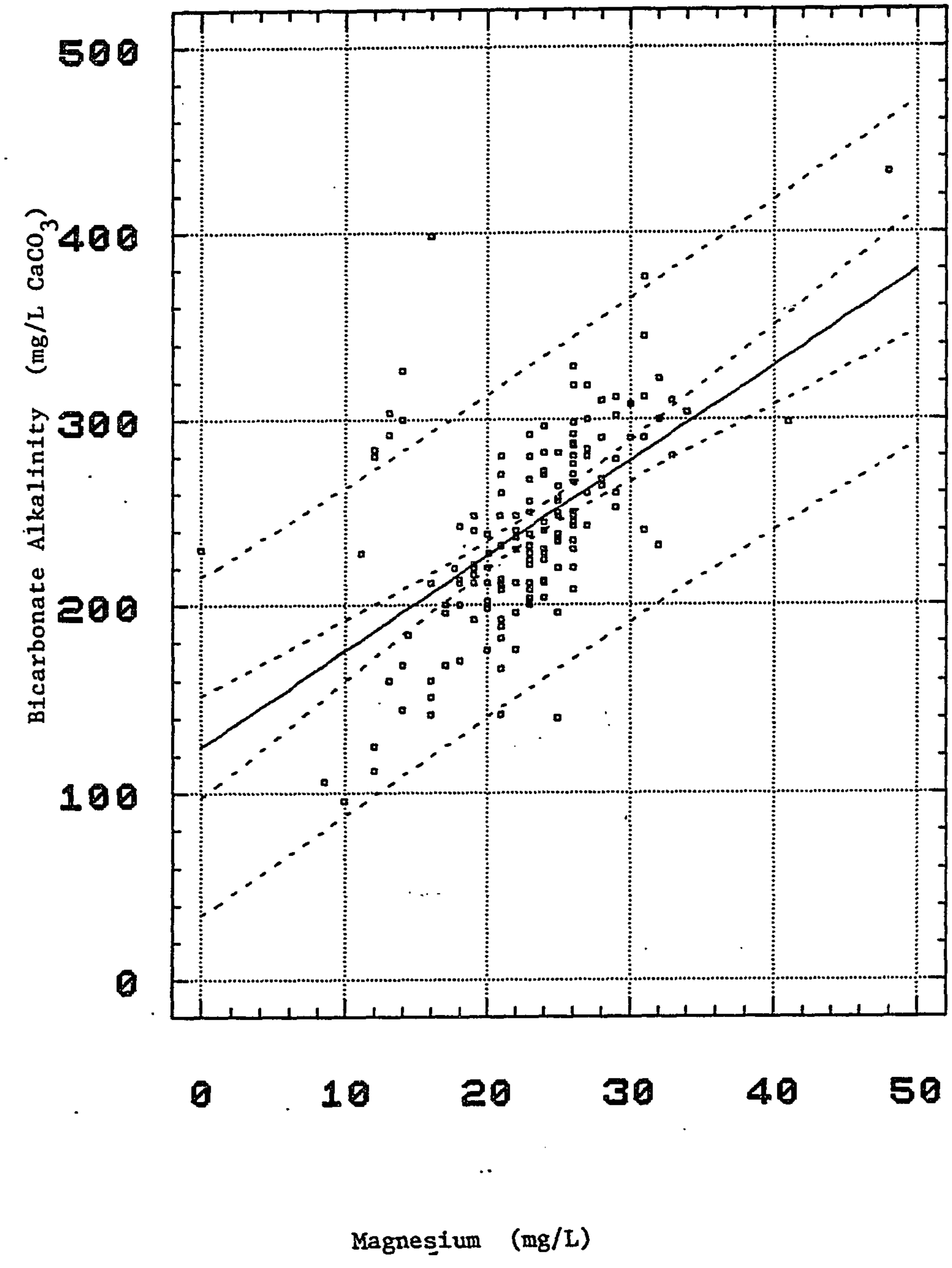


Figure 13. Regression Analysis of Bicarbonate Alkalinity and Magnesium for the Glacial Drift Aquifer.

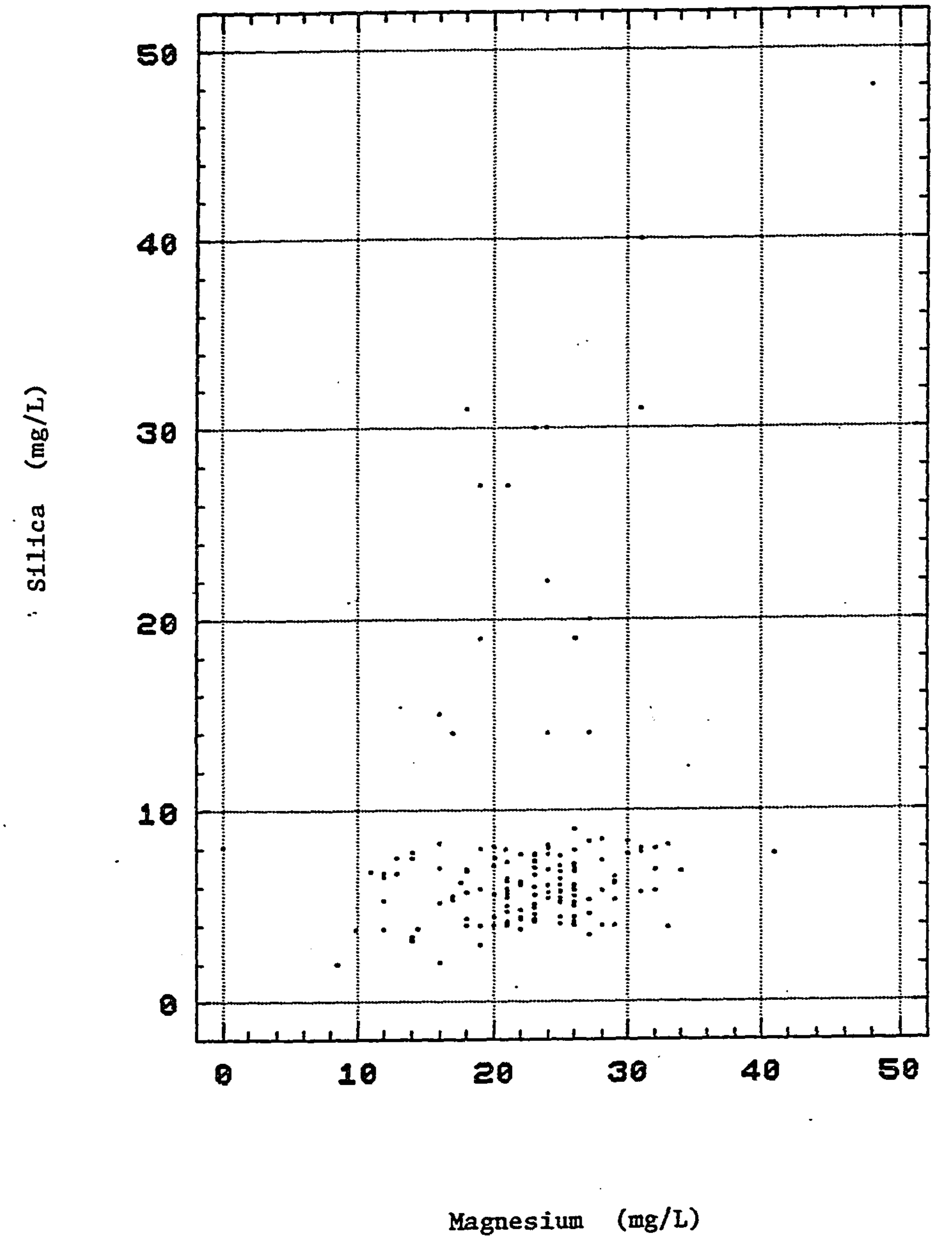


Figure 14. Scatter Plot of Magnesium and Silica for the Glacial Drift Aquifer.

magnesium may be contributed by the dissolution of magnesium-bearing silicates, e.g. forsterite (Mg_2SiO_4) or enstatite ($MgSiO_3$); or chlorite ($((MgFe)_6(AlSi)_3O_{10}(OH)_8$. The specific mineralogy of the glacial drift in Barry County is not known. Therefore, the minerals described are potential sources, not known sources. Concentrations of magnesium are between .02 mg/L and 48 mg/L in the non-degraded wells with a mean value of 23 mg/L.

Although most of the bicarbonate is a result of the dissolution of calcite, dolomite and other carbonates, part of the bicarbonate content of these waters originates from dissociation of carbonic acid produced when carbon dioxide enters the ground-water system. Inorganic carbon can exist in ground water as H_2CO_3, HCO_3^-, or CO_3^{2-}, depending the pH (Drever, 1988). The relationship of carbon species and pH is shown on Figure 15. Since the pH of most ground water is between 6 and 9, the dissolved carbon exists as the bicarbonate ion. The values for bicarbonate alkalinity range from 96 mg/L to 432 mg/L, with a mean of 241 mg/L.

Sulfate in ground water is usually derived from oxidation of metallic sulfides or dissolution of sulfate minerals. Sulfides in igneous and sedimentary clasts of the glacial drift are oxidized when they contact aerated water. Figure 16 is a scatter plot of iron and sulfate. This plot suggests a positive but not very strong relationship between these two parameters. The reaction

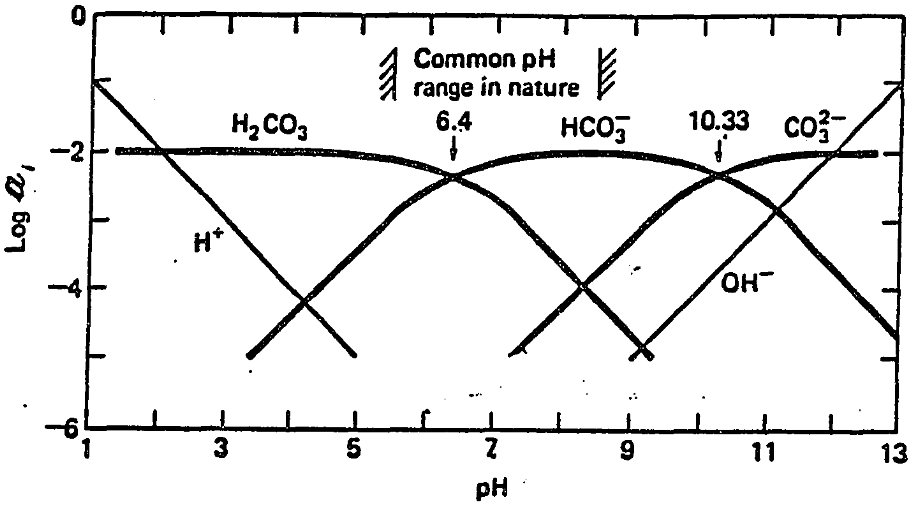


Figure 15. Activities of Different Species in the Carbonate System. As a function of ph, assume CO_2 = 10^{-2} atm. and temperature = 25 degrees celsius.

Source: Drever, James I., 1988, The Geochemistry of Natural Waters, 2nd Ed., Englewood Cliffs, NJ, Prentice Hall, p. 38.

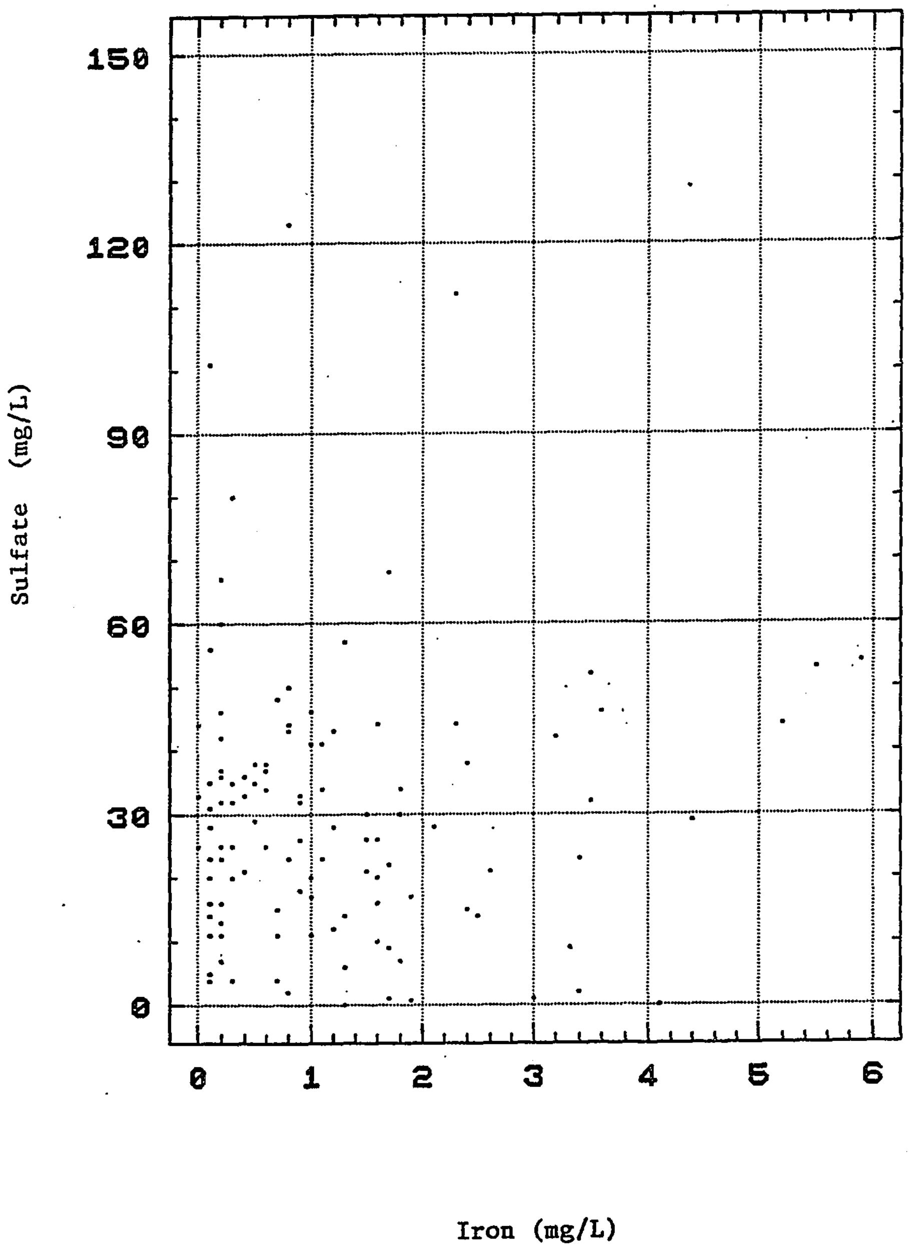


Figure 16. Scatter Plot of Iron and Sulfate for the Glacial Drift Aquifer.

for oxidation of pyrite (FeS_2) is:

$$FeS_2 + 8H_2O = 2SO_4^{2-} + Fe^{2+} + 16H^+$$

The plot also suggests that some sulfate is not produced by oxidation of FeS_2, and some iron is derived from other sources. The data are of minimal value due to the large amount of scatter. Sulfate concentrations range from 0 to 123 mg/L, with a mean value of 29.5 mg/L. The National Secondary Drinking Water Standards (NSDWS) established in July 1979 by the United States Environmental Protection Agency (U.S. EPA) recommends a maximum concentration of 250 mg/L for sulfate in drinking water. A complete reference is listed in Appendix B.

Possible sources for potassium are weathering and dissolution of potassium-bearing silicates such as orthoclase ($KALSi_3O_8$), leucite, muscovite, and biotite. Dissolution of these minerals and their alteration to clays releases both potassium ions and silica. The scatter plot of potassium and silica, however, suggests that most of the potassium in the ground water is being contributed from other sources (Figure 17). Concentrations of potassium in the background drift wells range from 0.5 mg/L to 6.7 mg/L, with a mean value of 2.0 mg/L.

Silica in natural water is hydrated and in the form of the monomolecular silicic acid, H_2SiO_4, or more accurately $Si(OH)_4$ (Hem, 1989). The majority of dissolved silica is produced from dissolution and alteration of various

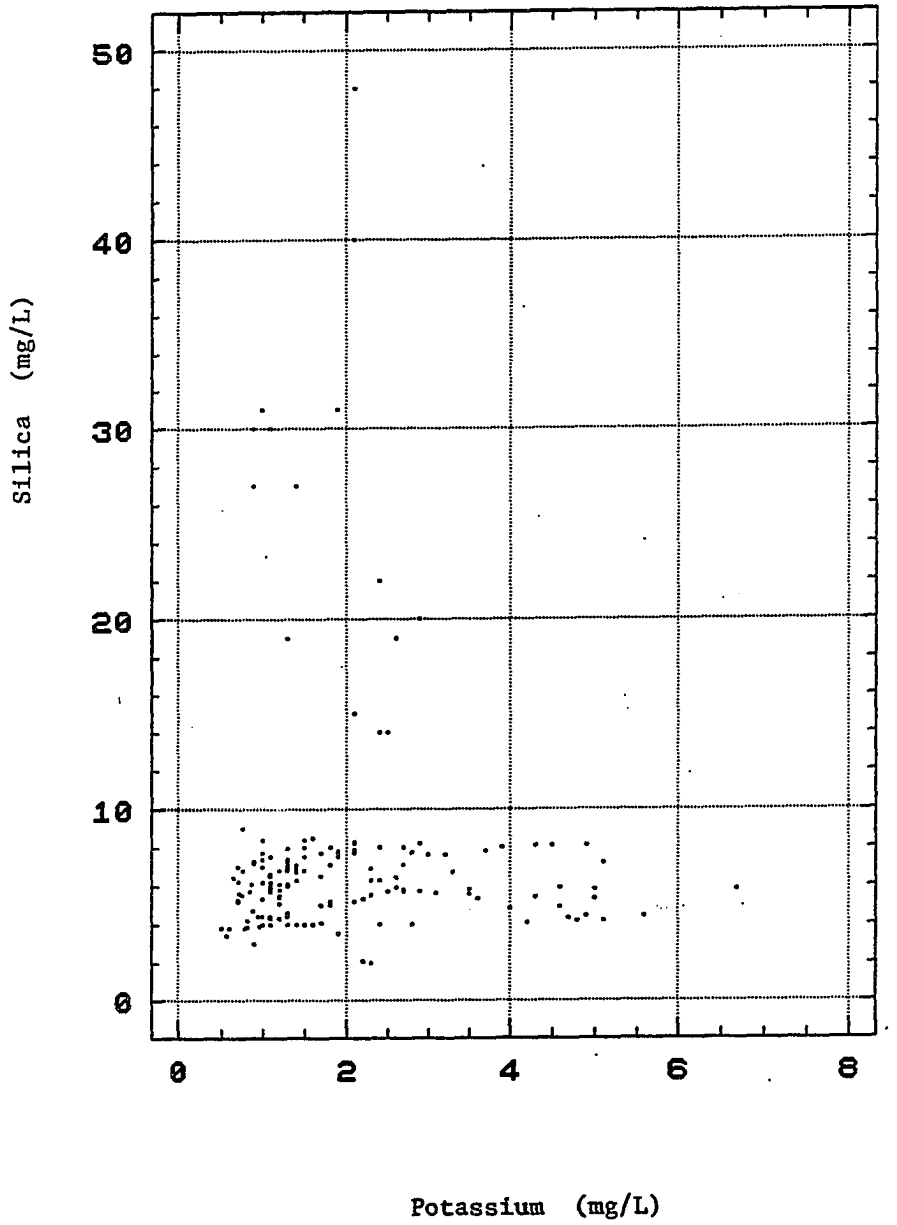


Figure 17. Scatter Plot of Potassium and Silica for the Glacial Drift Aquifer.

silicate minerals, such as albite:

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O = Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$$

Quartz and other amorphous forms of SiO_2 likely occur in igneous and sandstone clasts of the drift. However, their contribution to the dissolved silica concentration is probably minor, since these minerals are highly resistant to weathering (Hem, 1989). Silica values range between 2 and 48 mg/L, with a mean value of 8 mg/L.

The most likely source of barium in the drift is dissolution of witherite ($BaCO_3$). The scatter plot for barium and alkalinity (Figure 18) suggests a small positive trend. Another possible source for barium in the glacial drift is the mineral barite; however, the scatter plot for barium and sulfate shows no definite correlation (Figure 19). Barium concentrations range from 0.01 mg/L to 0.50 mg/L, with a mean of 0.10 mg/L. The National Primary Drinking Water Standards (NPDWS) established by the U.S. EPA in July 1979 lists a maximum allowable concentration for barium in drinking water as 1.0 mg/L (Appendix B).

Oxide, hydroxide, and sulfide compounds of iron are usually the chief sources of dissolved iron in ground water (Hem, 1989). In the normal pH range of ground water (6-9), iron is usually in the ferrous form Fe^{2+}. Above a pH of 4.8, the solubility of ferric iron (Fe^{3+}) is less than 0.01 mg/L. The concentration of Fe^{2+} is controlled by the redox

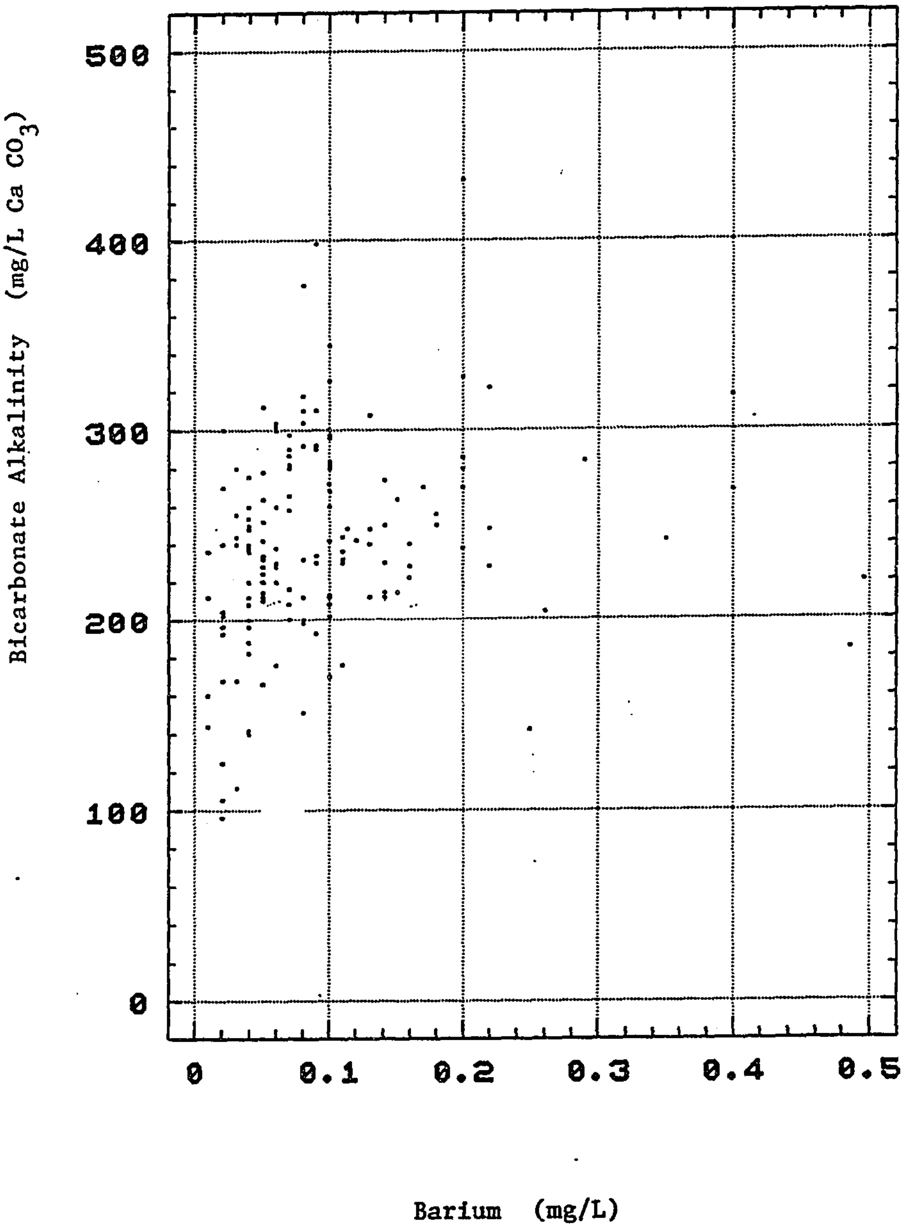


Figure 18. Scatter Plot of Barium and Bicarbonate Alkalinity for the Glacial Drift Aquifer.

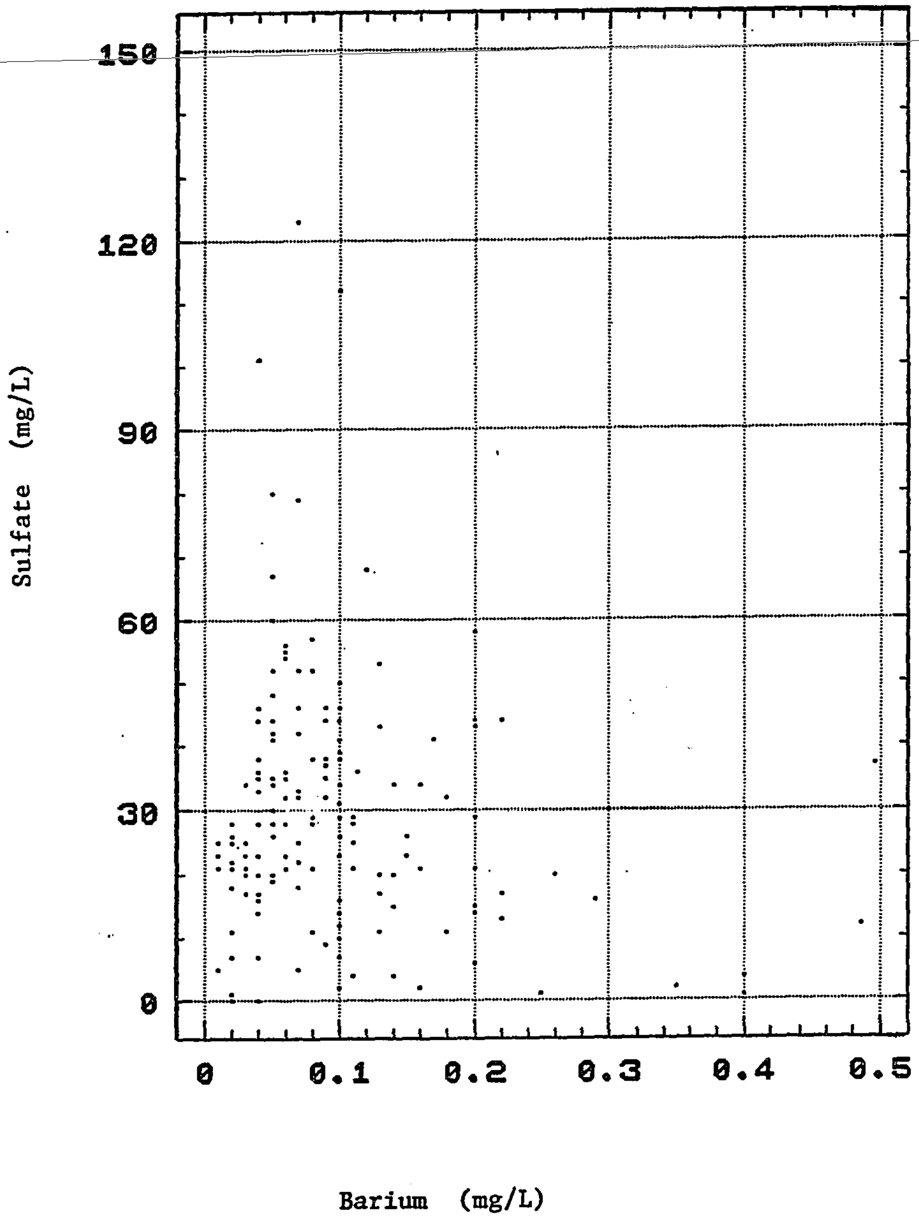


Figure 19. Scatter Plot of Barium and Sulfate for the Glacial Drift Aquifer.

state of the ground water. Redox potential is determined by oxygen content of recharge water, distribution and reactivity of organic matter and other potential reductants, distribution of redox buffers, and circulation rate of the ground water (Drever, 1988). The following reactions represent oxidation/reduction reactions involving iron which can occur in ground water:

$$Fe_2O_3 + 2e^- + 6H^+ = 2Fe^{2+} + 3H_2O$$

$$Fe_3O_4 + 2e^- + 8H^+ = 3Fe^{2+} + 4H_2O$$

$$FeS_2 + 8H_2O = 2SO_4^{2-} + 16H^+ + Fe^{2+} + 14e^-$$

The direction in which these reactions proceed will change with fluctuations in redox potential and pH. Since it is reasonable to assume that the pH does not vary widely in the study area due to carbonate buffering, the redox state of the ground water is likely the main influence on the iron concentration.

A small fraction of the iron may be derived from the dissolution of siderite ($FeCO_3$) in the sedimentary clasts of the glacial drift (Figure 20). No correlation was found between iron and silica or iron and magnesium. Concentrations of iron in these wells vary from 0.01 to 5.89 mg/L, with a mean of 1.13 mg/L. The NSDWS for iron is 0.3 mg/L (Appendix B).

Like iron, manganese is derived from oxide, hydroxide, and sulfide compounds, and plant debris. The manganese carbonate, rhodochrosite is also fairly common and could be

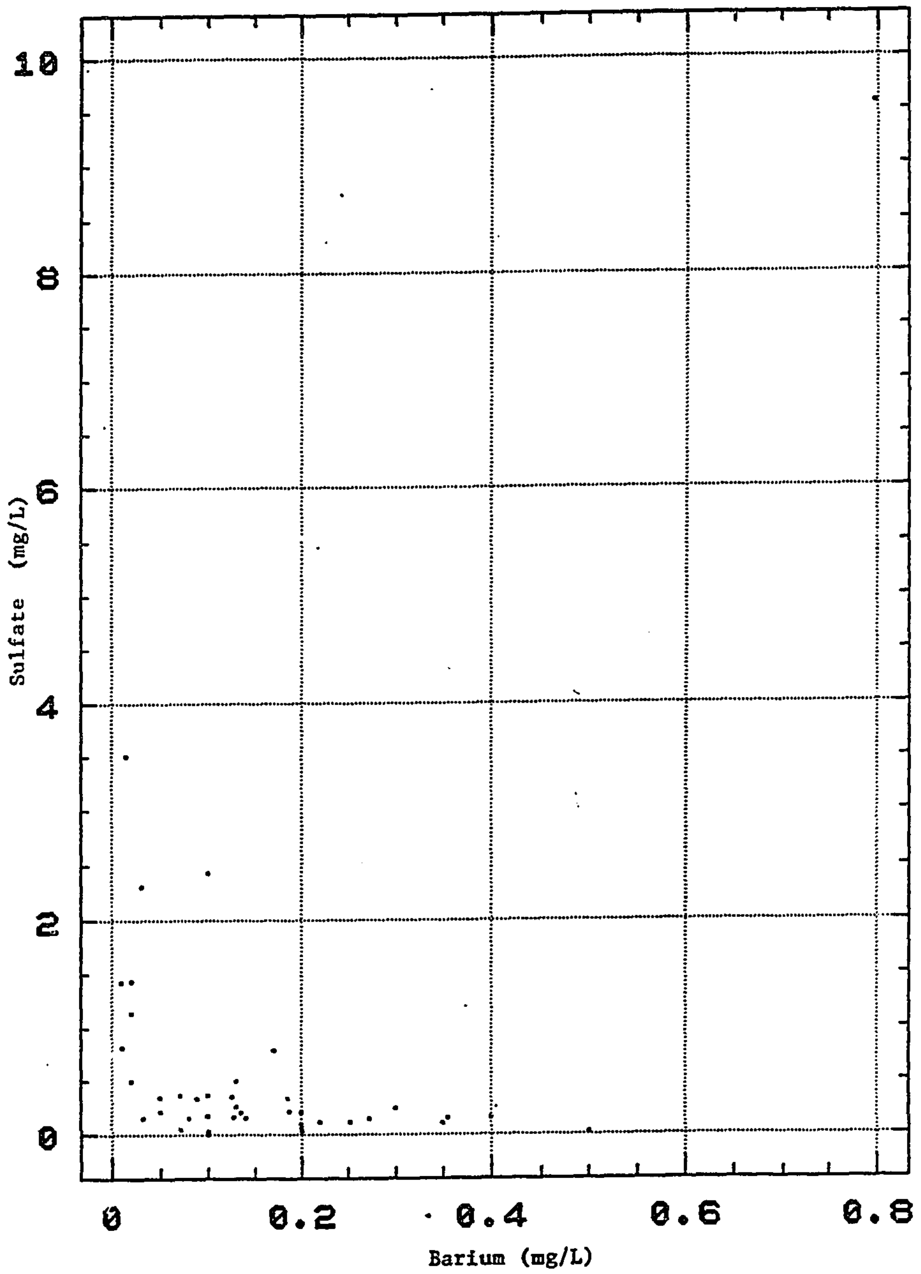


Figure 20. Scatter Plot of Iron and Bicarbonate Alkalinity for the Glacial Drift Aquifer.

a source of manganese in the drift. Figure 21 is the scatter plot for manganese and alkalinity. A small positive trend can be seen, but most of the manganese appears to originate from other sources. No correlation was found between manganese and silica (data not shown). Concentrations of manganese in the background drift wells range from 0.01 mg/L to 1.19 mg/L, with a mean of 0.08 mg/L. The NSDWS for manganese is 0.05 mg/L (Appendix B).

Sodium was detected in only five of the background drift wells. Values in these wells ranged from 1.1 to 61 mg/L, with a mean of 17.5 mg/L. Sources of sodium include precipitation, the weathering of albite, and the dissolution of halite. The average sodium concentration in precipitation over the west Michigan area is 0.14 mg/L (Drever, 1988). The sample set of five wells was too small to obtain a good correlation between sodium and silica. Halite residues might exist in the shale clasts in the drift, and dissolution of halite could provide some of the sodium detected.

Chloride concentrations in the glacial drift ground water of southwest Michigan are naturally very low. The dissolution of chloride-bearing minerals such as sodalite and apatite, which may be present in the igneous fraction of the drift materials, or halite residues that may occur in the sedimentary clasts of marine shales or sandstones, could contribute chloride to the ground water. A more

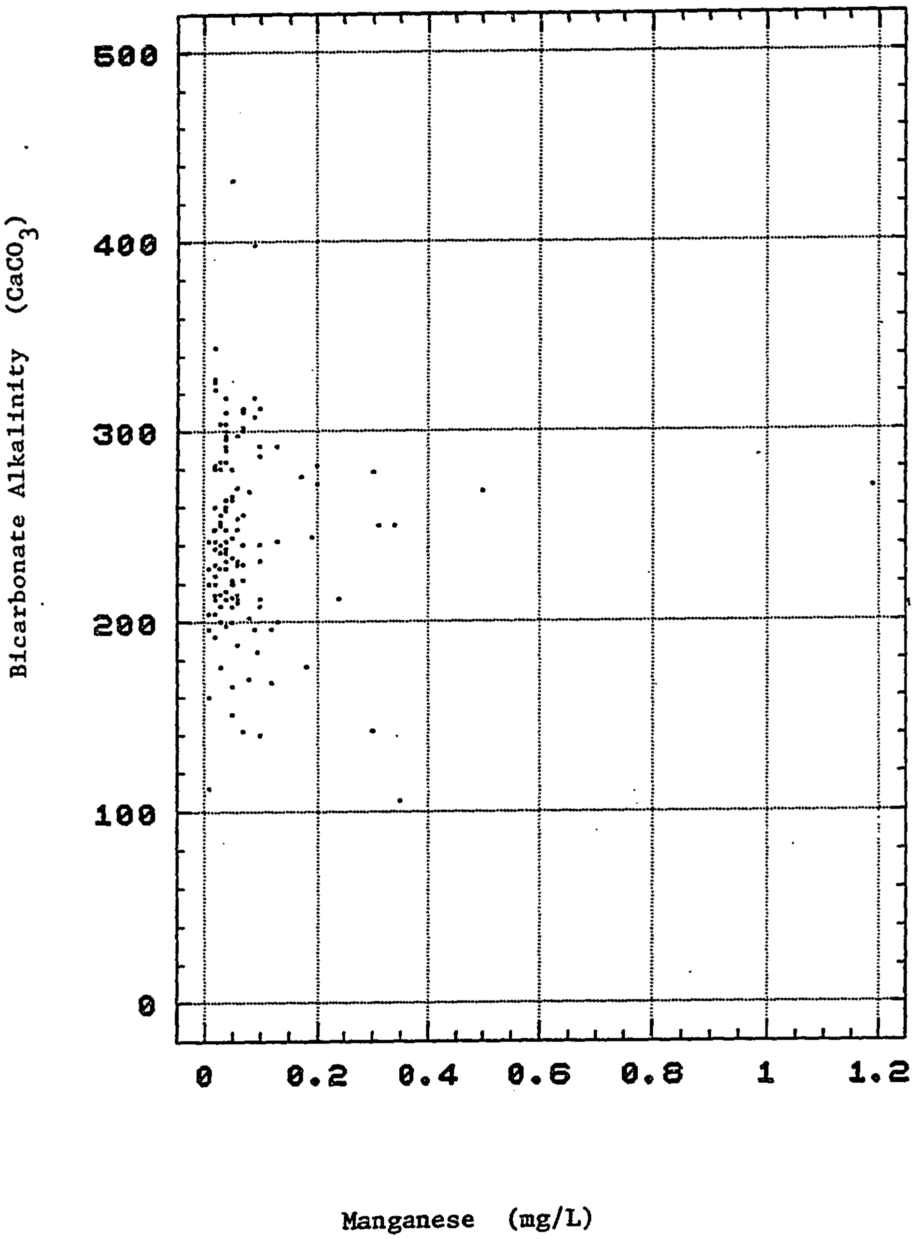


Figure 21. Scatter Plot of Manganese and Bicarbonate Alkalinity for the Glacial Drift Aquifer.

definite contributor is precipitation. The average chloride concentration in precipitation over west Michigan is about 0.15 milligrams per liter (Drever, 1988). The concentration of chloride in the non-degraded drift wells ranges from 1 mg/L to 8 mg/L, with a mean of 3.8 mg/L. The NSDWS for chloride is 250 mg/L (Appendix B).

The bulk of naturally occurring nitrate in ground water is produced by action of nitrogen-fixing bacteria in the soil zone. Nitrogen present in tissues of plants and animals is released as ammonia. Ammonia is oxidized first to nitrite, then to nitrate by purple photosynthetic bacteria. Nitrates also reach the subsurface directly through precipitation. Nitrate dissolved in rainwater is produced either from oxidation of nitrogen gas in the atmosphere or from photochemical oxidation of ammonia (Feth, 1966).

Geologic sources for nitrates include cave deposits, caliche deposits and playa lake deposits. Barry County contains none of these types of deposits. Nitrate is very scarce to absent in rock matrices (Feth, 1966). Nitrate concentrations in the non-degraded drift wells range from 0 to 4.9 mg/L, with a mean of .3 mg/L. The NPDWS for nitrate is 10 mg/L (Appendix B).

Sources for ammonium ions (NH_4^+) in these wells are similar to those for nitrate ions. Organic nitrogen is converted to an ammonium ion through ammonification in the soil zone when plants decompose. Ammonium is also present in precipitation. Most ammonium is oxidized to nitrate or adsorbed onto soil particles before reaching the water table. However, in reducing environments, NH_4^+ can be produced by a nitrate reduction reaction (Freeze and Cherry, 1979). Ammonium ions are also found in mineral lattices as a substitute for K^+ (Hem, 1989). Ammonium concentrations in the drift wells vary from 0 to 0.4 mg/L. The mean value is 0.10 mg/L.

Hardness values reported in terms of the equivalent concentration of calcium carbonate, range from 115 to 477 mg/L $CaCO_3$ with a mean value of 273 mg/L, for the background drift wells. Hardness can be approximated by substituting milligrams per liter of calcium and magnesium into the following equation:

$$\text{total hardness} = 2.5(Ca^{2+}) + 4.1(Mg^{2+})$$

Thus these values also are an indication of the calcium and magnesium content of the water, although hardness values do include concentrations of other metal ions. Ground water with a hardness concentration greater than 150 mg/L is categorized as "very hard." Ground water designated as "soft" has less than 60 mg/L (Freeze and Cherry, 1979). Ground water in Barry County is "hard" to "very hard." This is typical of the ground water in the glacial sediments of west Michigan.

Specific electrical conductance provides an indication of ionic concentrations in the ground water, since electrical conductivity is directly proportional to total dissolved solids. The range of values for electrical conductivity in the background glacial drift wells is 177 to 748 micromhos per centimeter. The mean value is 413.4 umhos/cm. It is used as a means for comparing the general water chemistry of aquifers.

As mentioned before, field pH measurements were not obtained for wells sampled in this study. Although pH measurements were made in the laboratory, gains or losses of carbon dioxide as well as oxidation of ferrous iron in samples that are opened and exposed to atmosphere in the laboratory can change the pH value as much as a full unit when compared to the field value (Hem, 1989). Therefore laboratory pH values are not considered reliable indicators of in-situ conditions.

The pH of ground water is directly influenced by reactions involving hydrolysis, dissociation of acids, dissolution of solids and oxidation/reduction. For example, the dissociation of carbonic acid produces H^+. Oxidation of pyrite also produces H^+. H^+ is a reactant in the dissolution of carbonate and silicate minerals. Increases in the activity of the hydrogen ion result in an increase in the acidity of ground water. A range of pH values for ground water in the glacial drift in Barry County can only be estimated by the types of ions present.

The high bicarbonate concentration indicates that the pH is in a range common to most ground water, between 6 and 9 (Figure 15). Lack of field pH and temperature measurements limits the amount of quantitative analysis that can be done on these samples. Future studies of individual townships or other smaller areas must include these field parameters.

Degraded Drift Wells

The degraded drift wells were divided into those with elevated chloride, those with elevated nitrate, and those with elevated ammonium concentrations. These three parameters are most diagnostic for ground water affected by human activity, because there are no known natural sources for high concentrations of these ions in the glacial drift of southwest Michigan. Summary statistics for each sample set are given in Tables 2, 3, and 4.

Chloride concentrations in the degraded wells vary between 10 and 97 milligrams per liter. The mean value is 27.3 mg/L, compared to 3.8 mg/L in the non-degraded drift wells. The only natural source for elevated chloride levels in the glacial drift ground water would be inflow of ground water from the Coldwater Shale. However, samples collected from wells in the area underlain by this formation (in the southwest part of Barry County) show the lowest chloride concentrations in Barry County. Other sources for increased chloride include use of sodium

Table 2

Summary Statistics for Chloride-degraded Wells

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Total alkalinity	mg/l-CaCO3	33	249	248	61	76	389	313	212	288	-0.03
Ammonium	mg/l	24	0.15	0.04	0.44	0.03	2.20	2.17	0.03	0.08	4.80
Barium	mg/l	32	0.07	0.06	0.05	0.01	0.25	0.24	0.04	0.09	1.67
Calcium	mg/l	33	92	84	29	34	200	166	75	109	1.75
Chloride	mg/l	33	27.3	16	23.7	10.0	97.0	87	14.0	26.0	2.08
Spec. Conductance	umhos/cm	32	559	534	158	259	1000	741	464	605	0.73
Total hardness	mg/l-CaCO3	33	324	310	73	141	518	377	289	354	0.34
Iron	mg/l	16	0.93	0.35	1.36	0.02	5.50	5.48	0.20	1.20	2.83
Magnesium	mg/l	33	28	25	9	9	56	47	23	31	0.86
Manganese	mg/l	16	0.10	0.06	0.10	0.01	0.39	0.38	0.04	0.10	2.19
Nitrate	mg/l	33	3.4	1.8	4.8	0.0	21.6	21.6	0.0	4.5	2.17
Potassium	mg/l	33	4.0	2.6	3.8	0.8	16.0	15.2	1.5	4.7	2.10
Silica	mg/l	33	6	5.6	3	3	20	17	4.6	6.5	3.10

Table 2--Continued

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Sodium	mg/l	13	18.9	15.0	9.8	0.0	34.0	34	14.0	26.0	-0.15
Sulfate	mg/l	33	39	33	28	3	123	120	23	45	1.61

Table 3

Summary Statistics for Nitrate-degraded Wells

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Total alkalinity	mg/l-CaCO3	22	227	216	45	144	316	172	196	268	0.15
Ammonium	mg/l	8	0.04	0.04	0.01	0.03	0.05	0.02	0.03	0.05	0.28
Barium	mg/l	22	0.05	0.04	0.04	0.01	0.15	0.14	0.03	0.08	1.00
Calcium	mg/l	22	84	77	30	50	200	150	70	89	2.97
Chloride	mg/l	13	20.2	15	13.6	8.0	45.0	37	9.0	26.0	0.96
Spec. Conductance	umhos/cm	22	488	492	95	281	612	331	428	584	-0.54
Total hardness	mg/l-CaCO3	22	303	305	47	197	393	196	276	341	-0.31
Iron	mg/l	4	--	--	--	--	--	--	--	--	--
Magnesium	mg/l	22	26	24	9	10	56	46	23	29	1.92
Manganese	mg/l	2	--	--	--	--	--	--	--	--	--
Nitrate	mg/l	21	8.6	7.1	3.9	5.1	21.6	16.5	6.1	9.8	2.15
Potassium	mg/l	22	4.2	2.5	4.1	0.8	15.0	14.2	1.1	5.3	1.49
Silica	mg/l	22	6	5.5	3	3	20	17	4.5	6.4	3.53

Table 3--Continued

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Sodium	mg/l	4	--	--	--	--	--	--	--	--	--
Sulfate	mg/l	22	24	22.5	8	12	44	32	18	30	0.84

-- Statistics not calculated due to small sample size

Table 4

Summary Statistics for Ammonium-degraded Wells

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Total alkalinity	mg/l-CaCO3	11	277	266	75	200	400	200	212	358	0.53
Ammonium	mg/l	11	1.04	0.85	0.64	0.50	2.60	2.1	0.60	1.11	1.83
Barium	mg/l	11	0.16	0.08	0.23	0.04	0.80	0.76	0.04	0.15	2.74
Calcium	mg/l	11	71	76	17	28	94	66	66	82	-1.53
Chloride	mg/l	5	4.8	3	3.9	1.0	9.0	8	2.0	9.0	0.46
Spec. Conductance	umhos/cm	11	429	434	84	327	616	289	356	472	0.85
Total hardness	mg/l-CaCO3	11	269	255	85	108	468	360	235	297	0.72
Iron	mg/l	8	3.69	4.10	1.85	0.20	5.50	5.3	2.60	5.20	-1.02
Magnesium	mg/l	11	19	19	8	3	36	33	16	25	0.16
Manganese	mg/l	10	0.13	0.10	0.10	0.04	0.31	0.27	0.07	0.20	1.06
Nitrate	mg/l	11	0.8	0.0	1.7	0.0	4.9	4.9	0.0	0.4	2.05
Potassium	mg/l	11	2.0	1.9	1.2	0.6	3.4	2.8	0.9	3.2	0.04
Silica	mg/l	11	11	6	11	1	34	33	5	8.7	1.77

Table 4--Continued

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Sodium	mg/l	1	--	--	--	--	--	--	--	--	--
Sulfate	mg/l	11	16	12	18	0	55	55	0	26	1.15

-- Statistics not calculated due to samll sample size chloride or calcium chloride in road deicing operations. The wells containing increased chloride are distributed sporadically around the county. All residences with wells containing degraded water are located on major county roads, but many other residences on these roads are unaffected. Non-degraded wells located along major county roads could be screened in discharge zones where the ground water is migrating up from the water table. In addition discontinuous clay layers in the glacial drift could be acting as a barrier to migration of chloride-degraded water to the well screen. The stratigraphy of individual wells was not investigated in this study.

Elevated concentrations of chloride could be the result of degradation from septic tank effluent. One study demonstrated that domestic sewage can contain between 20 and 50 mg/L of chloride (Cantor, Knox, and Fairchild, 1977). Therefore septic systems are a potential source of high chloride concentrations in ground water (Feth, 1966).

Nitrate concentrations range from 5.1 to 21.6 mg/L in the nitrate-degraded glacial drift wells. The mean value is 8.6 mg/L. The background wells have concentrations ranging from 0 to 4.9 milligrams per liter. The nitrate-degraded wells, like the chloride-degraded wells, are randomly distributed. Nitrate is a common cause of ground water degradation because nitrogen is a major component of agricultural fertilizers. An estimated 50% of applied nitrogen fertilizer infiltrates to ground-water reservoirs (Cantor et al., 1977). When precipitation and irrigation exceed plant requirements, plant roots no longer absorb nitrate ions from the soil water and substantial amounts of nitrate can reach the water table.

Nitrate also enters ground water directly from septic tank effluent. The nitrate ion is highly soluble and unretarded by adsorption onto aquifer materials. A California study of domestic sewage showed that effluent can increase concentrations of nitrate by 20-40 mg/L in excess of background values (Feth, 1966). Nitrogen is released to the subsurface as ammonia nitrogen and as nitrate nitrogen. In an oxidizing environment, ammonia nitrogen will be converted to nitrate. Septic systems that are located above vulnerable aquifers can contribute substantially to the deterioration of ground water quality by nitrate.

Ammonium can also enter ground water via septic tanks and inefficient septic systems. One study of conventional septic systems (Cantor et al., 1977) revealed that 10 to 78 mg/L of ammonia nitrogen reaches the water table, depending on the adsorption capacity of the soil. Concentrations in the degraded wells are much lower than this, between 0.5 and 2.6 mg/L, with a mean value of 1.04 mg/L. Specific causes of elevated ammonium and nitrate concentrations in individual wells were not investigated in this study.

Background/Degraded Well Comparison

The purpose for classifying glacial drift wells as background or degraded was to determine whether other parameters in the degraded wells deviated from natural background variations. A comparison of data from degraded wells with that from background wells was performed using the two-sample tests described earlier. Results of these tests are shown in Tables 5, 6, and 7. Statistical differences were found for several parameters.

In samples collected from the chloride-degraded wells, concentrations of calcium, magnesium, potassium and nitrate were increased. Specific electrical conductance and hardness values were also increased. Bicarbonate concentrations were similar to those in the background glacial drift water. The differences can be displayed on box-and-whisker plots (Figure 22). Elevated hardness, calcium and magnesium values suggest that chloride-degraded recharge either contains higher calcium and magnesium (from calcium chloride or calcium/magnesium acetate compounds used in road deicing), or causes increased dissolution of calcite and dolomite. Since bicarbonate values are not affected, the first option seems more plausible. Increased nitrate may indicate that the degradation of these wells is in part due to releases of sewage effluent which contains both chloride and nitrate.

Table 5

Two-sample Test Results from Comparison of Background and Chloride-degraded Wells

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values		Decision***
			Background	Degraded	
Alkalinity	equal	MWW	239	248	Similar
Ammonium	unequal	95% CI	0.1	0.15	Similar
Barium	unequal	95% CI	0.1	0.07	Different
Calcium	unequal	95% CI	71	92	Different
Chloride	unequal	95% CI	3.8	27.3	Different
Spec. Conductance	unequal	95% CI	413	559	Different
Hardness	unequal	95% CI	273	324	Different
Iron	equal	MWW	0.8	0.35	Similar
Magnesium	unequal	95% CI	23	29	Different
Manganese	equal	MWW	0.04	0.06	Similar
Nitrate	unequal	95% CI	0.3	3.4	Different
Potassium	unequal	95% CI	2	4	Different
Silica	unequal	95% CI	8	6	Different
Sodium	unequal	95% CI	17.5	18.9	Similar

Table 5--Continued

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Background	Median/Mean Values Degraded	Decision***
Sulfate	unequal	95% CI	29.5	39	Similar

* Procedure tests the hypothesis that the ratio of sample variances is equal to 1.0 at the 95% confidence level.

** For unequal variances, the 95% confidence level for the difference in means is used. For equal variances, the Mann-Whitney-Wilcoxin test for the difference in medians is used.

*** Similar=sample means or medians come from similar populations, and are equal at the 5% level of significance.
Different=sample means or medians are not equal at the 5% level of significance.

Table 6

Two-sample Test Results from Comparison of Background and Nitrate-degraded Wells

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Background	Degraded	Decision***
Alkalinity	equal	MWW	239	216	Similar
Ammonium	unequal	95% CI	0.1	0.04	Different
Barium	unequal	95% CI	0.1	0.05	Different
Calcium	unequal	95% CI	71	84	Similar
Chloride	unequal	95% CI	3.8	20.2	Different
Spec. Conductance	equal	MWW	401	491.5	Different
Hardness	equal	MWW	269.5	305	Different
Iron	N/A	N/A	N/A	0.35	N/A
Magnesium	unequal	95% CI	25.9	22.8	Similar
Manganese	N/A	N/A	N/A	N/A	N/A
Nitrate	unequal	95% CI	0.32	8.62	Different
Potassium	unequal	95% CI	1.98	4.18	Different
Silica	unequal	95% CI	7.8	6	Different
Sodium	N/A	N/A	N/A	N/A	N/A

Table 6--Continued

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Background	Median/Mean Values Degraded	Decision***
Sulfate	unequal	95% CI	29.5	24.1	Different

* Procedure tests the hypothesis that the ratio of sample variances is equal to 1.0 at the 95% confidence level.

** For unequal variances, the 95% confidence level for the difference in means is used. For equal variances, the Mann-Whitney-Wilcoxin test for the difference in medians is used.

*** Similar=sample means or medians come from similar populations, and are equal at the 5% level of significance.
Different=sample means or medians are not equal at the 5% level of significance.

N/A Not analyzed due to small sample size

Table 7

Two-sample Test Results from Comparison of Background and Ammonium-degraded Wells

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Background	Degraded	Decision***
Alkalinity	equal	MWW	239	266	Similar
Ammonium	unequal	95% CI	0.1	1.04	Different
Barium	unequal	95% CI	0.1	0.16	Different
Calcium	equal	MWW	70	76	Similar
Chloride	unequal	95% CI	3.8	4.8	Similar
Spec. Conductance	equal	MWW	401	434	Different
Hardness	unequal	95% CI	273	269	Similar
Iron	equal	MWW	0.8	4.1	Different
Magnesium	equal	MWW	22.8	19	Similar
Manganese	equal	MWW	0.04	0.1	Different
Nitrate	equal	MWW	0	0	Different
Potassium	equal	MWW	1.5	1.9	Different
Silica	unequal	95% CI	7.8	10.7	Similar
Sodium	N/A	N/A	N/A	N/A	N/A

Table 7--Continued

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Background	Degraded	Decision***
Sulfate	equal	MWW	26	12	Different

* Procedure tests the hypothesis that the ratio of sample variances is equal to 1.0 at the 95% confidence level.

** For unequal variances, the 95% confidence level for the difference in means is used. For equal variances, the Mann-Whitney-Wilcoxin test for the difference in medians is used.

*** Similar=sample means or medians come from similar populations, and are equal at the 5% level of significance.
Different=sample means or medians are not equal at the 5% level of significance.

N/A Not analyzed due to small sample size

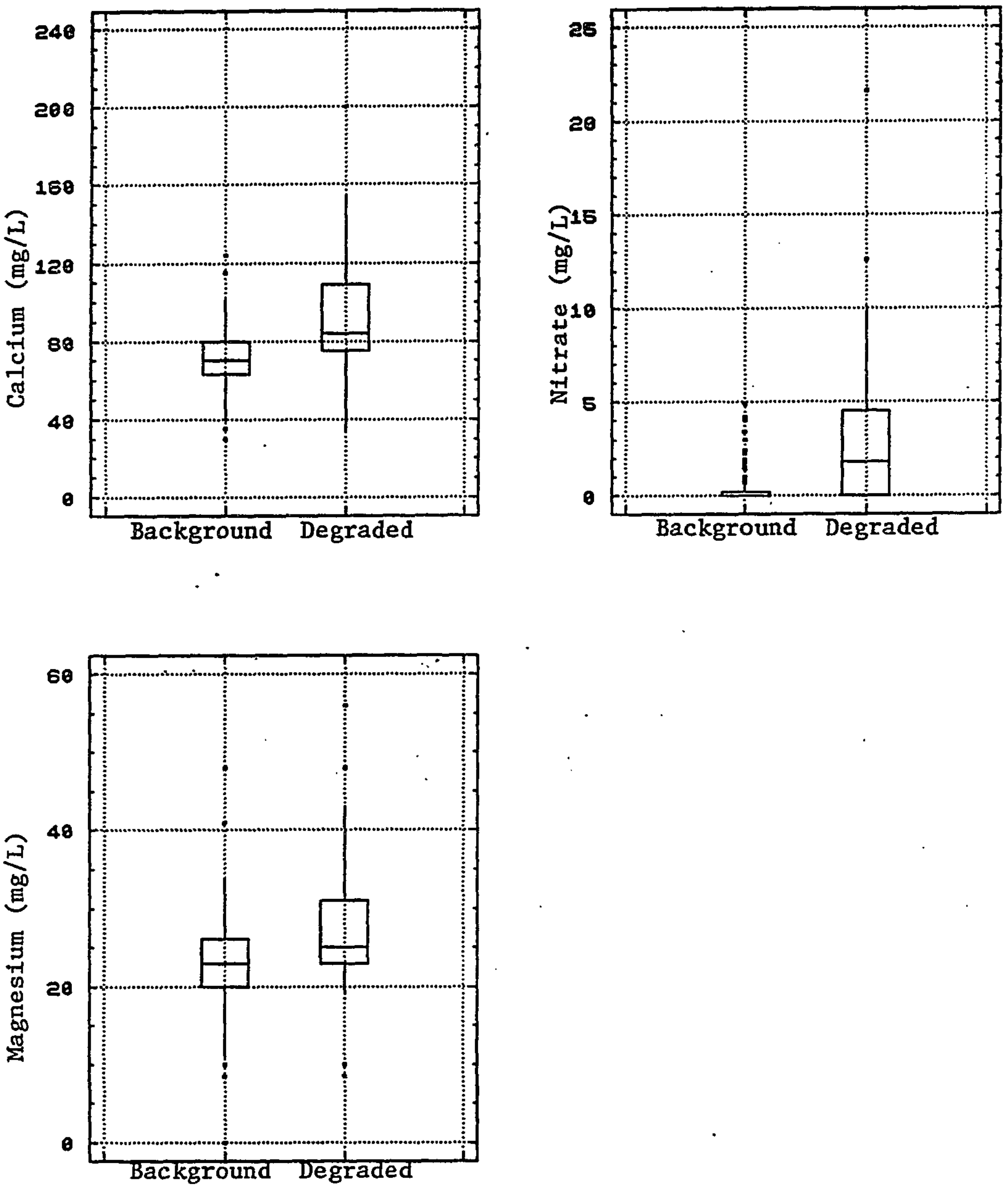


Figure 22. Concentrations of Calcium, Magnesium, and Nitrate in the Chloride-degraded Glacial Drift Ground Water.

Samples collected from the nitrate-degraded wells also showed increases in conductivity, hardness and calcium (Figure 23). In addition, potassium, sodium and chloride values were elevated. Magnesium and bicarbonate values were similar to background. The cause for increase in potassium and sodium concentrations is not known. Both ions are found in sewage effluent. Releases of septic tank effluent may cause increases in potassium and sodium concentrations. Potassium is also present in agricultural fertilizers which could infiltrate down to the water table. Elevated potassium in samples collected from nitrate-degraded wells could also be the result of degradation by agricultural fertilizers.

Samples collected from wells degraded by ammonium showed increases in iron and manganese. The remaining parameters were statistically similar. Increases in these redox controlled parameters imply lower redox conditions. The sulfate concentration was lower in the ammonium-degraded wells also. Although the Mann-Whitney-Wilcoxin test showed sulfate in the two data sets to be statistically similar, the hypothesis of equal means or medians was 2 percentage points away from being rejected. A decrease in sulfate would also be indicative of lower redox conditions. Because other parameters associated with septic tank effluent, such as calcium, magnesium, chloride, nitrate, and potassium are statistically similar for the

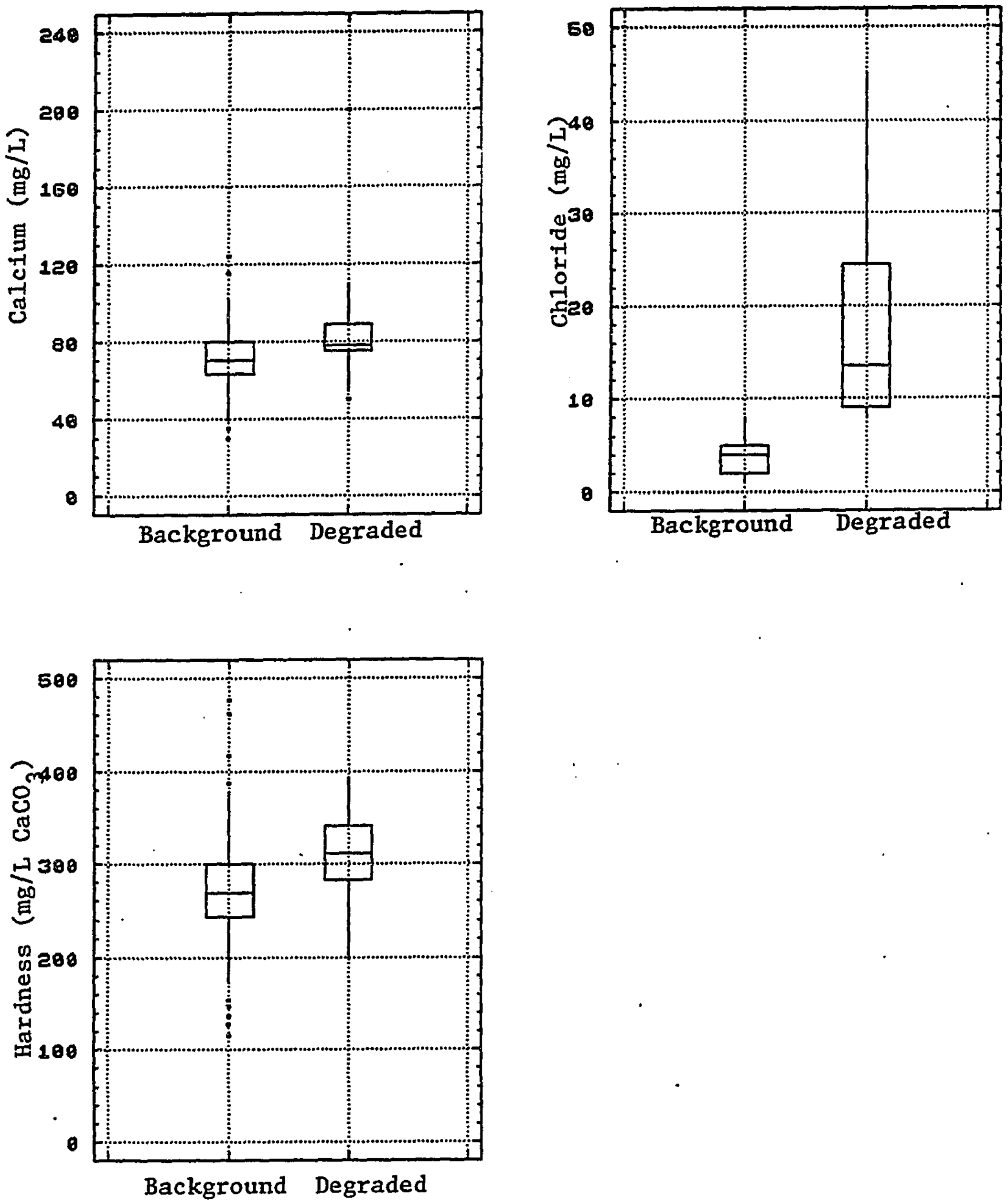


Figure 23. Concentrations of Calclium, Chloride, and Hardness in the Nitrate-degraded Glacial Drift Ground Water.

background drift and ammonium-degraded drift wells, the wells with high NH_4^+ might simply represent a natural variation in the ground-water chemistry rather than human degradation.

Bedrock Wells

Data from the bedrock well set consist of 46 chemical analyses from domestic wells, most of which are screened in the Marshall Sandstone. Summary statistics for chemical species in bedrock wells are given on Table 8. In general, the water quality of the bedrock aquifer is similar to that of the glacial drift aquifer. Parameters with the highest concentrations in bedrock samples are calcium, magnesium and bicarbonate. Ranges of concentration for these parameters are within those values for the glacial drift wells, with the exception of two high calcium values of 300 and 537 mg/L. The two bedrock wells with samples containing high calcium concentrations also have high sulfate concentrations.

Sulfate values in samples collected from the bedrock wells are similar to those collected from the glacial drift. Concentrations vary between 0 and 1310 mg/L with a mean value of 70 mg/L. The value of 1310 mg/L was not included in the statistical analyses. Mean value for the glacial drift wells is 29 mg/L. Three of the bedrock wells contained sulfate levels over the EPA NSDWS of 250 mg/L.

Table 8

Summary Statistics for Bedrock Wells

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Total alkalinity	mg/l-CaCO3	44	246	252	45	144	336	192	217	285.5	-0.26
Ammonium	mg/l	43	0.19	0.14	0.13	0.03	0.60	0.57	0.11	0.24	1.33
Barium	mg/l	44	0.16	0.13	0.15	0.01	0.80	0.79	0.06	0.20	2.21
Calcium	mg/l	43	81	67.3	46	41	300	259	58.1	82	4.29
Chloride	mg/l	12	25.8	2	51.1	1.0	178.0	177	1.0	32.0	2.80
Spec. Conductance	umhos/cm	44	546	447	352	305	1760	1455	381	514	2.83
Total hardness	mg/l-CaCO3	44	311	269	123	191	649	458	243	315.5	2.01
Iron	mg/l	39	1.58	1.00	1.51	0.10	5.50	5.40	0.40	2.50	1.31
Magnesium	mg/l	44	21	21	6	0.01	34	33.9	18.05	25	-0.68
Manganese	mg/l	42	0.05	0.04	0.04	0.01	0.20	0.19	0.02	0.07	2.24
Nitrate	mg/l	44	0.1	0.0	0.2	0.0	0.6	0.6	0.0	0.0	1.96
Potassium	mg/l	44	2.4	1.9	1.6	0.7	8.3	7.6	1.35	2.85	1.88
Silica	mg/l	44	8	7	5	4	26	22	6.22	7.35	2.56

Table 8--Continued

Parameter	Units	Sample Size	Mean	Median	Standard Deviation	Minimum	Maximum	Range	Lower Quartile	Upper Quartile	Skewness
Sodium	mg/l	8	49.8	39.5	39.1	12.0	129.0	117	19.5	69.5	1.29
Sulfate	mg/l	43	70	21	156	0	957	957	14	50	4.74

The two wells with highest concentrations of sulfate, 1310 and 957 mg/L, contained calcium concentrations of 537 and 81.2 milligrams per liter respectively. These calcium and sulfate concentrations most likely reflect wells that are screened in the gypsum-bearing Michigan Formation, instead of the Marshall Sandstone.

Background Drift/Bedrock Well Comparison

Apparent similarities between ground water in the glacial and bedrock aquifers was examined using two-sample tests. Results are shown in Table 9. No statistical differences were evident at the 95% confidence level for calcium, magnesium, alkalinity, hardness, chloride, and silica. Similarities between ground water in the glacial drift and bedrock aquifers are also obvious on box-and-whisker plots of these parameters (Figures 24 and 25). This similarity is further supported by the Piper Trilinear diagram, on which ground water from both aquifers plots in the same regions (Figure 26).

Differences exist in concentrations of ammonium, barium, iron, manganese, sulfate and potassium in ground water from the two aquifers. These parameters were more concentrated in ground-water samples collected from the bedrock aquifer and may in part explain higher specific conductance in the bedrock aquifer. Potassium values range from 0.7 to 8.3 mg/L, with a mean value of 1.9 mg/L.

Table 9

Two-sample Test Results from Comparison of Background Drift and Bedrock Wells

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Background	Median/Mean Values Bedrock	Decision***
Alkalinity	equal	MWW	239	252	Similar
Ammonium	unequal	95% CI	0.1	0.19	Different
Barium	unequal	95% CI	0.1	0.16	Different
Calcium	unequal	95% CI	71	81	Similar
Chloride	unequal	95% CI	3.8	25.8	Similar
Spec. Conductance	unequal	95% CI	413	546	Different
Hardness	unequal	95% CI	273	311	Similar
Iron	equal	MWW	0.8	1	Different
Magnesium	equal	MWW	23	20.9	Similar
Manganese	unequal	95% CI	0.08	0.05	Different
Nitrate	unequal	95% CI	0.32	0.08	Different
Potassium	unequal	95% CI	1.98	2.36	Different
Silica	unequal	95% CI	7.8	8.3	Similar
Sodium	N/A	N/A	N/A	N/A	N/A

Table 9--Continued

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values		Decision***
			Background	Bedrock	
Sulfate	unequal	95% CI	29.5	70	Different

* Procedure tests the hypothesis that the ratio of sample variances is equal to 1.0 at the 95% confidence level.

** For unequal variances, the 95% confidence level for the difference in means is used. For equal variances, the Mann-Whitney-Wilcoxin test for the difference in medians is used.

*** Similar=sample means or medians come from similar populations, and are equal at the 5% level of significance.
Different=sample means or medians are not equal at the 5% level of significance.

N/A Not analyzed due to small sample size

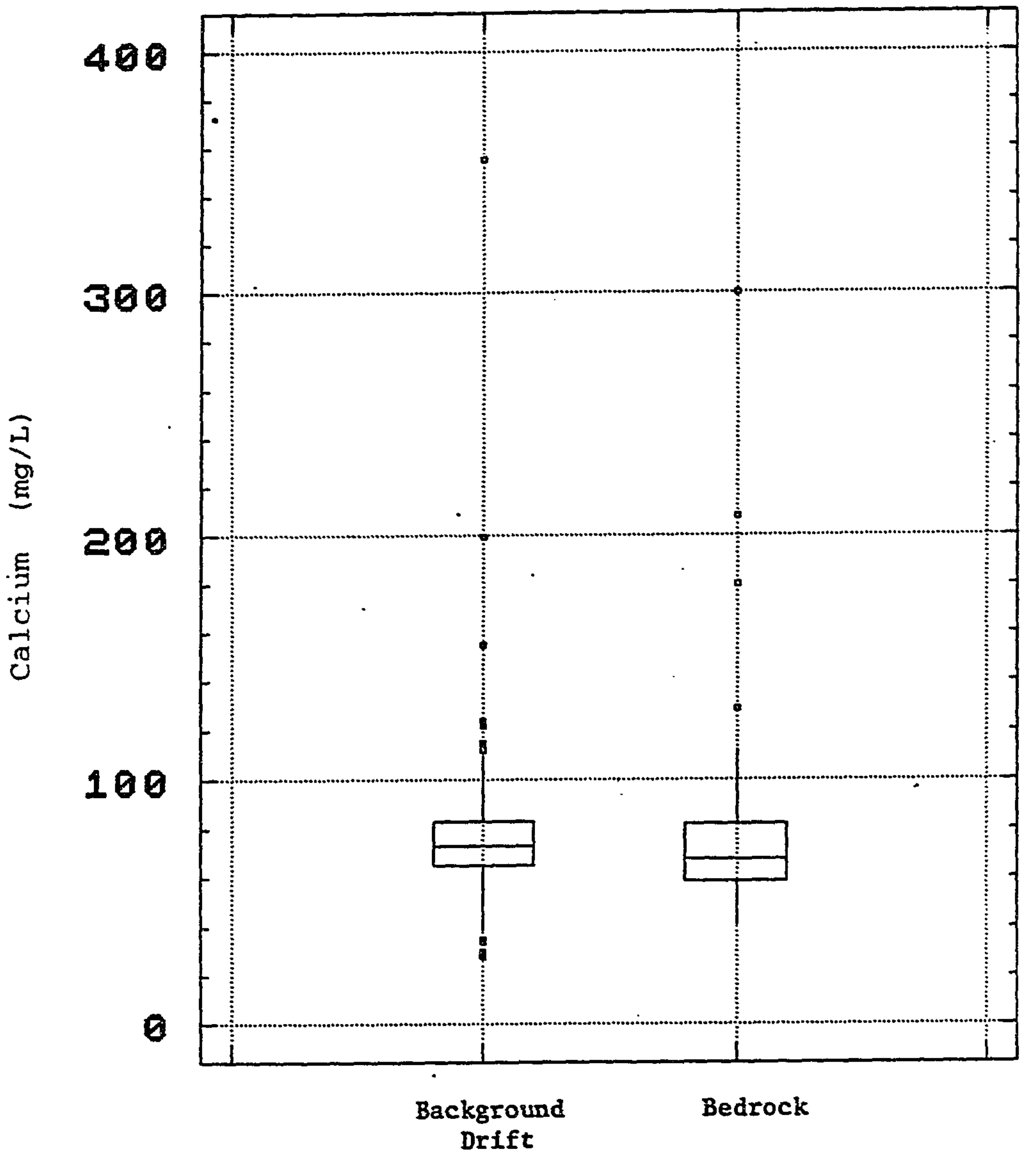


Figure 24. Calcium Concentrations in the Background Drift and Bedrock Ground Water.

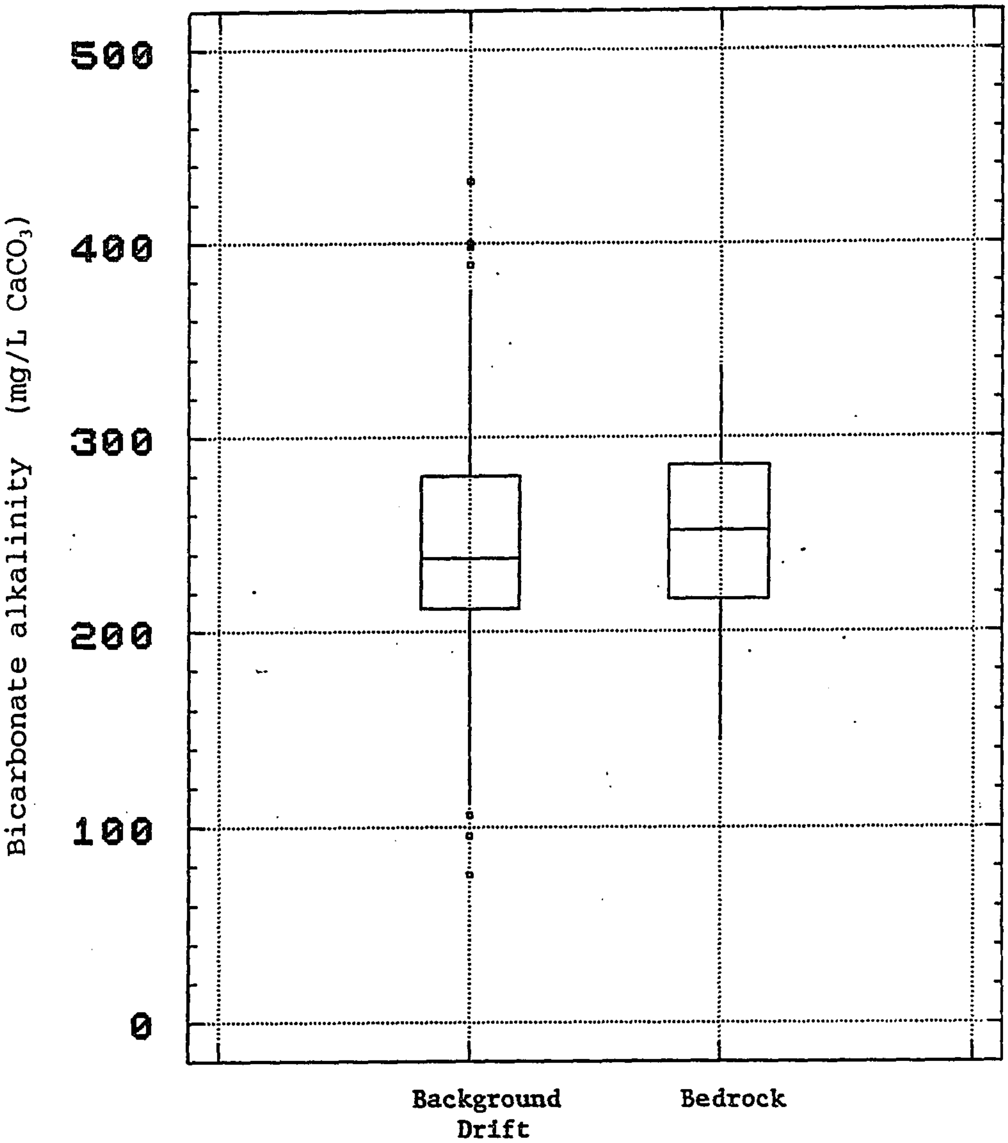


Figure 25. Bicarbonate Alkalinity Concentrations in the Background Drift and Bedrock Ground Water.

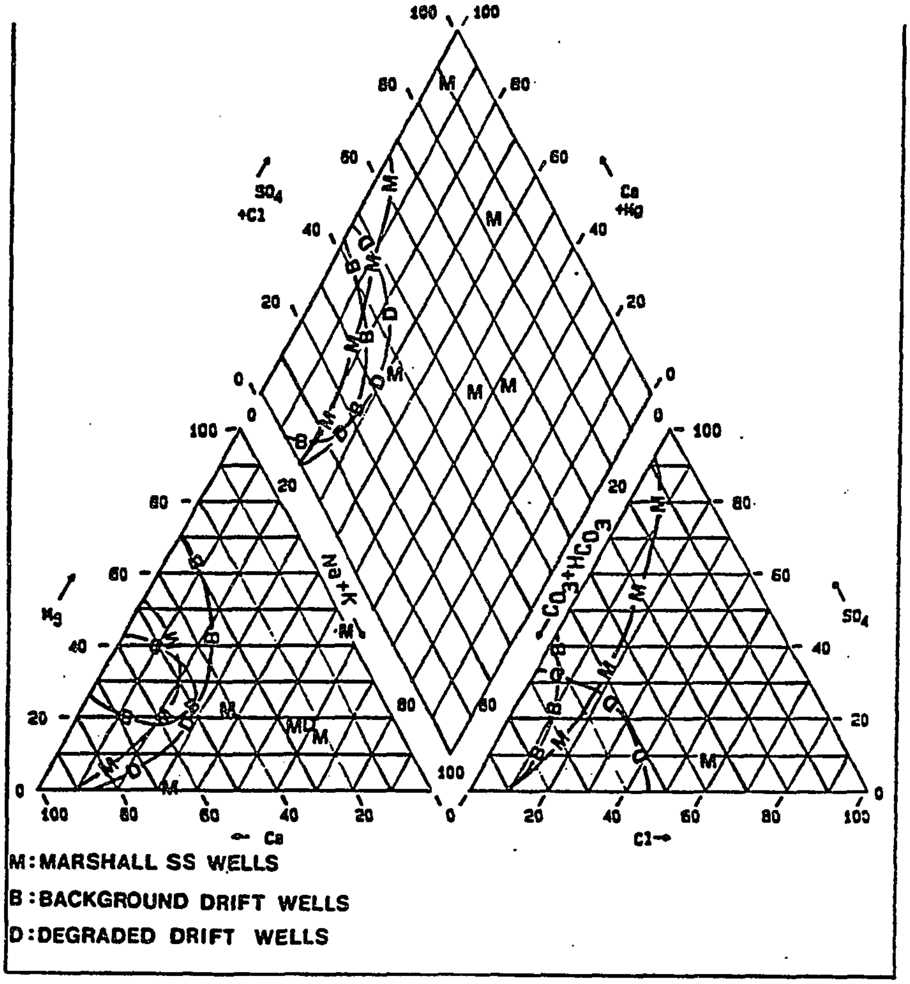


Figure 26. Piper Trilinear Diagram. Lower left triangle shows percentage of cations; lower right triangle shows percentage of anions; and diamond shows combined percentages of cations and anions. Anomalous values plotted as single points.

Barium values are between 0.10 and 0.80 mg/L, with a mean of 0.16 mg/L. The cause for the increase in potassium is uncertain. The Marshall Sandstone does contain potassium-bearing feldspars and mica; however, no correlation was evident on a scatter plot (data not shown) between potassium and silica for these wells. Scatter plots of barium versus alkalinity and sulfate (Figures 27 and 28), suggest that additional barium is probably coming from dissolution of witherite, and not from dissolution of barite.

Iron concentrations in ground water from bedrock are higher than those of glacial drift ground water. Values vary between 0.1 and 5.5 mg/L, with a mean concentration of 1.6 mg/L. The mean value for the glacial drift wells is 1.13 mg/L. Increase in iron concentration is most likely caused by lower redox conditions in the bedrock. Organic carbon present in the sandstone or in the recharge from the glacial drift may serve as an electron donor in dissolution of iron oxides and reduction of iron to the more soluble ferrous form. Additional iron may also be coming from dissolution of siderite ($FeCO_3$) as suggested by the scatter plot of iron versus alkalinity (Figure 29).

The increase in ammonium combined with a decrease in nitrate concentration, also suggests lower redox conditions in the bedrock. The ammonium concentrations range from 0.03 and 0.6 mg/L. The mean concentration in ground water

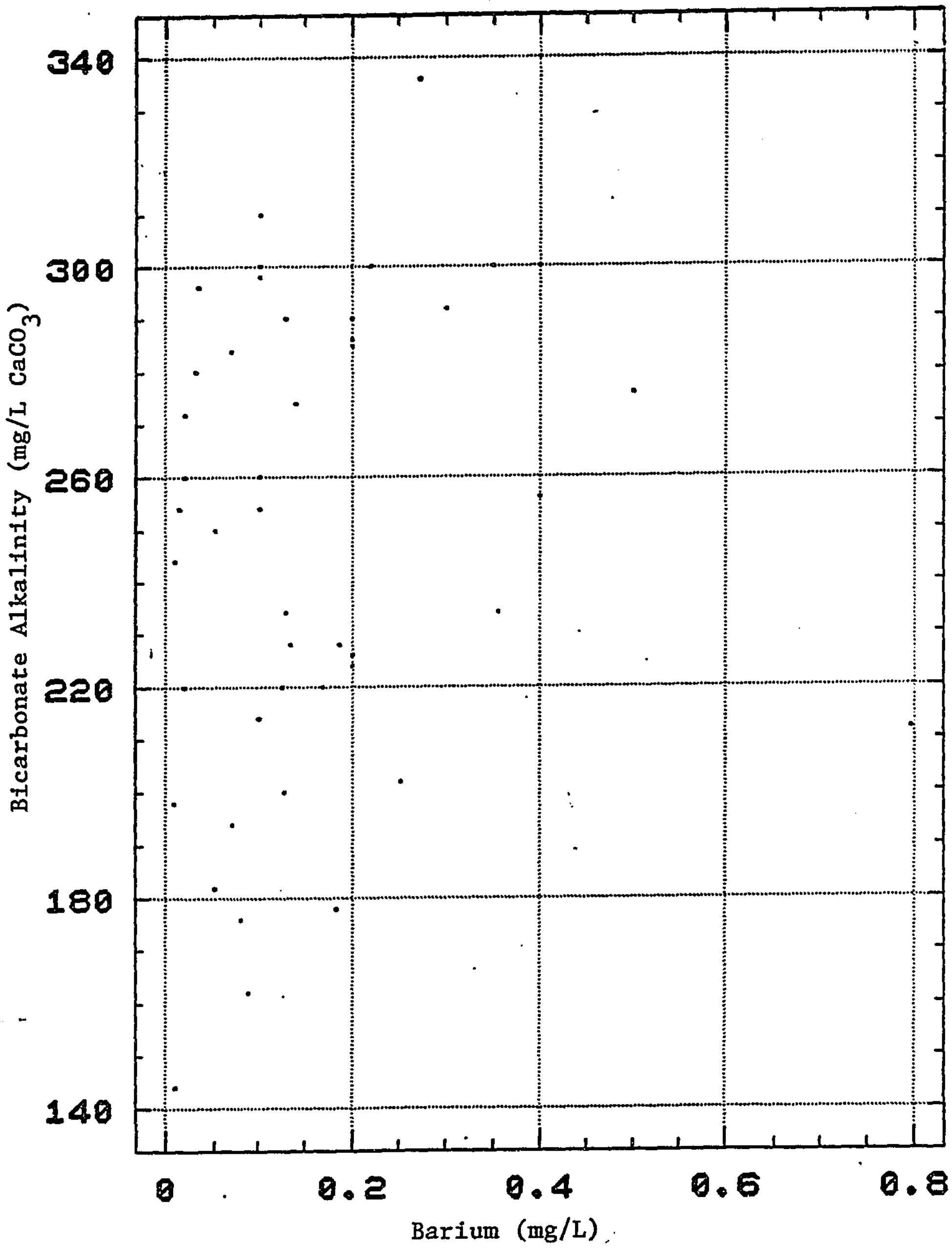


Figure 27. Scatter Plot of Barium and Bicarbonate Alkalinity for the Bedrock Aquifer.

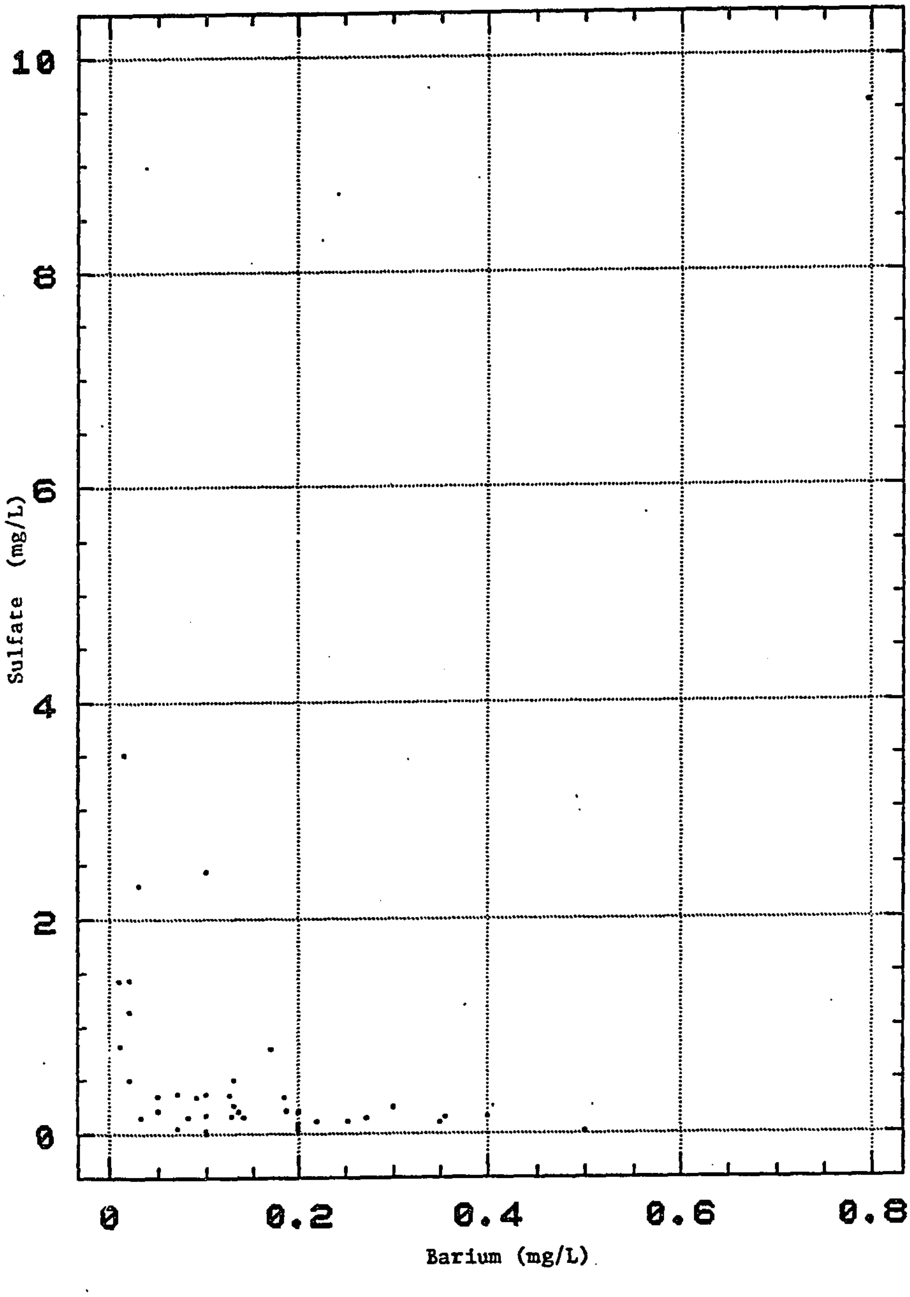


Figure 28. Scatter Plot of Barium and Sulfate for the Bedrock Aquifer.

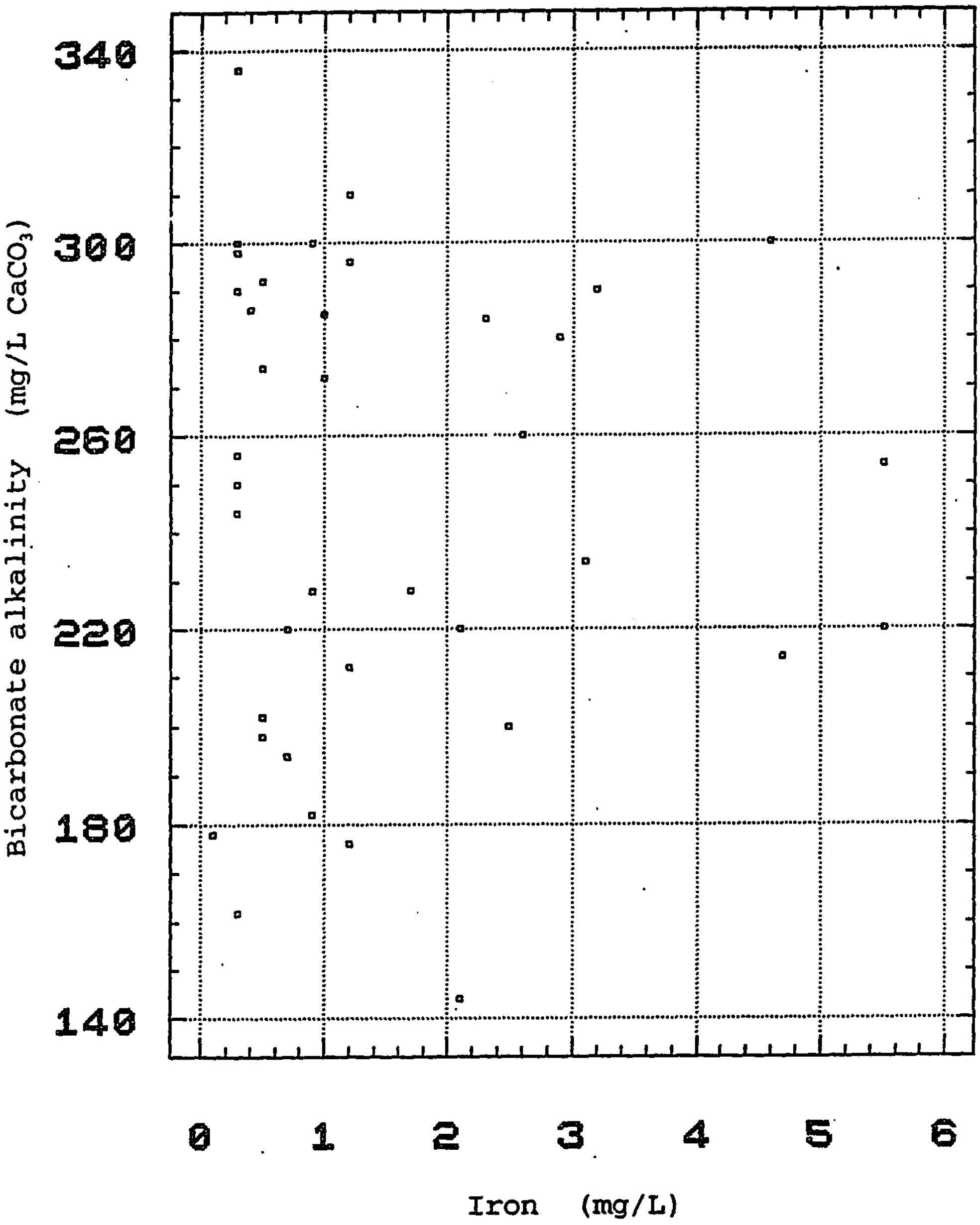


Figure 29. Scatter Plot of Iron and Bicarbonate Alkalinity for the Bedrock Aquifer.

from bedrock is 0.19 mg/L, compared to a mean of 0.10 mg/L in the background drift water.

Discussion

The ground water of the glacial drift aquifer in Barry County is a calcium-magnesium-bicarbonate water, classified by Freeze and Cherry (1979) as a Type-II glacial deposit ground water. This type of ground water is typical of glacial deposits in Michigan and southern Ontario (Freeze and Cherry, 1979). The primary chemical control of ground water quality in the glacial drift aquifer is open system dissolution of carbonate minerals in the drift. Rain percolating through the soil zone becomes enriched in carbon dioxide, typically to a partial pressure of 10^{-2} atmospheres. The supply of carbon dioxide is constant under open system conditions. Carbonic acid produced from carbon dioxide dissolving in ground water lowers the pH. Carbonic acid dissociates into bicarbonate ions and hydrogen ions. As the concentration of hydrogen ions increases, the pH decreases (Drever, 1988). As acidic ground water migrates though the vadose zone and comes in contact with carbonate minerals, the carbonates dissolve, releasing carbonate ions. Carbonate ions join with H^+ to form bicarbonate ions, reducing the activity of H^+ and consequently increasing the pH. Therefore carbonate minerals in the glacial drift act as a natural buffering system for pH fluctuations. Thermodynamic modeling performed on an area in northwest Calhoun County, near but outside the study area, suggests the ground water is in approximate chemical equilibrium with calcite and somewhat undersaturated with respect to dolomite (Western Michigan University, 1989). Lack of negative correlation between calcium and sodium, as well as between calcium and potassium, suggests that ion exchange is not a significant control on the hydrochemistry and that available exchange sites on aquifer materials are already saturated with calcium and magnesium rather than other cations.

The background water quality of the drift aquifer as measured by concentrations of the parameters in this study is acceptable for domestic purposes. Of the parameters in this study that are listed in the U.S. EPA drinking water standards only iron and nitrate were found to be higher than recommended standards. Iron concentrations above 0.3 mg/L are found in 64% of samples collected from the background glacial drift wells. Iron solubility is controlled principally by pH and redox conditions in the ground water. The presence of oxidized iron minerals and organic debris may favor reduction of ferric iron and production of a higher ferrous iron concentration. Ground water that is high in dissolved iron could indicate a regional or local contact between oxidizing and reducing conditions (Hem, 1989). No correlation however, exists between iron content and well depth for the background drift wells (data not shown).

Statistical comparison of degraded and background drift wells suggests that the chloride and nitrate degraded data sets represent ground water that deviates from natural background variations of the water chemistry in the drift aquifer. Although chloride levels do not exceed EPA NSDWS, they are indicative of the susceptibility of the drift aquifer to contamination. Elevated nitrate levels also demonstrate the susceptibility of the drift to non-point source contamination, and are of greater concern because of the potential health threat to infants and livestock. Five of the wells are above the EPA NPDWS of 10 mg/L for nitrate. In addition, the fact that these degraded wells are uniformly distributed around the county and are screened at a range of depths, suggests that the entire drift aquifer is vulnerable to degradation. The degraded wells were excluded from the remainder of the study in order to examine factors controlling the background water quality of the glacial drift.

The ground-water quality of the bedrock aquifer is within EPA drinking water standards for all parameters except iron. Ground-water samples collected from 31 of 46 bedrock wells have iron concentrations greater than the EPA SDWS of 0.3 mg/L. Ground water in the bedrock aquifer like the glacial drift water is a calcium-magnesium-bicarbonate water. Concentrations of calcium, magnesium, and bicarbonate in ground water from the bedrock are statistically similar to those from glacial drift ground water. The similarity of the major ion chemistry suggests that water in the bedrock aquifer is derived from the glacial drift aquifer.

Concentrations of the minor ions ammonium and iron in bedrock ground water were statistically higher than concentrations in the glacial drift ground water. These increases imply evolution of ground water within the bedrock aquifer. Longer residence times, slower flow velocities and the presence of organic matter could all contribute a reduced redox potential. Increases in barium and potassium may point to some changes in mineralogy, such as a greater abundance of barite ($BaSO_4$) in the overlying Michigan Formation, or a greater abundance of potassium silicate minerals in the Marshall Sandstone.

CHEMICAL CHANGES ALONG FLOW PATHS

Both the hydrogeology and hydrochemistry of the glacial drift and Marshall Sandstone aquifers demonstrate that the glacial drift is recharging the bedrock aquifer. This relationship suggests that mechanisms controlling drift water chemistry also control water chemistry of the Marshall Sandstone, at least initially. The remainder of this report explores other possible influences on background water chemistry. In addition to chemical controls already discussed: open system dissolution of carbonates, pH, and redox potential, certain physical controls must be examined. One of these variations in the water chemistry along ground-water flow paths.

Recharge/Transition/Discharge Comparisons

Results of two-sample analyses for changes along a flow path are given in Table 10. Statistically, only one difference were found between the recharge and discharge wells. Ammonium values were higher in samples collected from the recharge wells. All other parameters were similar. In addition, box-and-whisker plots of recharge, transition, and discharge wells illustrate the similarity in the data sets. Figure 30 represents a typical plot for most major ions. The typical systematic increase in ion

Table 10

Two-sample Test Results from Comparison of Background Recharge and Discharge Wells

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Recharge	Median/Mean Values Discharge	Decision***
Alkalinity	equal	MWW	236	234	Similar
Ammonium	unequal	95% CI	0.12	0.07	Different
Barium	unequal	95% CI	0.1	0.09	Similar
Calcium	equal	MWW	70	70	Similar
Chloride	equal	MWW	5	4	Similar
Spec. Conductance	equal	MWW	387	400	Similar
Hardness	equal	MWW	268	278	Similar
Iron	equal	MWW	0.6	1.1	Similar
Magnesium	equal	MWW	23	24	Similar
Manganese	equal	MWW	0.05	0.04	Similar
Nitrate	unequal	95% CI	0.25	0.12	Similar
Potassium	equal	MWW	1.3	1.5	Similar
Silica	equal	MWW	5.9	6.35	Similar
Sodium	N/A	N/A	N/A	N/A	N/A

Table 10--Continued

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Recharge	 Discharge	Decision***
Sulfate	equal	MWW	28	26	Similar

* Procedure tests the hypothesis that the ratio of sample variances is equal to 1.0 at the 95% confidence level.

** For unequal variances, the 95% confidence level for the difference in means is used. For equal variances, the Mann-Whitney-Wilcoxin test for the difference in medians is used.

*** Similar=sample means or medians come from similar populations, and are equal at the 5% level of significance.
Different=sample means or medians are not equal at the 5% level of significance.

N/A Not analyzed due to small sample size

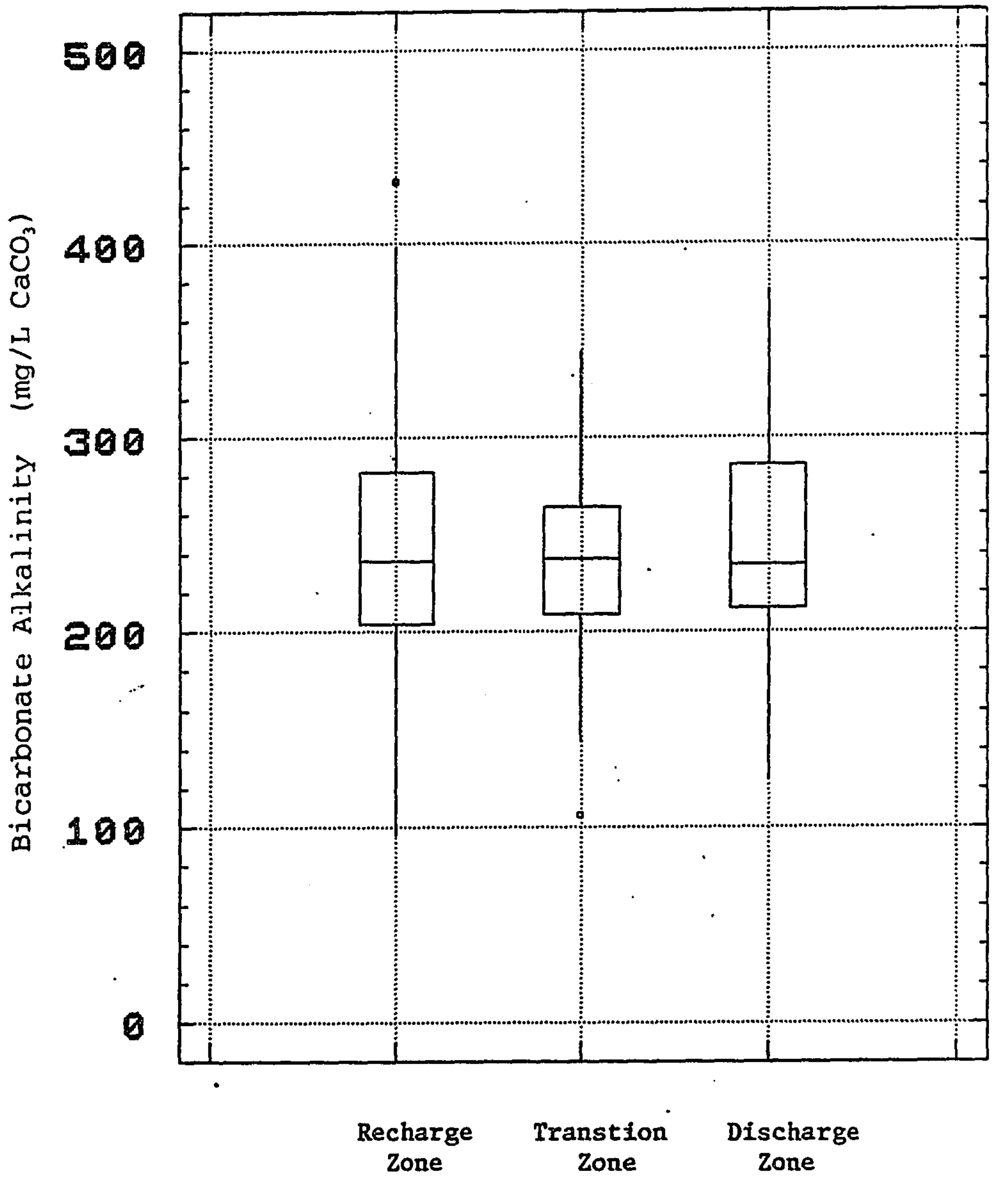


Figure 30. Bicarbonate Alkalinity Concentrations in the Recharge, Transition, and Discharge Zones of the Glacial Drift Aquifer.

concentration from recharge zone to discharge zone is absent. Iron did show a slight increase from recharge to discharge. Although this increase was not statistically significant, the hypothesis of equal means was one percentage point away from being rejected. Figure 31 illustrates the trend for iron. The increase in iron along the flow path may suggest that redox potential declines along the flow path or at least in the vicinity of discharge areas.

Discussion

As ground water migrates along flow paths from recharge to discharge areas, increases in most of the major chemical constituents occur in many aquifers (Freeze and Cherry, 1979). Lack of a systematic increase in the Barry County data could be a result of several factors. First, because wells sampled are uniformly distributed around Barry County, they do not represent the corresponding recharge and discharge zones of specific flow systems. In addition, an equal amount of recharge and discharge wells were not chosen for sampling. Therefore, true changes along an individual flow path from beginning to end may be hidden; for example although a well in a recharge zone was chosen to be sampled, the well in the discharge zone for that same flow path may not have been chosen. Second, the wells sampled may represent chemical concentrations along

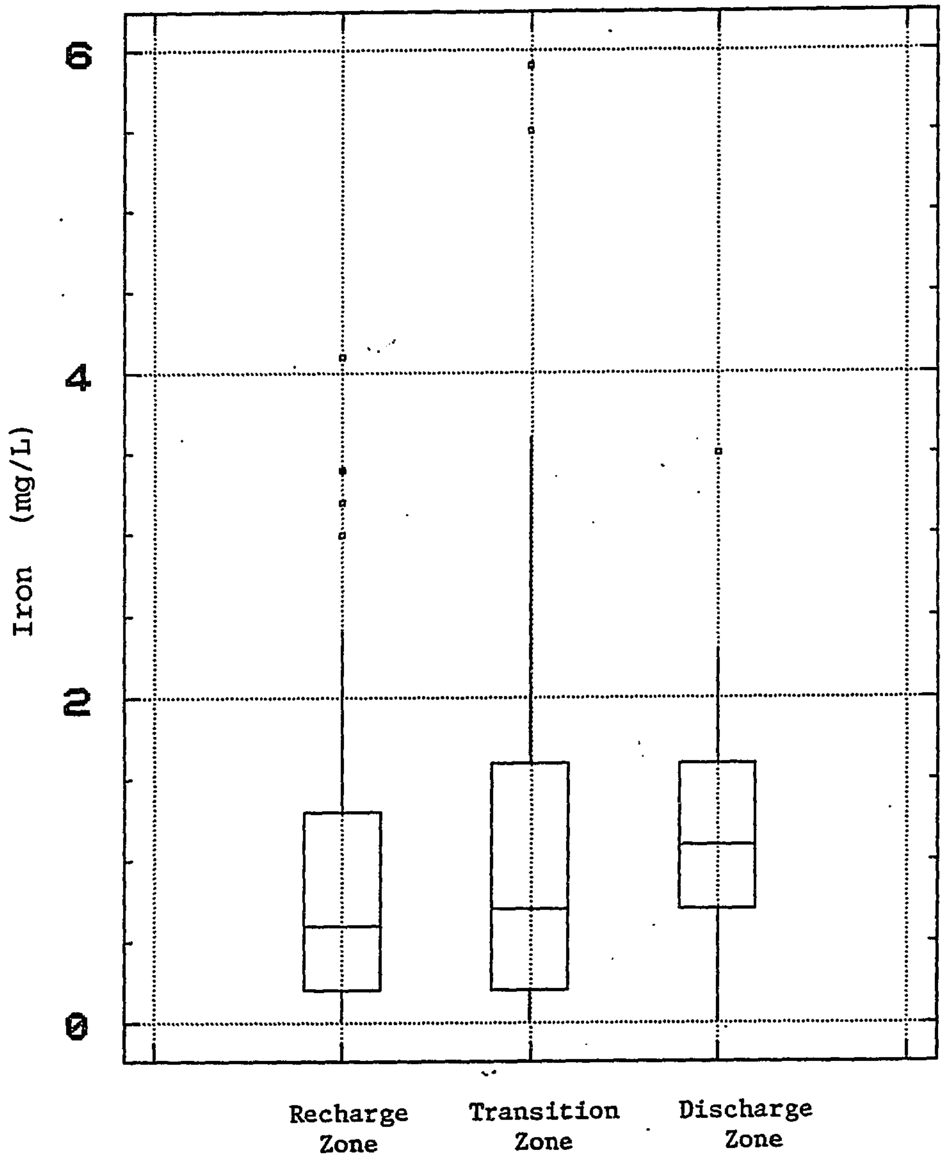


Figure 31. Concentrations of Iron in the Recharge, Transition, and Discharge Zones of the Glacial Drift Aquifer.

the horizontal or lateral portion of a flow path while normal chemical changes are likely occurring along vertical gradients. Third, ground-water recharge may vary in chemical quality depending on differences in vegetation, permeability, and mineralogy of the soil zone. The amount and type of vegetation determines the availability and distribution of organic matter in the soil zone. Decaying organic matter releases CO_2 which dissolves in ground water and decreases pH. The less permeable the soil zone, the longer acidic ground water stays in contact with materials in the soil zone. In contrast, the more permeable the soil zone, the faster infiltration occurs. Precipitation which infiltrates rapidly retains more dissolved oxygen gained during exposure to the atmosphere. Highly oxygenated ground water has a higher redox potential. In recharge areas with sandy or gravelly soils, shallow ground water commonly contains detectable oxygen (greater than about 0.1 mg/L). In recharge areas with silty or clayey soils, detectable oxygen is typically absent in shallow ground water (Freeze and Cherry, 1979). Such variation at the recharge area would result in differences in water quality unrelated to gradual changes along a flow path. Fourth, Reardon et al. (1980) demonstrated that ground water in a climatic and geologic setting similar to the study area reached equilibrium with carbonate minerals in the vadose zone, prior to reaching the water table. In the absence of ion exchange or other chemical reactions, major ions would not be expected to undergo large changes in concentration along short to moderate flow paths.

INFLUENCE OF LANDFORMS

In glacial interlobate regions such as Barry County, the variety of glacial landforms is a possible factor in water quality variations. This hypothesis was investigated by separating the background data set into samples from wells screened in morainal deposits (including till plains) and samples from wells screened in outwash deposits. One significant difference between these two landforms is the presence of fine-grained sediment interbedded with sand and gravel aquifer materials in the moraine and till plains.

Moraine/Outwash Comparison

Moraine and outwash ground-water samples were compared graphically and statistically using box-and-whisker plots and two-sample tests. Statistical results for calcium, magnesium, alkalinity, and sulfate are illustrated in Figure 32. Obvious differences illustrated on these plots were tested statistically. Results of the two-sample tests are shown on Table 11. Hardness, specific conductance, calcium, magnesium, alkalinity, barium, and sulfate were found to have statistically higher concentrations in ground water from the moraine wells. Concentrations of potassium and silica in the moraine samples were similar to concentrations in the outwash samples. Concentrations of

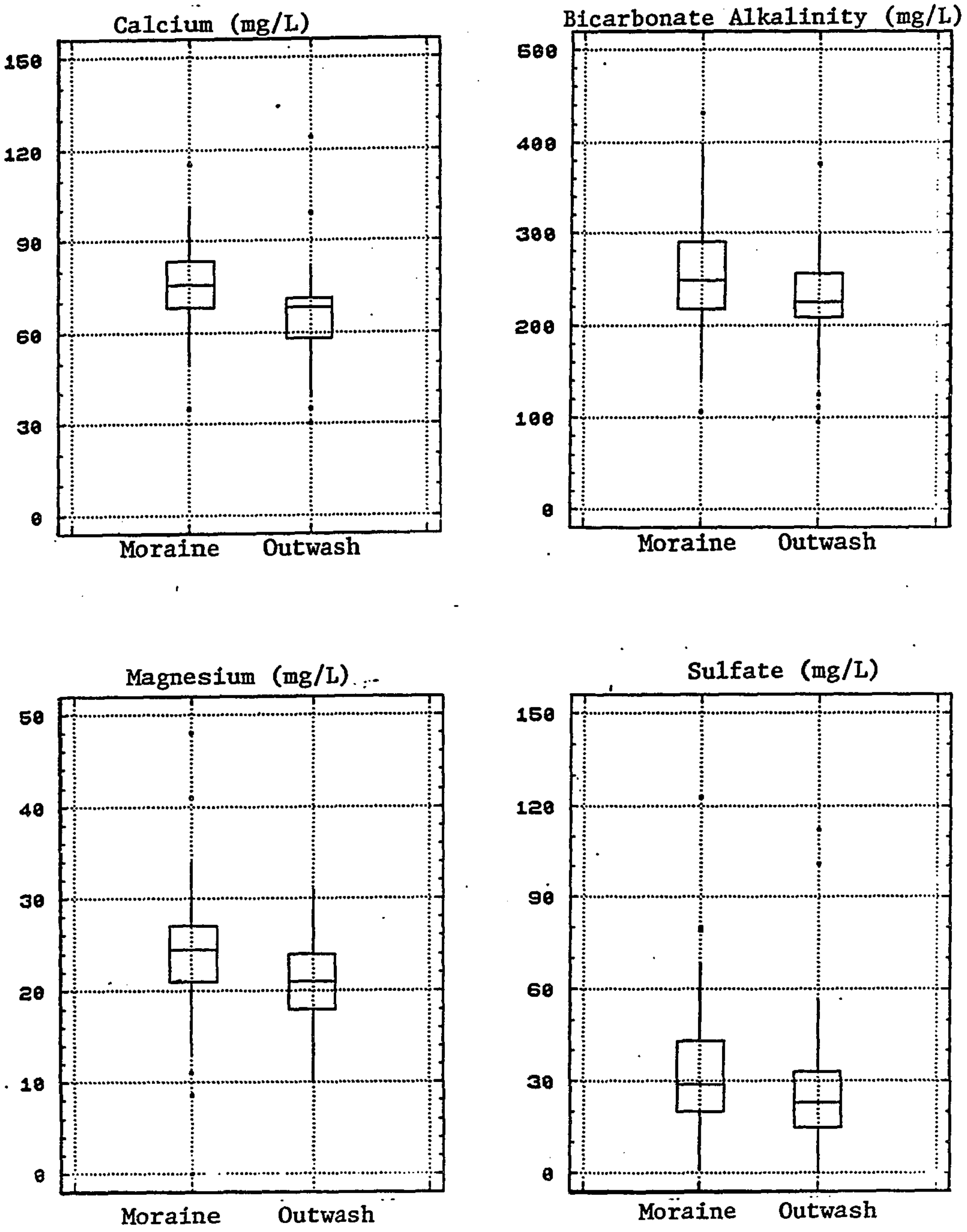


Figure 32. Concentrations of Calcium, Magnesium, Bicarbonate Alkalinity, and Sulfate in the Moraine and Outwash Ground Water.

Table 11

Two-sample Test Results from Comparison of Background Moraine and Outwash Wells

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Moraine	Outwash	Decision***
Alkalinity	equal	MWW	248	224	Similar
Ammonium	equal	MWW	0.06	0.06	Different
Barium	unequal	95% CI	0.11	0.08	Similar
Calcium	equal	MWW	75.5	68	Similar
Chloride	equal	MWW	2.5	3	Similar
Spec. Conductance	equal	MWW	422	373	Similar
Hardness	equal	MWW	281.5	259	Similar
Iron	unequal	95% CI	1.25	0.98	Similar
Magnesium	unequal	95% CI	24	21	Similar
Manganese	unequal	95% CI	0.07	0.08	Similar
Nitrate	equal	MWW	0	0	Similar
Potassium	unequal	95% CI	2.03	1.67	Similar
Silica	unequal	95% CI	8.5	7.1	Similar
Sodium	N/A	N/A	N/A	N/A	N/A

Table 11--Continued

Parameter	Sample variances*	Statistical Test used**	Median/Mean Values Moraine	Outwash	Decision***
Sulfate	equal	MWW	29	23	Similar

* Procedure tests the hypothesis that the ratio of sample variances is equal to 1.0 at the 95% confidence level.

** For unequal variances, the 95% confidence level for the difference in means is used. For equal variances, the Mann-Whitney-Wilcoxin test for the difference in medians is used.

*** Similar=sample means or medians come from similar populations, and are equal at the 5% level of significance.
Different=sample means or medians are not equal at the 5% level of significance.

N/A Not analyzed due to small sample size

the conservative parameters, nitrate and chloride, and the redox indicators, iron, manganese, and ammonia also were statistically similar between the moraine and outwash ground-water samples (Table 11).

Discussion

The results of the statistical analyses demonstrate that the type of glacial landform in which a well is screened can influence ground-water quality. Higher concentrations of most chemical parameters found in the moraine ground water could be explained in two ways. First, fine-grained sediment interbedded within the moraines and till plains has a marked effect on ground-water movement. Glacial till and silty materials have hydraulic conductivities ranging from 10^{-12} to 10^{-4} meters per second, while sandy and gravelly materials commonly vary between 10^{-5} and 1 meter per second (Freeze and Cherry, 1979). Morainal deposits also tend to be poorly sorted compared to outwash deposits, resulting in more tortuous flow paths. Slow flow and long residence time characterize ground-water movement in the moraines. A longer residence time provides more time for ground water to react with aquifer materials, resulting in a larger concentration of dissolved solids.

Mineralogy may also play a role in the higher chemical concentrations found in the moraine. Sediments containing a large fine-grained fraction may have a larger amount of reactive minerals than the outwash sediment. In addition, the fine fraction represents a larger surface area for ground water to contact. These factors combined with longer residence time may explain the higher ion concentrations in ground water of the moraines.

It is interesting to note that the higher content of clay in the moraine materials does not appear to protect the wells cased in the moraine from ground water degradation. The chloride-, nitrate-, and ammonium-degraded wells were also classified as moraine or outwash wells, although they were not included in the statistical analyses. Approximately 50% of the chloride-degraded wells, 50% of the nitrate degraded wells, and 50% of the ammonium-degraded wells were located in moraines. These percentages suggest the clayey materials interbedded in the moraine deposits are probably discontinuous and do not provide protection against contamination from surface sources on a regional scale. This does not mean, however, that certain clay-rich areas of the moraine could not act as effective barriers to the migration of contaminants from the surface.

CONCLUSIONS

The results of this study provide valuable information on the aquifers in Barry County, Michigan. First, chemical similarities and hydraulic head differences between the glacial drift and Marshall Sandstone aquifers indicate that the water in the bedrock is derived from the drift, and that the drift recharges the bedrock throughout most of the county. Therefore, in considering methods of waste disposal and land use, the county cannot assume that the drift and bedrock aquifers are isolated from each other. Contamination in the shallow drift aquifers could eventually reach the bedrock aquifer.

Second, the concentrations of all studied chemical constituents, with the exception of chloride, nitrate, and iron in the drift and bedrock aquifers provide water quality acceptable for domestic use. About one quarter of the glacial drift wells sampled show ground water degradation from chloride and nitrate. Higher levels of ammonium were also observed, however it is not clear that these levels result from human activity. Elevated concentrations of chloride and nitrate reveal the susceptibility of the glacial drift aquifer to contamination through land use and/or waste disposal practices. High concentrations of these parameters were not found in the bedrock aquifer. High concentrations of iron in many of the bedrock and drift wells may make the ground water aesthetically unacceptable in parts of the county.

Third, the ground water quality of glacial drift is controlled primarily by open-system dissolution of carbonate minerals. This process has produced a calcium-magnesium-bicarbonate type water in the drift and the bedrock aquifer. Because these reactions regulate the pH of the ground water, they also influence dissolution of other minerals. By comparison to carbonate dissolution, redox reactions appear only to influence the concentration of iron. Ion exchange does not appear to affect the water chemistry significantly. The natural buffering effect of the carbonate minerals and the apparent absence of ion exchange activities for the parameters studied could influence the design of and operation of waste management systems. Further investigation of the chemical processes occurring in the aquifers, such as geochemical modeling, will require field pH, Eh, and temperature data for samples collected from the wells.

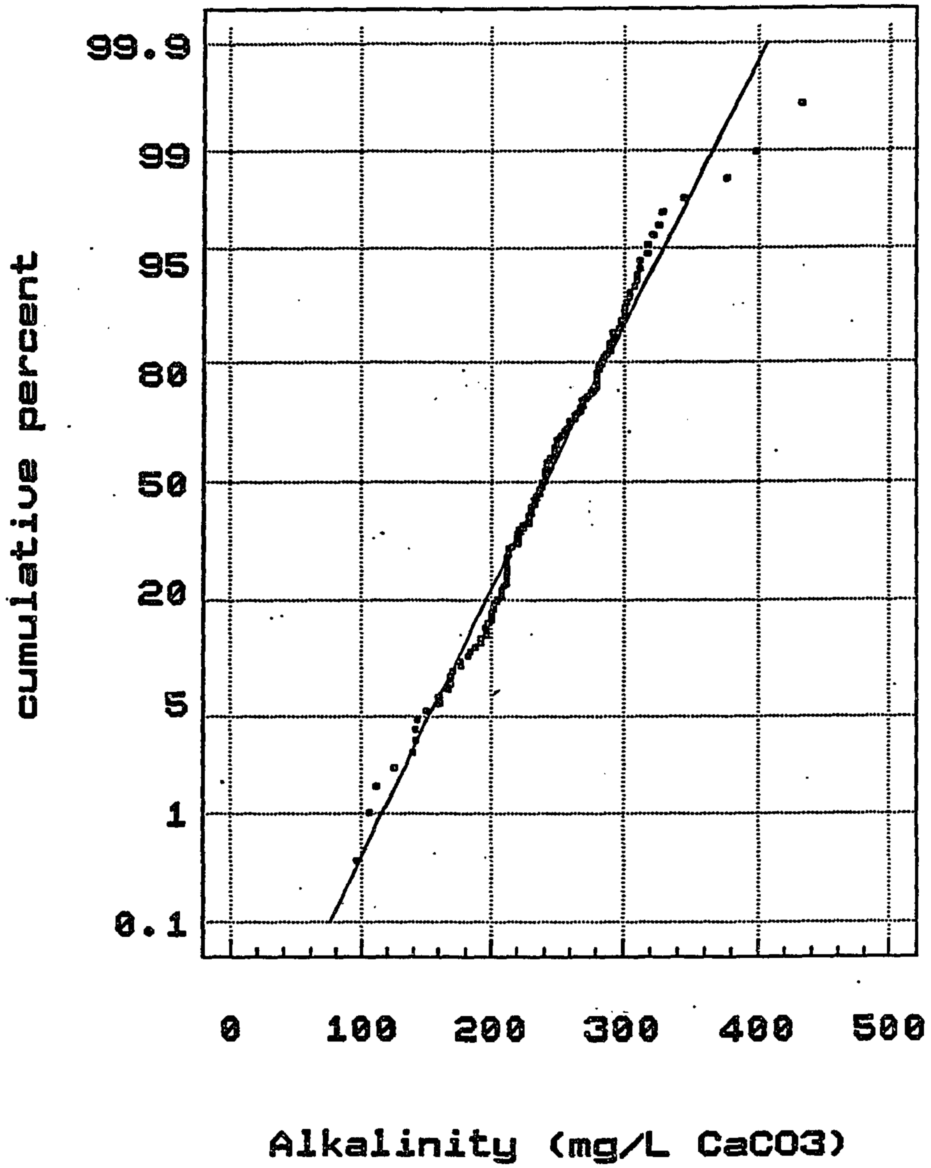
Fourth, the ground-water quality of the drift is also affected by physical factors. Redox-sensitive parameters appear to increase slightly along flow paths. Landforms also appear to influence the ground-water quality in the Barry County aquifers. Concentrations of the major ions are significantly higher in wells screened in the moraines than in wells screened in the outwash. These differences likely result from longer residence time of the ground water in the moraine. However, although the moraines contain greater amounts of fine sediment, longer flow paths, and slower flow velocities, it cannot be assumed that these areas are less susceptible to contamination than the outwash areas on a regional scale.

Appendix A

Normal Probability Plots

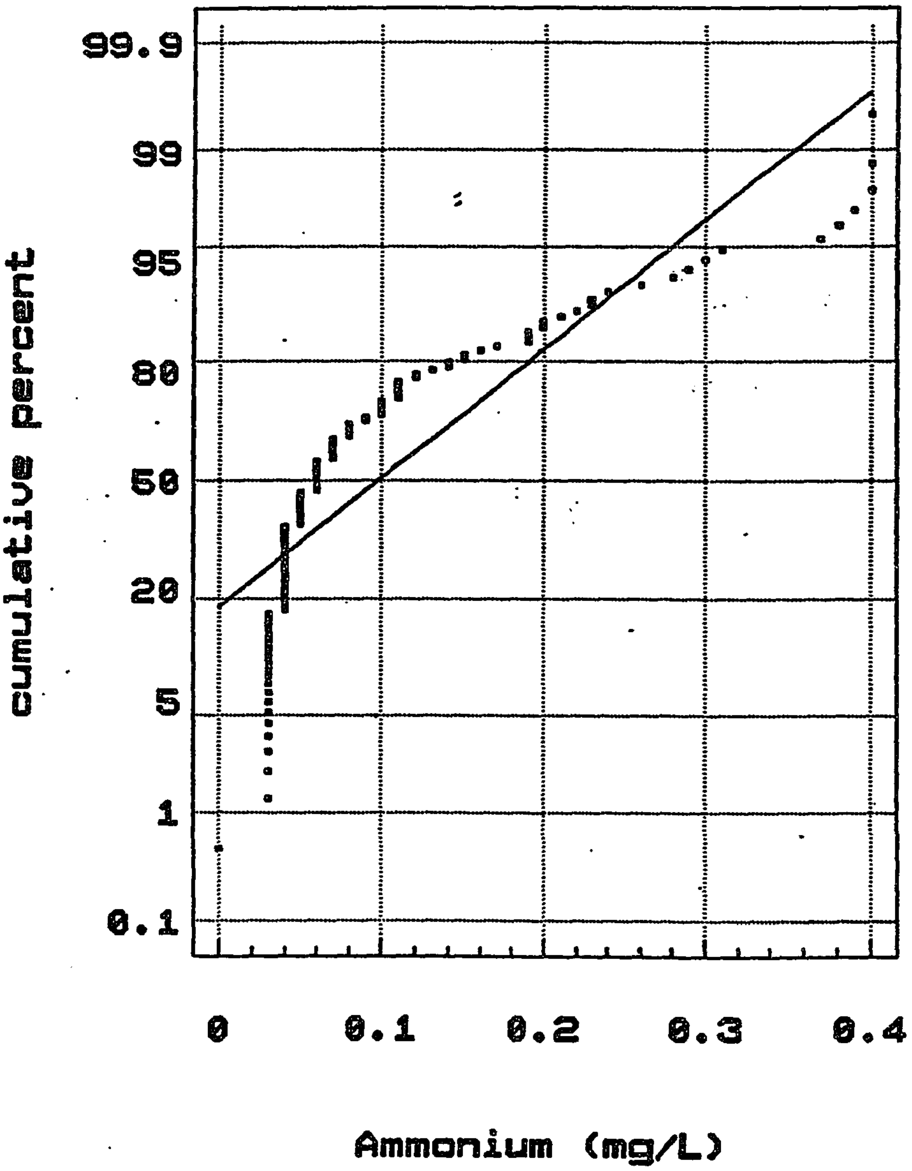
Normal Probability Plot

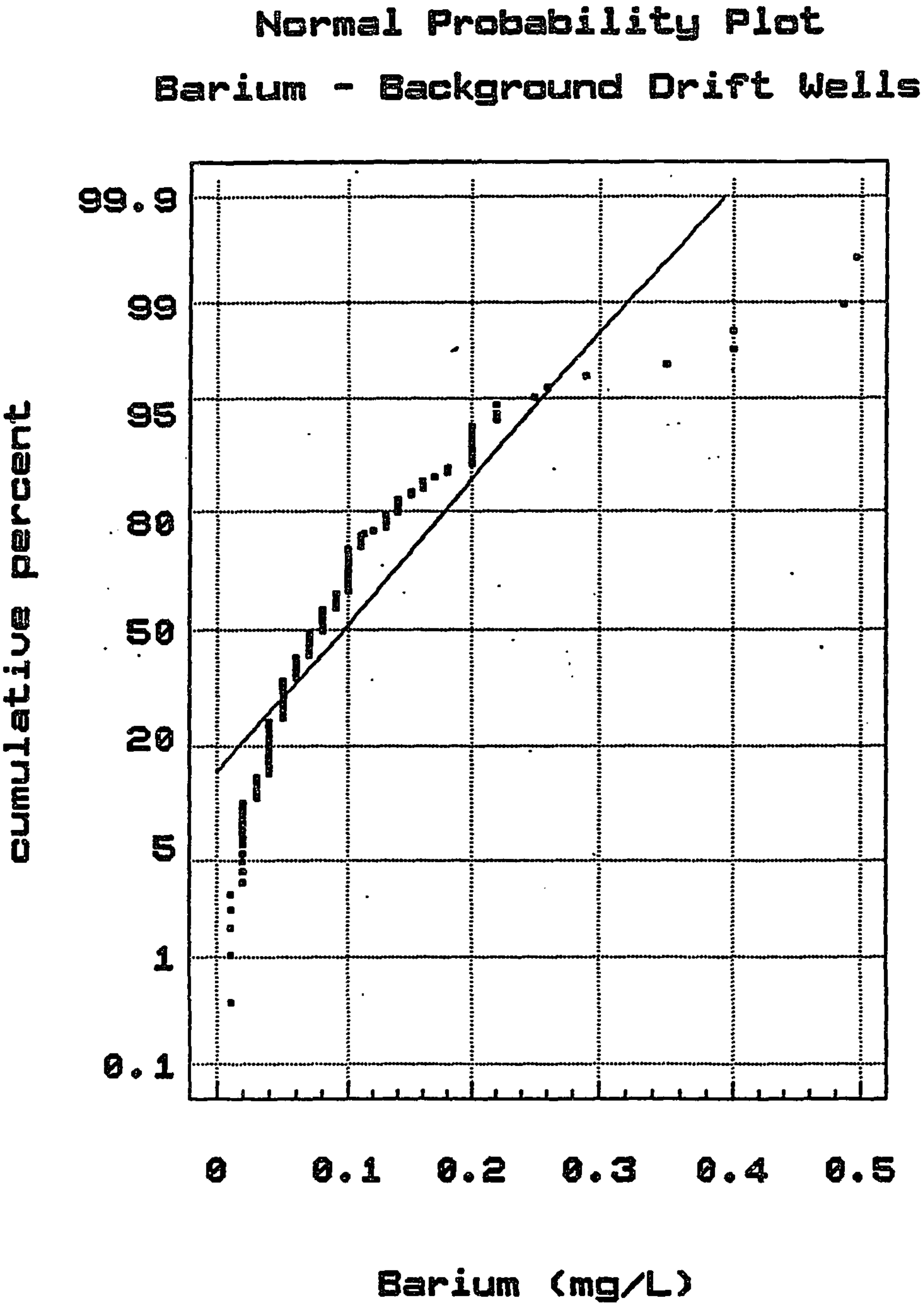
Alkalinity - Background Drift Wells



Normal Probability Plot

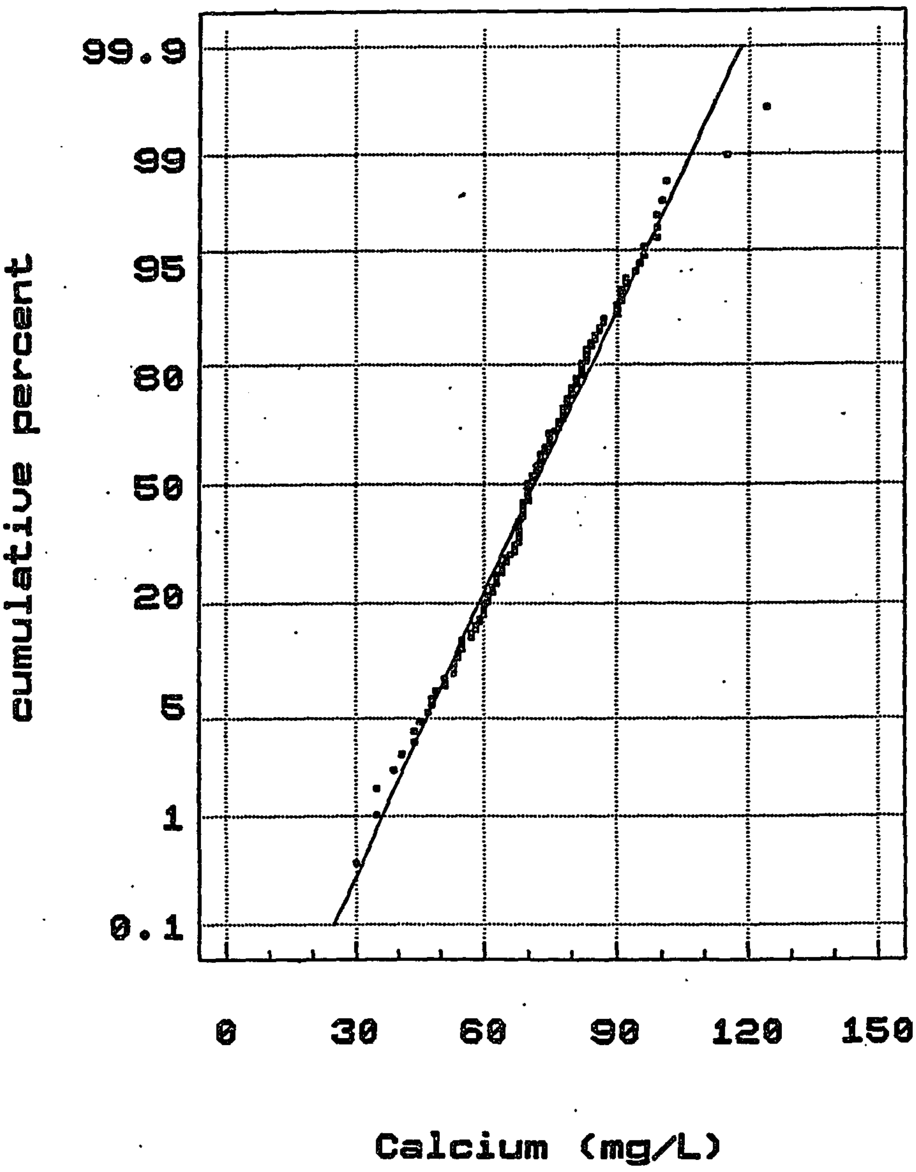
Ammonium - Background Drift Wells

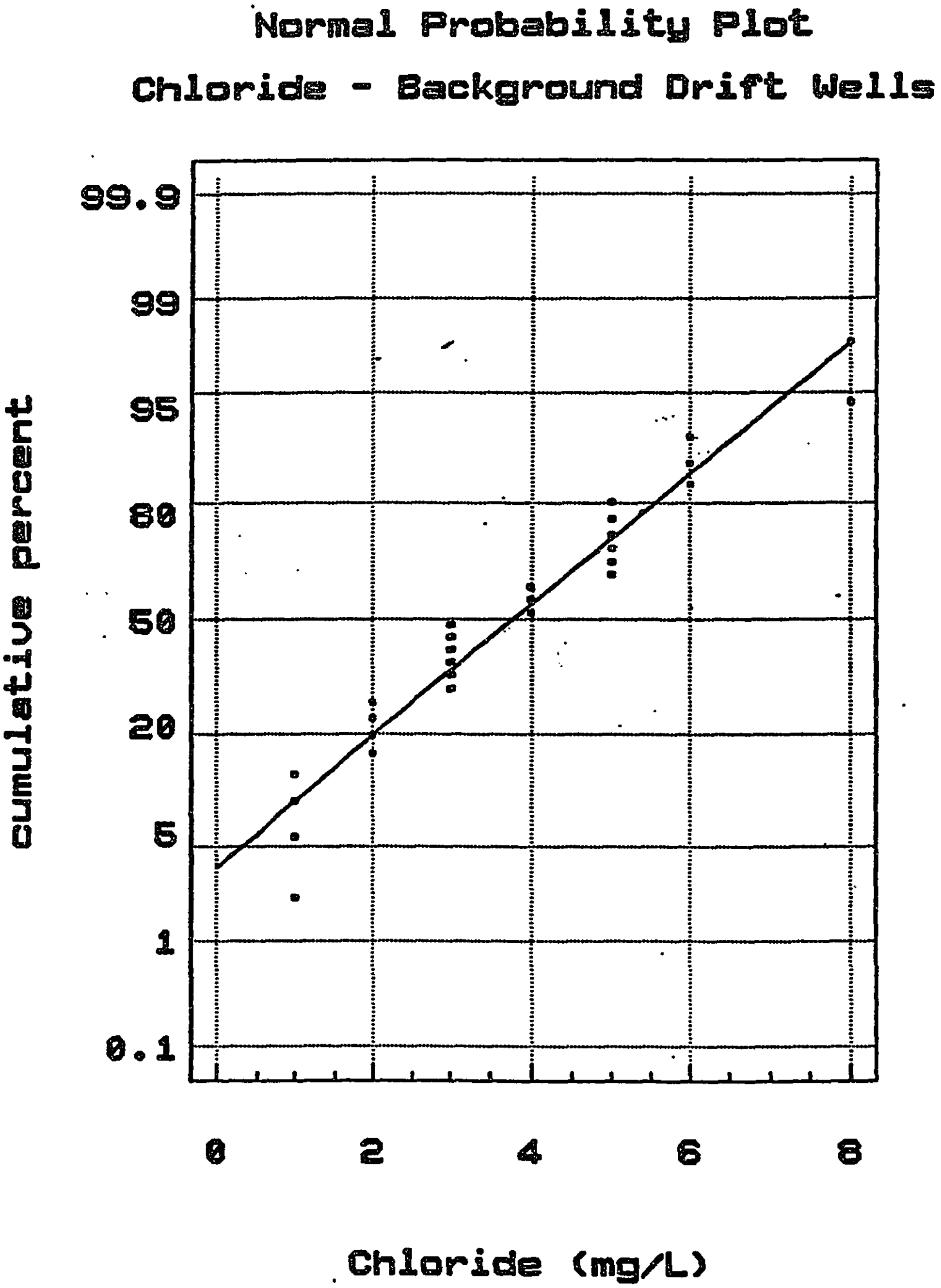



Normal Probability Plot
Barium - Background Drift Wells
99.9
99
95
80
50
20
5
1
0.1
cumulative percent
0
0.1
0.2
0.3
0.4
0.5
Barium (mg/L)

Normal Probability Plot

Calcium - Background Drift Wells

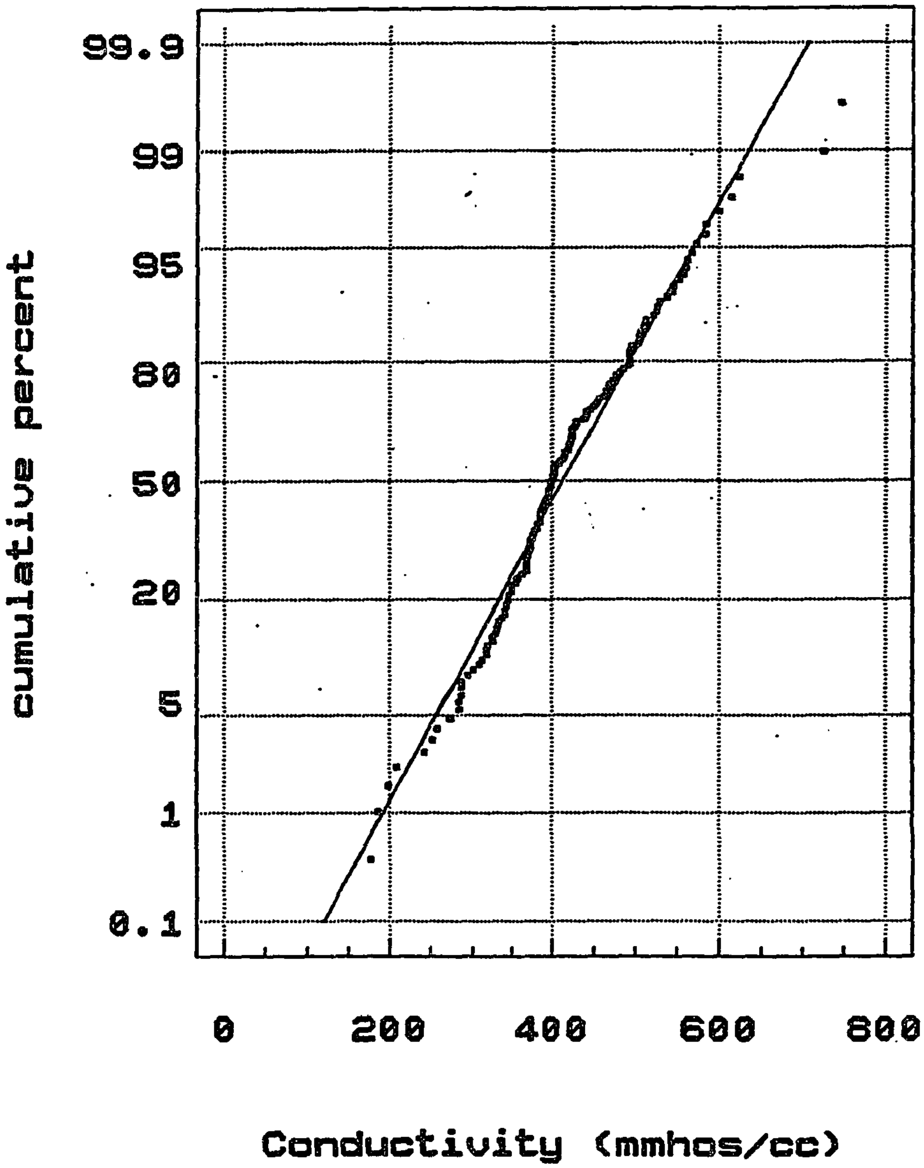


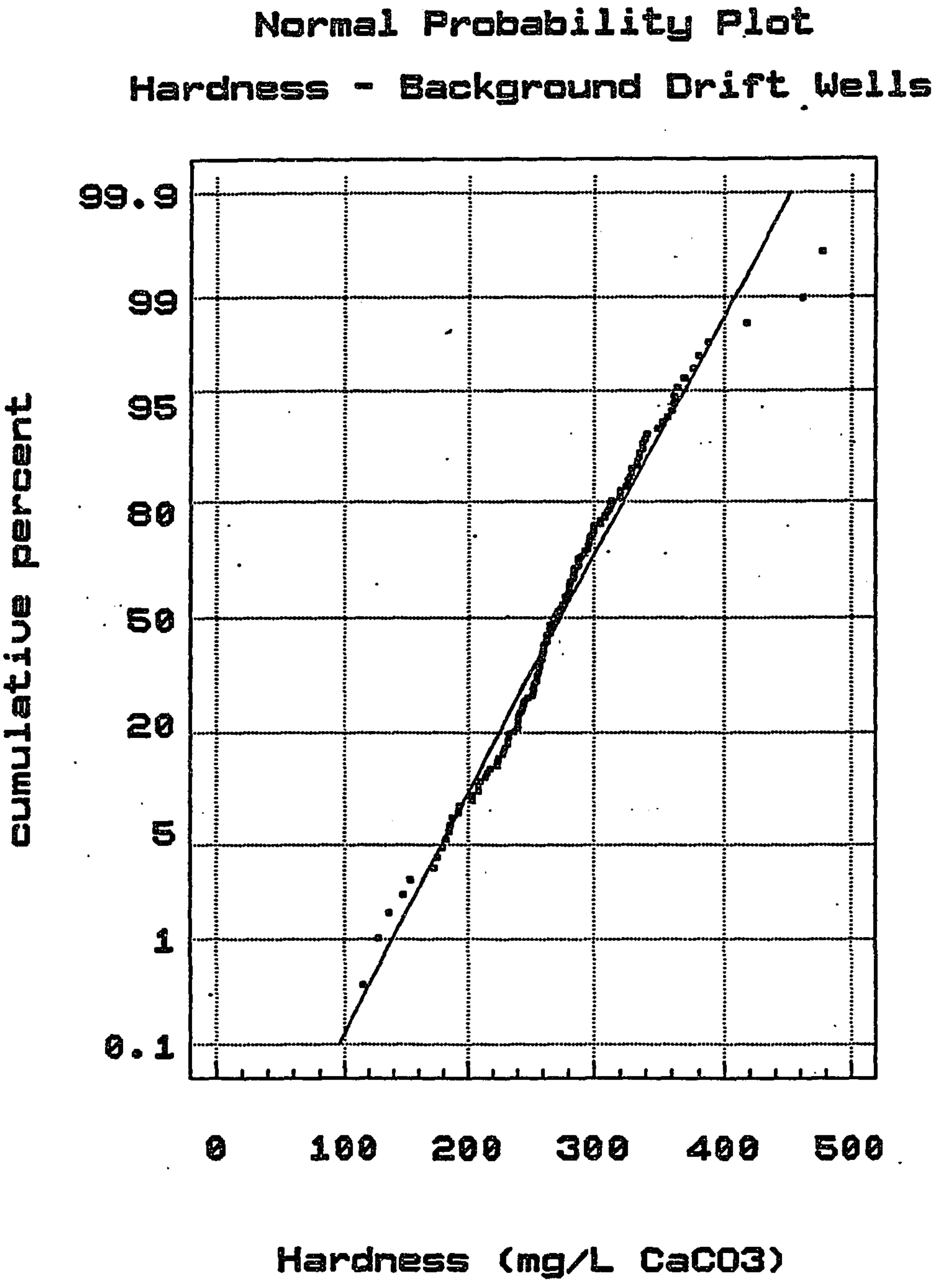


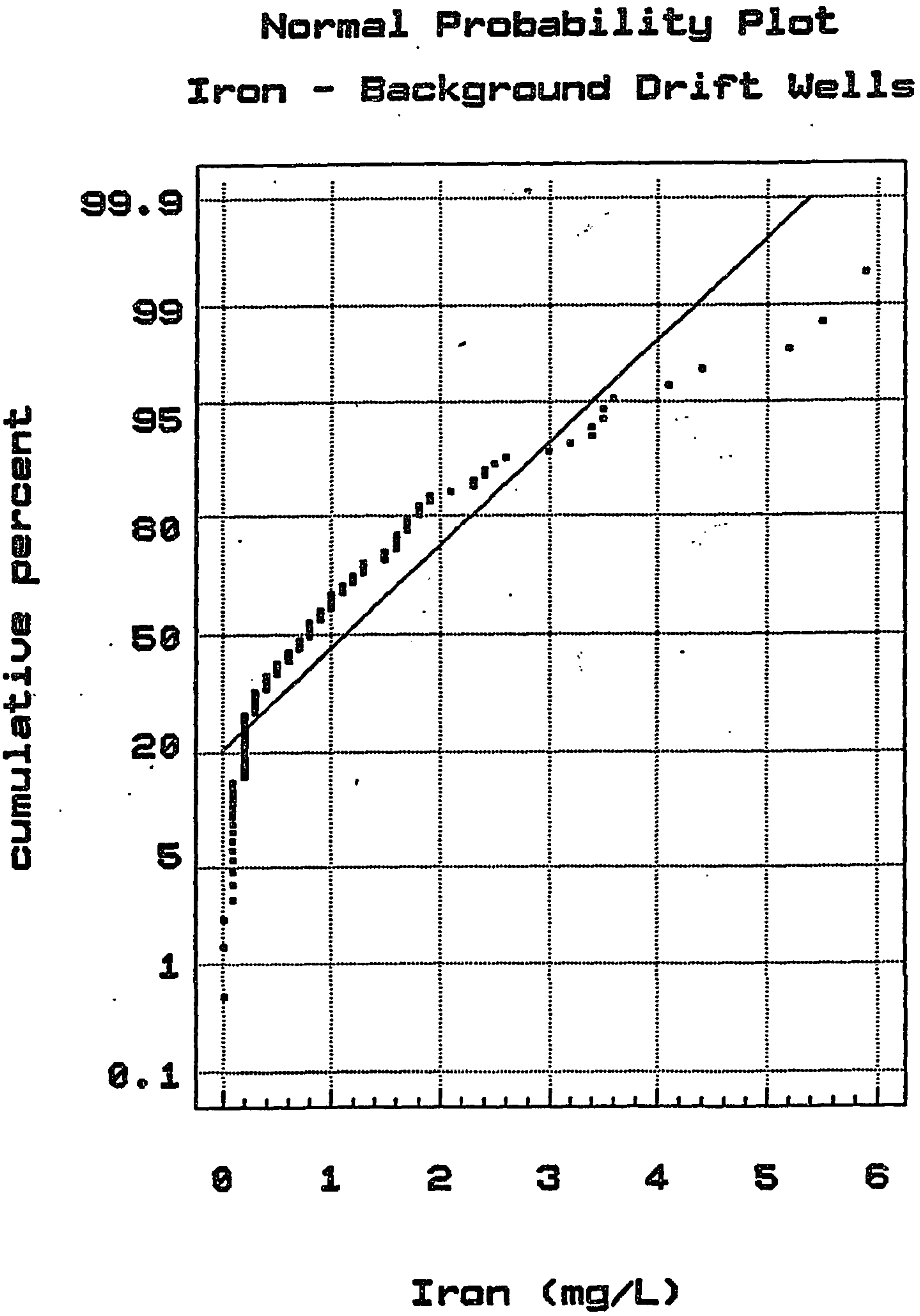
Normal Probability Plot

Chloride - Background Drift Wells

Normal Probability Plot
Conductivity - Background Drift Wells

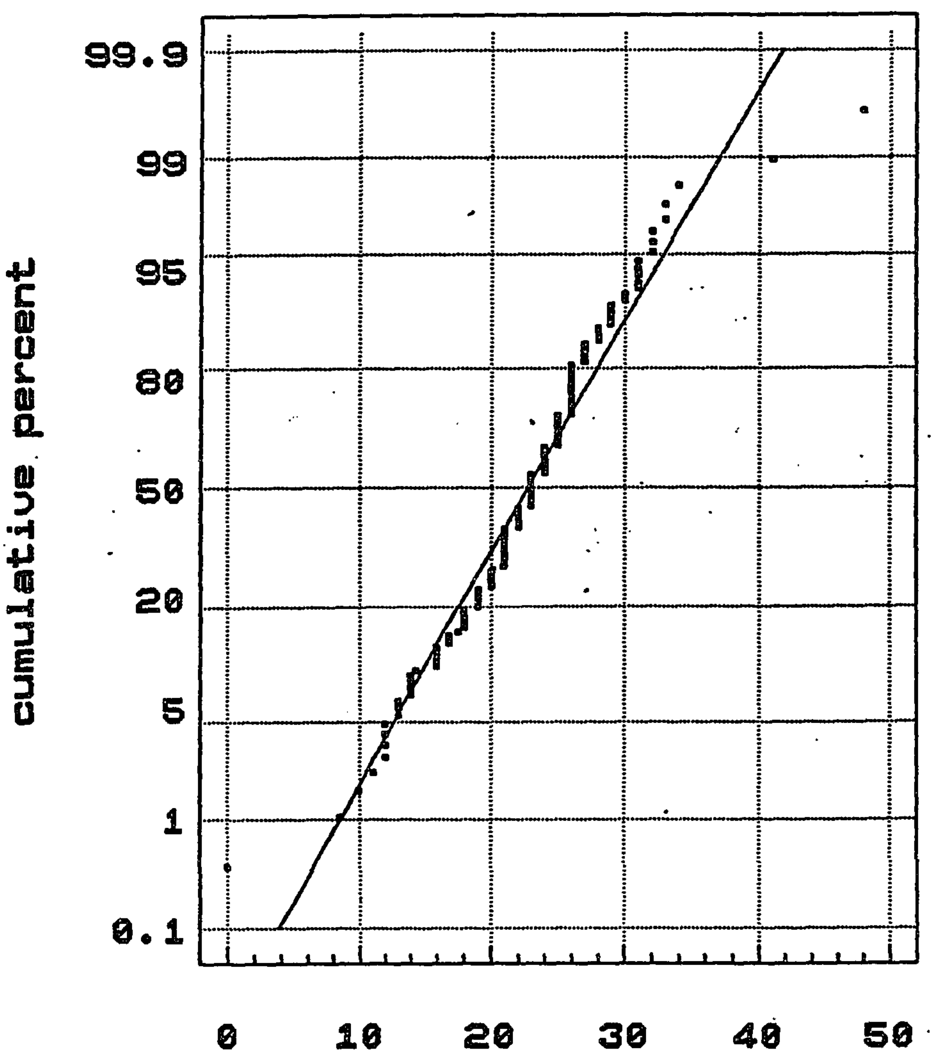



Normal Probability Plot
Hardness - Background Drift Wells
cumulative percent
99.9
99
95
80
50
20
5
1
0.1
0
100
200
300
400
500
Hardness (mg/L CaCO3)

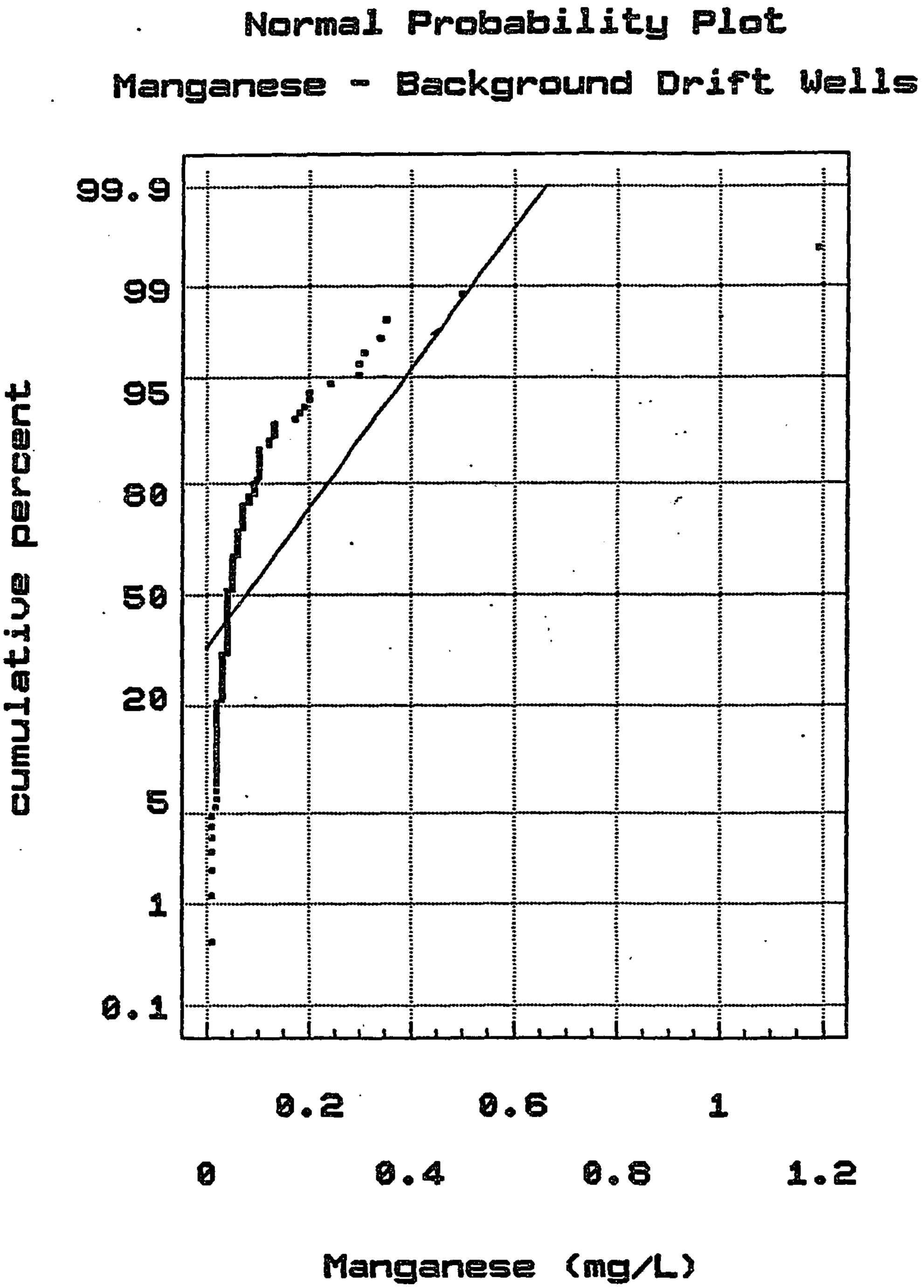

Normal Probability Plot
Iron - Background Drift Wells
cumulative percent
99.9
99
95
80
50
20
5
1
0.1
0
1
2
3
4
5
6
Iron (mg/L)

Normal Probability Plot

Magnesium - Background Drift Wells

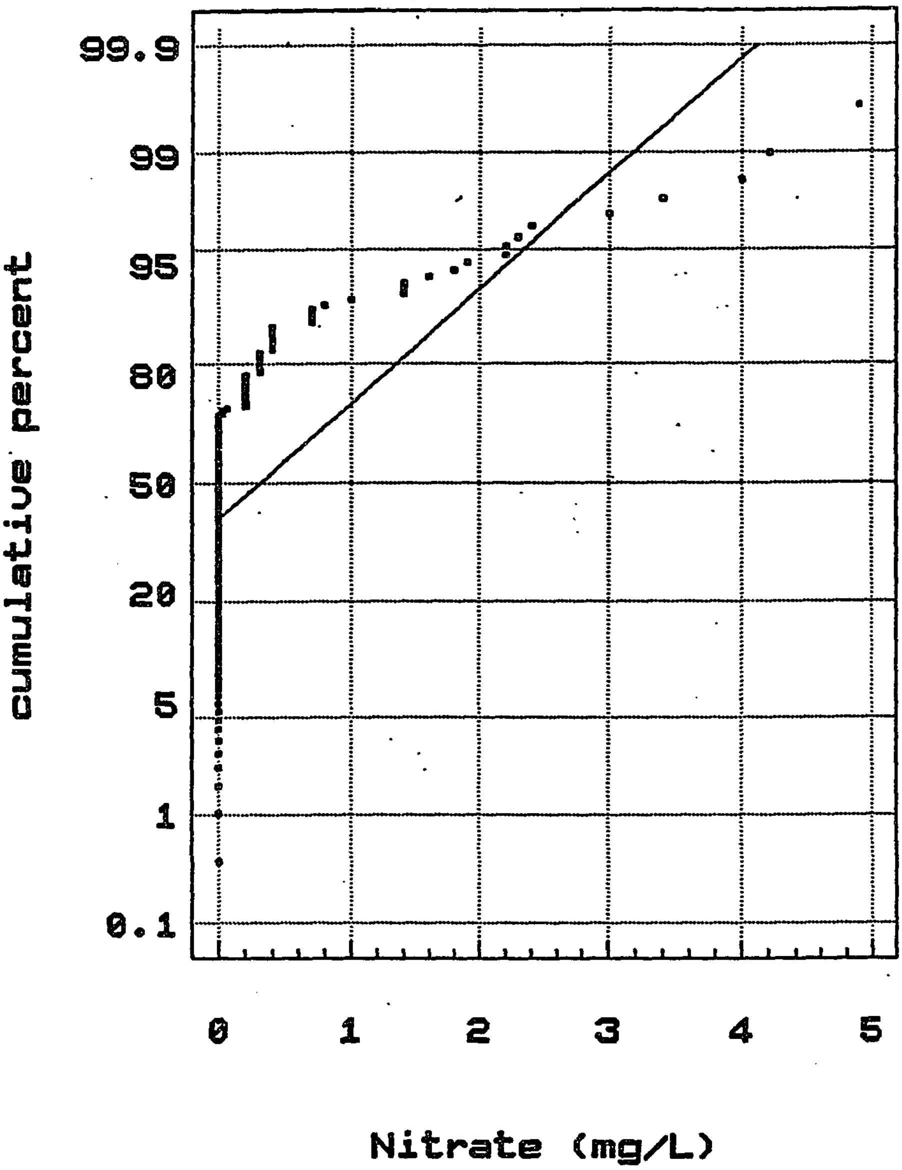


Magnesium (mg/L)


Normal Probability Plot
Manganese - Background Drift Wells
cumulative percent
99.9
99
95
80
50
20
5
1
0.1
0.2
0.6
1
0
0.4
0.8
1.2
Manganese (mg/L)

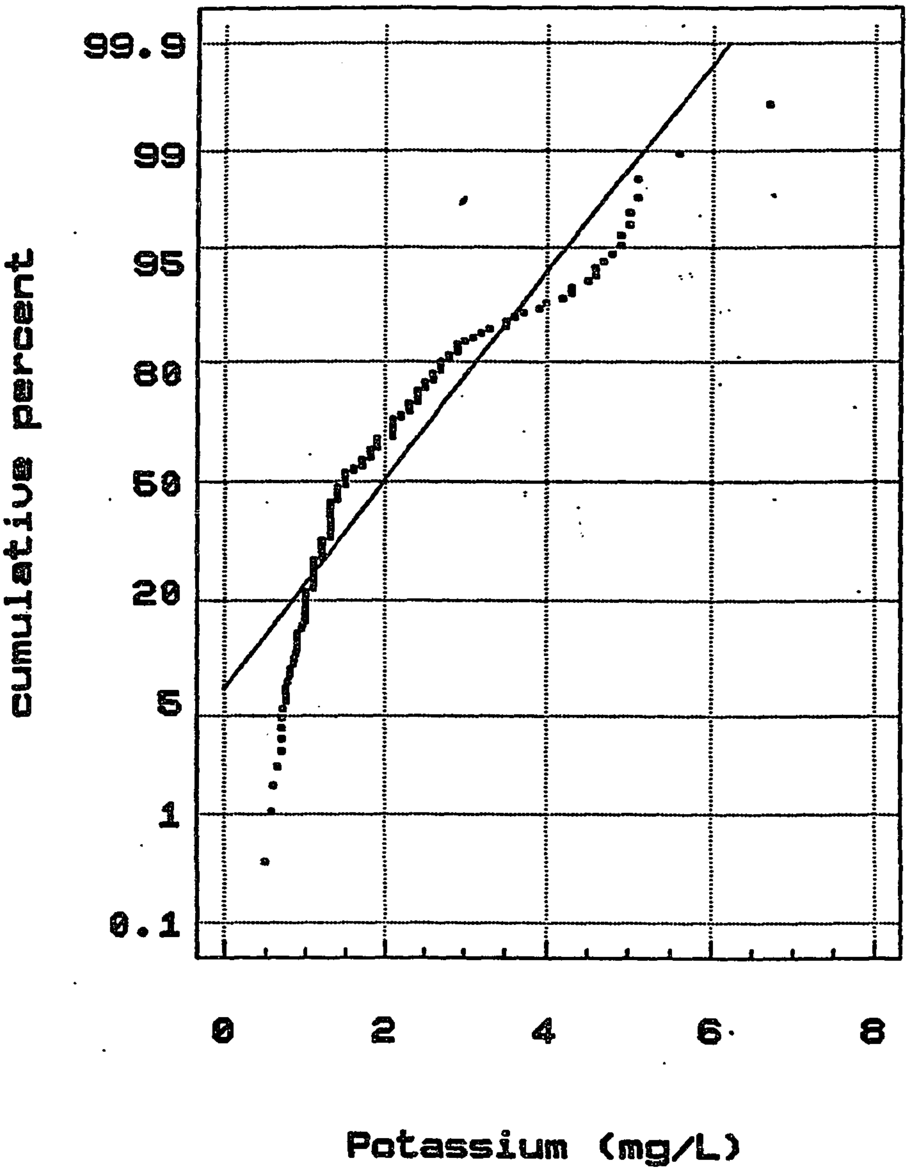
Normal Probability Plot

Nitrate - Background Drift Wells



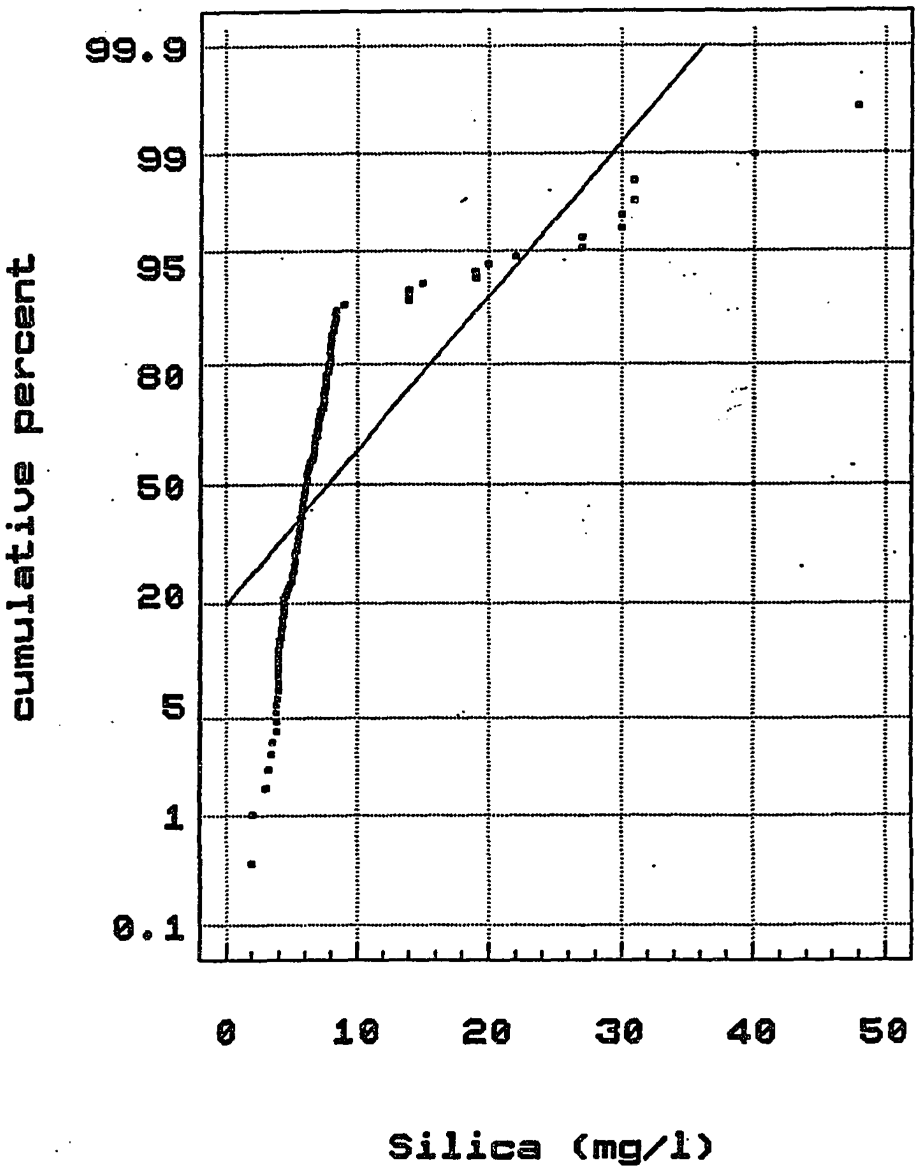
Normal Probability Plot

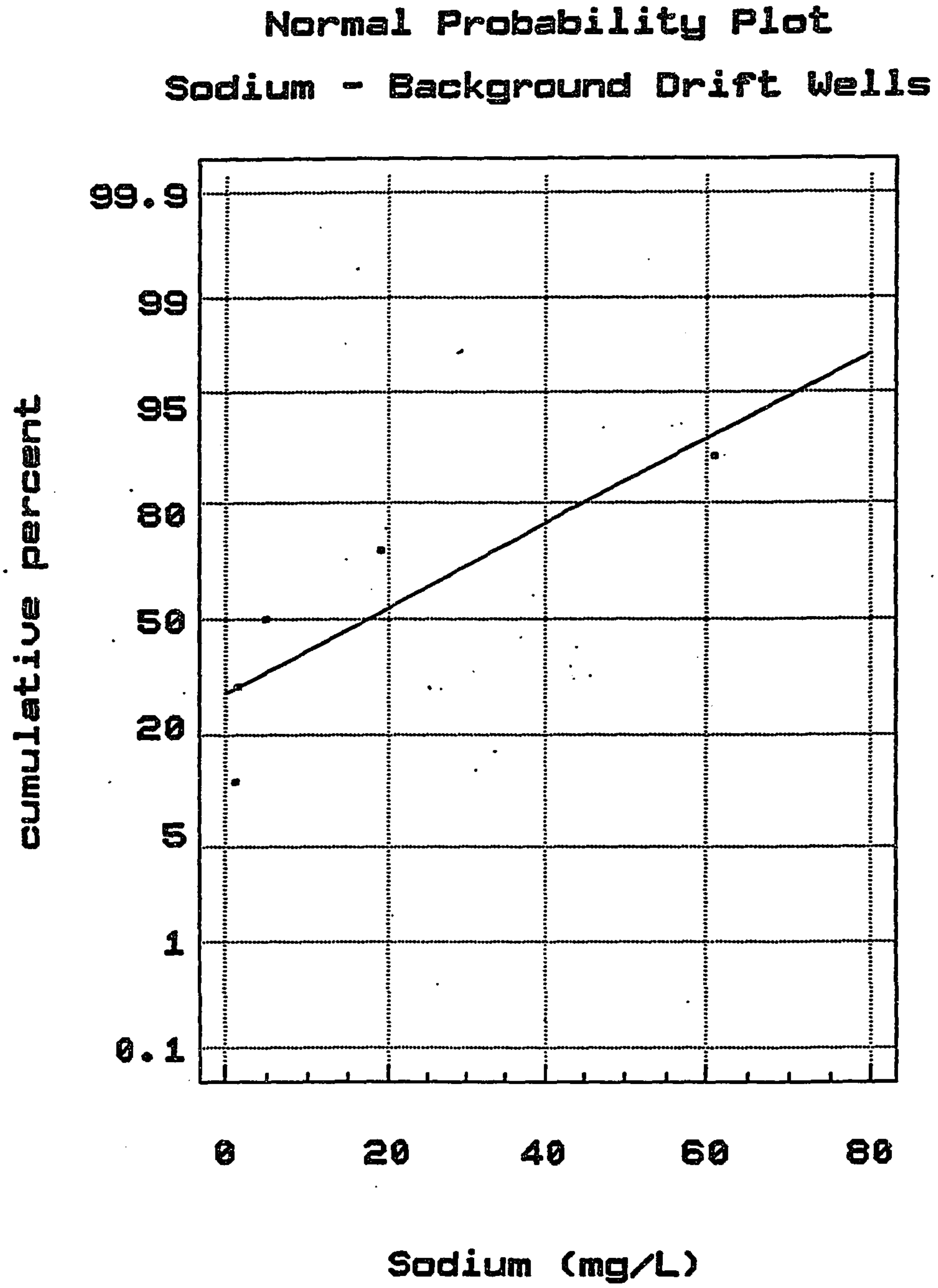
Potassium - Background Drift Wells

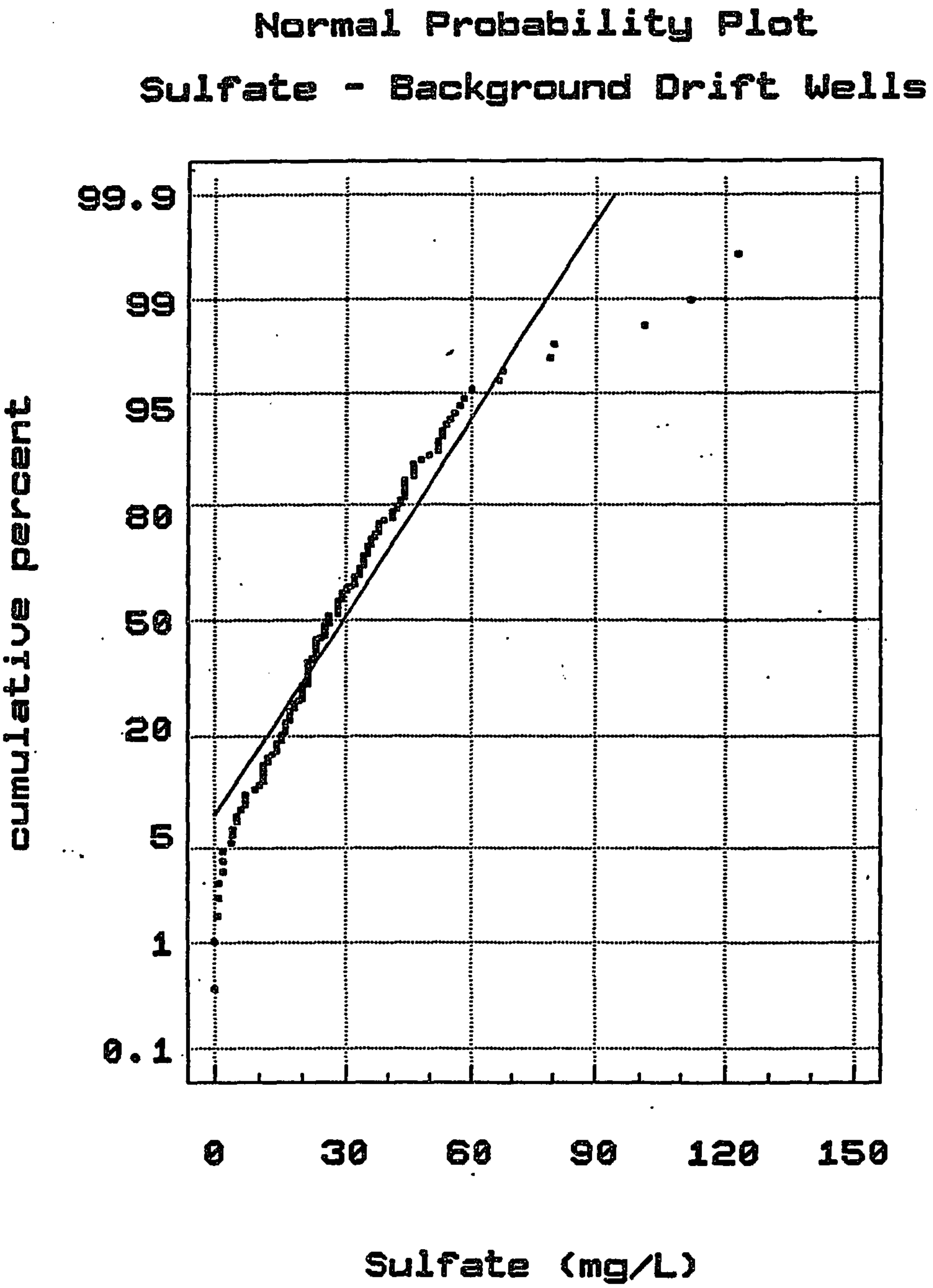


Normal Probability Plot

Silica - Background Drift Wells




Normal Probability Plot
Sodium - Background Drift Wells
cumulative percent
99.9
99
95
80
50
20
5
1
0.1
0
20
40
60
80
Sodium (mg/L)


Normal Probability Plot
Sulfate - Background Drift Wells
cumulative percent
99.9
99
95
80
50
20
5
1
0.1
0
30
60
90
120
150
Sulfate (mg/L)

Appendix B

EPA National Drinking Water Standards

NATIONAL PRIMARY DRINKING WATER STANDARDS (MG/LITER)

AUGUST 1990

	Secondary Maximum Contaminant Level	Proposed Secondary Maximum Contaminant Level
Aluminum	0.05(h)	0.05 mg/l(g)
Chloride	250 mg/l(d)	
Color	15 color units(d)	
Copper	1 mg/l(d)	
Corrosivity	non-corrosive(d)	
o-Dichlorobenzene	0.01(h)	0.01 mg/l(g)
p-Dichlorobenzene	0.005(h)	0.005 mg/l(g)
Ethylbenzene	0.03(h)	0.03 mg/l(g)
Fluoride	2 mg/l(f)	
Foaming agents	0.5 mg/l(d)	
Hexachlorocyclopentadiene		0.008
Iron	0.3 mg/l(d)	
Manganese	0.05 mg/l(d)	
Monochlorobenzene		0.1 mg/l(g)
Odor	3 threshold odor number	
pH	6.5-8.5(d)	
Pentachlorophenol	0.03(h)	0.03 mg/l(g)
Silver	0.09(h)	0.09 mg/l(g)
Styrene	0.01(h)	
Sulfate	250 mg/l(d)	
Toluene	0.04(h)	0.04 mg/l(g)
Total dissolved solids	500 mg/l(d)	
Xylene (total)	0.02(h)	0.02 mg/l(g)
Zinc	5 mg/l(d)	

REFERENCES:

(a) 50 Federal Register 45902 (November 13, 1985)
(b) 52 Federal Register 25690 (July 8, 1987)
(c) 53 Federal Register 31515 (August 18, 1988)
(d) 44 Federal Register 42196 (July 19, 1979)(e) 40 CFR 141.11
(f) 50 Federal Register 47156 (November 14, 1985)
(g) Fact Sheet. Drinking Water Regulations Under the Safe Drinking Water Act. September 1988. Criteria and Standards Division, Office of Drinking Water, U.S. Enviornmental Protection Agency
(h) 54 Federal Register 22062 (May 22, 1989)
(i) 54 Federal Register 27544 (June 29, 1989)
(j) Update for Table of Drinking Water Standards and Health Advisories. May 7, 1990. Office of Drinking Water, U.S. EPA.
(k) 40 CFR 141.12
(l) 55 Federal Register 30370 (July 25, 1990)

NATIONAL PRIMARY DRINKING WATER STANDARDS (MG/LITER)

AUGUST 1990

INORGANICS	MAXIMUM CONTAMINANT Level	MAXIMUM CONTAMINANT Level Goal	PROPOSED MAXIMUM CONTAMINANT Level	PROPOSED MAXIMUM CONTAMINANT Level Goal
Antimony			0.01/0.005(l)	0.003(l)
Arsenic	0.05(e)	0.05(e)		
Asbestos			fibers/liter(h)	fibers/liter(h)
Barium	1.00(e)	5.0(h)	5.0(h)	
Beryllium			0.001(1)	0
Cadmium	0.01(e)	0.005(h)	0.005(h)	
Chromium	0.05(e)	0.1(h)	0.1(h)	
Copper			1.3(c)	1.3(c)
Cyanide			0.2(l)	0.2(l)
Fluoride	4.0(f)	4.0(f)		
Lead	0.05(e)	0.005(c)	0(c)	
Mercury	0.002(e)	0.002(h)	0.002(h)	
Nickel			0.1(l)	0.1(l)
Nitrate (as N)	10.0(e)	10(h)	10.0(h)	
Nitrate + nitrite			10(h)	10.0(h)
Selenium	0.01(e)	0.05(h)	0.05(h)	
Silver	0.05(e)			
Sulfate			400/500(l)	400/500(l)
Thallium			0.002/0.001(l)	0.0005(l)
ORGANICS				
Acrylamide			(h)**	0(h)
Adipates [Di(ethylhexyl)adipate]			0.5(l)	0.5(l)
Alachlor			0.002(h)	0(h)
Aldicarb			0.01(h)	0.01(h)
Aldicarb sulfone			0.04(h)	0.04(h)
Aldicarb sulfoxide			0.01(h)	0.01(h)
Atrazine			0.003(h)	0.003(h)
Benzene	0.005(b)	0(b)		
Benz(a)anthracene			0.0002(l)	0(l)
Benzo(a)pyrene			0.0002(l)	0(l)
Benzo(b)fluoranthene			0.002(l)	0(l)
Benzo(k)fluoranthene			0.0002(l)	0(l)
Butylbenzyl phthalate			0.1(l)	0.1(l)
Carbofuran			0.04(h)	0.04(h)
Carbon tetrachloride	0.005(b)	0(b)		
Chlordane			0.002(h)	0(h)
Chrysene			0.0002(l)	0(l)
2,4-D	0.1(e)	0.07(h)	0.07(h)	
Dalapon			0.2(l)	0.2(l)

** *Treatment technique.*

BIBLIOGRAPHY

Boggs, S. Jr., 1987, Principles of Sedimentology and Stratigraphy, Columbus, Ohio, Merrill Publishing Company, p. 380-393.

Cantor, L.W., Knox, R.C., and Fairchild, D.M., 1977, Ground Water Quality Protection, New York, Lewis Publishers, p. 67-118.

Cummings, T.R., 1980, Chemical and Physical Characteristics of Natural Ground Waters in Michigan: U.S. Geological Survey, Open-File Report 80-953, p. 34.

Dorr, J.A. Jr., and Eschman, D.F., 1977, Geology of Michigan, Ann Arbor, Michigan, University of Michigan Press, p. 81-135.

Drever, J.I., 1988, The Geochemistry of Natural Waters, 2nd Ed., Englewood Cliffs, New Jersey, Prentice Hall, p. 1-13, 48-124, 281-326.

Feth, J.H., 1966, Nitrogen Compounds in Natural Water-A Review, Water Resources Research, Vol. 2, No. 1, p. 41-58.

Freeze, R.A., and Cherry, J.A., 1979, Groundwater, Engelwood Cliffs, New Jersey, Prentice Hall, p. 106-134, 149-154, 193-197, 240, 279-286, 413-456.

Gillespie, R.J., Humphreys, D.A., Baird, N.C., and Robinson, E.A., 1986, Chemistry, Boston, Allyn and Bacon Inc., p. 175-188, 240-260, 567-584.

Golden Software Inc., 1988, SURFER User's Guide, Golden, Colorado.

Hem, J.D., 1989, Study and Interpretation of the Chemical Characteristics of Natural Water: U.S. Geological Survey Water-Supply Paper 2254, 3rd Ed.

Lilienthal, R.T., 1974, Subsurface Geology of Barry County, Michigan: Michigan Department of Natural Resources Report of Investigation 15.

Monaghan, G.W. et al., 1986, Wisconsinan Drift Stratigraphy of the Lake Michigan Lobe, Southwestern Michigan: Geological Society of America Bulletin, Vol. 97, p. 329-334.

Monnett, V.B., 1948, Mississippian Marshall Formation of Michigan: Bulletin of the American Association of Petroleum Geologists, Vol. 32, p. 629-688.

Reardon, E.J., Mozeto, A.A., and Fritz, P., 1980, Recharge in Northern Clime Calcareous Soils: soils, water, chemical, and carbon-14 evolution: Geochemica et Cosmochemica Acta, Vol. 44, p. 1723-1735.

Robertson, W.D., Cherry J.A., and Sudicky E.A., 1991, Ground-Water Contamination from Two Small Septic Systems on Sand Aquifers: Ground Water, Vol. 29, No. 1, p. 82-92.

Selby, M.J., 1985, Earth's Changing Surface, Oxford, Clarendon Press, p. 417-467.

Siegel, Sidney, 1956, Nonparametric Statistics, New York, McGraw-Hill Book Company, p. 1-30.

Simms, Craig S., 1988, Report on the Aquifers of Barry County, Michigan: Southwest Michigan Groundwater Survey.

Statistical Graphics Corporation, 1987, STATGRAPHICS User's Guide, Rockville, Maryland.

Thoen, Greg, 1988, Barry County Surficial Geology: Landforms: U.S. Department of Agriculture-Soil Conservation Service, supplement to Barry County Soil Survey.

Western Michigan University, 1989, unpublished data, Department of Geology, thermodynamic modeling of ground water in Calhoun County, Michigan.