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THE GEOCHEMISTRY AND ISOTOPIC CHEMISTRY OF SALINE GROUND WATER DERIVED FROM NEAR-SURFACE DEPOSITS OF THE SAGINAW LOWLAND, MICHIGAN BASIN

By

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ABSTRACT

THE GEOCHEMISTRY AND ISOTOPIC CHEMISTRY OF SALINE GROUND WATER DERIVED FROM NEAR-SURFACE DEPOSITS OF THE SAGINAW LOWLAND, MICHIGAN BASIN

By

Laura Santina Badalamenti

Near-surface ground water in the Saginaw Lowland is characterized by relatively high salinities and light isotopic values of del oxygen-18 and del deuterium. The source of the salinity and isotopically light water and the cause of their occurrence is unclear. It is hypothesized (1) that the source of the isotopically light water is meteoric water that recharged the system when the climate was much cooler (perhaps glacial meltwater of the Pleistocene Epoch); (2) that the source of salinity is the upward advection or diffusion of brines; and (3) that their occurrence is due to slow flushing of the water in argillaceous deposits by recent meteoric water.

Isotopic ranges in the ground water were as follows: del oxygen-18, -8.7 o/oo to -17.91 o/oo; del deuterium, -56.5 o/oo to -126.7 o/oo; and del carbon-13 -7.9 o/oo to -15.4 o/oo. Del oxygen-18 and del deuterium plot along the meteoric-water line, ranging from modern-day meteoric to extremely light values. The range of dissolved solids is 145 to 13115 mg/l.

It is concluded that the argillaceous deposits, which act as aquitards, retain meteoric water formed at cooler

temperatures and brines which have diffused or advected upward. These conclusions are consistent with the fact that the Saginaw Lowland regional ground-water system is a discharge zone. In addition, the outer perimeter of the Saginaw Lowland is a transition zone to fresher, modern-day meteoric recharge.

ACKNOWLEDGEMENTS

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INTRODUCTION

This study examines the extent of isotopically-depleted ground water in the Saginaw Lowland of the Michigan basin and investigates several hypotheses based primarily on previous work of Long et al. (1988) in Bay County of the Saginaw Lowland. The occurrence of isotopically-depleted ground water is compared to regional lithology and ground-water geochemistry in order to test the following hypotheses regarding characteristics of the ground water system in the Saginaw Lowland:

Hypothesis 1: the ground water system contains isotopically-depleted meteoric water that recharged the system when the climate was much cooler (perhaps glacial meltwater of the Pleistocene Epoch);

Hypothesis 2: the ground water system contains saline water derived from brines deep in the Michigan basin; and

Hypothesis 3: the isotopically-depleted water and saline water are retained in the ground water system by the combined affects of aquitards, low regional horizontal hydraulic gradients, and a regional ground-water discharge zone.

This study also attempted to verify that the additional processes identified by Long et al. (1986, 1988) in the Bay County ground water system are also affecting the Saginaw Lowland system. The additional processes include water-rock interactions including calcium carbonate equilibrium and stability with potassium aluminosilicate minerals; and biological reduction of sulfate.

The study was also used to estimate whether the data reduction techniques used in the Bay County study (Long et al., 1986, 1988), will produce interpretable results on more widely-spaced data points.

SECTION 1 - DEFINITION OF THE PROBLEM AND PAST WORKS

1.1 Definition of the Problem

Long et al. (1986, 1988) hypothesized that the following processes are occurring in the near-surface ground water system of Bay County, Michigan: 1) upward diffusion of local formation brines into the near-surface ground water and mixing of the brines with surface water as suggested by ternary diagrams of major cations and anions; 2) water-rock interactions, including calcium carbonate equilibrium as suggested by calcite saturation indices, and stability with the potassium aluminosilicate minerals, as suggested by a potassium aluminosilicate mineral activity plot of groundwater samples with points clustered along the boundary of muscovite and potassium feldspar; 3) the biological reduction of sulfate within the drift and bedrock, as suggested by the correlation of decreased sulfate (due to consumption by microbes) and increased del sulfur-34 values (due to selective assimilation of sulfur-32 by microbes resulting in isotopic enrichment of sulfur-34 in the ground water); and 4) the mixing of present-day meteoric water with meteoric water formed at cooler temperatures (possibly Pleistocene in age) as suggested by oxygen and deuterium stable isotopic values.

This study examines the extent of isotopically-depleted ground water in the Saginaw Lowland of the Michigan basin,

which encompasses Bay County (investigated by Long et al., 1988). The occurrence of isotopically-depleted ground water is compared to regional lithology and ground-water geochemistry in order to test several hypotheses outlined in the Introduction. This study evaluates a large geochemical data set with the aid of statistical, graphical and computer modeling techniques of data reduction. The statistical data reduction techniques are the Student's t-Test and multivariate factor analysis. The graphical data reduction techniques include ternary diagrams, frequency histograms, and x-y plots. The computer modeling technique used is chemical modeling with WATEQF. The research allows the comparison of interpretations made on ground-water processes from a data set composed of a large number of samples (about four hundred) taken in a one-county area with a data set composed of a small number of samples (about one hundred) taken from a seven county area. The extent of sulfate reduction in the Saginaw Lowland is briefly examined.

1.2 Past Works

Stable isotopes of oxygen and deuterium give insight into the origin of ground water, and reflect physical and chemical processes which have affected the ground water. In low-salinity ground water, oxygen-18 and deuterium concentrations are conservative; they are unaffected by physical, chemical or geological processes. However, in the hydrosphere, oxygen-18 and deuterium concentrations are not

conservative (Frape and Fritz, 1982). Craig (1961 a) demonstrated a linear relationship between concentrations of oxygen-18 and deuterium in meteoric waters which have not undergone large amounts of evaporation. Samples of meteoric water will plot along the meteoric water line (MWL) as described by Craig (1961 a).

The shallow geologic deposits in the Saginaw Lowland area of the east-central Michigan basin (Figure 1.1) yield isotopically-depleted, saline ground water, as reported by Badalamenti et al. (1988) and Long et al. (1988). Long et al. (1988) found that ground water from the glacial deposits and near-surface bedrock in Bay County, Saginaw Lowland (see Figure 1.2 for location) has del oxygen-18 values ranging from -6.93 o/oo to -18.46 o/oo; and del deuterium values ranging from -47.3 o/oo to -137.4 o/oo. The concentrations of oxygen-18 and deuterium are reported according to the standard of Craig (1961 b). These values plot along the MWL of Craig (1961 a) indicating meteoric origin of the ground water. They interpret these data to indicate that during the Pleistocene epoch, isotopically-light meteoric water recharged the system, and has since mixed with modern-day meteoric water producing a variable isotopic composition in the ground water. These observations and conclusions are consistent with conclusions of Desaulniers et al. (1981) (study area location shown on Figure 1.1).

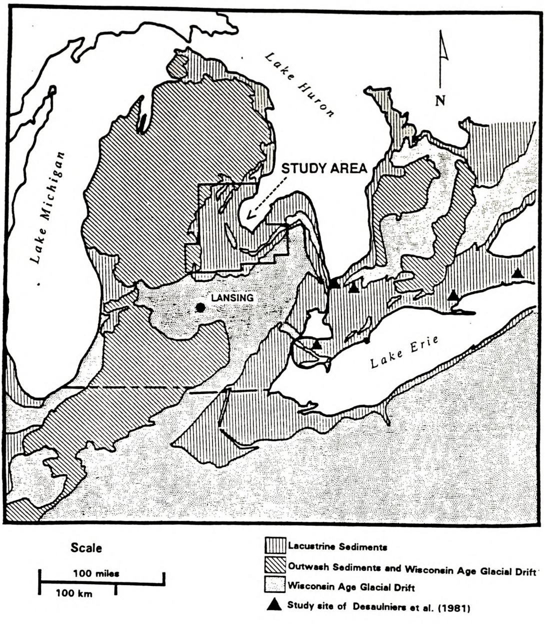


Figure 1.1 Surficial geology of the Michigan basin, with locations of the Saginaw Lowland, Simcoe and Greater Lansing study areas.

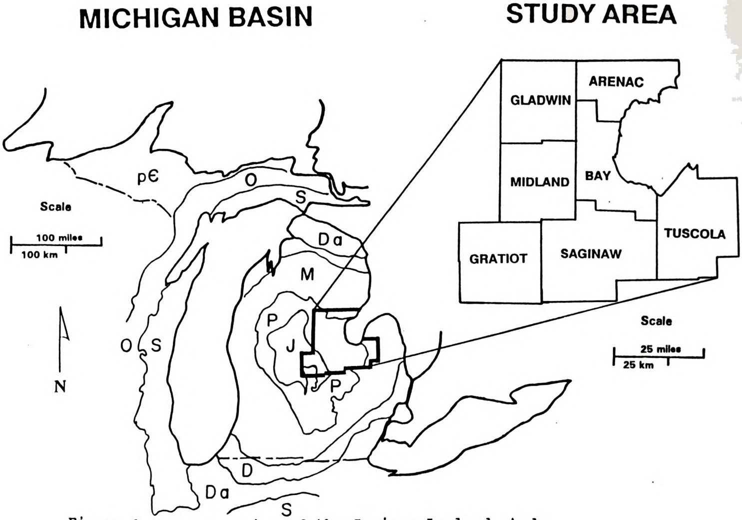


Figure 1.2 Location of the Saginaw Lowland study area, with generalized bedrock geology.

The shallow geologic deposits in the Saginaw Lowland, primarily lacustrine sediments and glacial drift, are characterized as aquitards (see Figure 1.1 for distribution of the aquitards). The ground water in these deposits has total dissolved solids concentrations of up to 53,000 mg/L (Long et al., 1986). The ratios of bromide to chloride concentrations for ground water samples compared to samples of meteoric water and local brines suggest that the ground water samples have been geochemically influenced by brines. The upward migration of brines from deeper in the Michigan basin via diffusion or advection may be producing salinity in the ground water (Long et al., 1988).

Isotopically-light ground water has been identified in aquifers by Clayton et al. (1966); Fritz et al. (1974); Perry et al. (1982); and Siegel and Mandle (1984). The origin of isotopically-light ground water in aquifers has been interpreted as recharge during a period when the climate was cooler than present day.

Isotopically-light ground water is frequently found in association with near-surface aquitards. The Quaternary argillaceous deposits of the Great Lakes region, considered aquitards, produce ground water significantly depleted in isotopes compared with modern-day meteoric water (Desaulniers et al., 1981; and Bradbury, 1984). Although the role of aquitards in affecting the hydrogeochemistry of ground water is becoming understood (Back, 1986), their role

in controlling the isotopic composition of ground water has been little studied. Aquitards have low hydraulic conductivity values, are composed of fine-grained reactive minerals, and have predominantly vertical ground-water flow direction (Back, 1986). They often produce water of poor quality. For example, the dissolution of reactive minerals in the aquitard deposits can produce mineralized water. Aquitards can control flow patterns of ground water, and thereby determine the distribution of different chemical types of ground water.

Long et al. (1988) hypothesize that ground-water salinity and isotopic depletion are due to the effect of aquitards in the ground water system. Modern meteoric recharge to the system is inhibited by the presence of relatively thick glaciolacustrine deposits, impermeable glacial till, and shale; and a low regional ground-water flow gradient. Long et al. hypothesize that the "glacial" water is retained in these deposits, because modern-day recharge water is only slowly "flushing" the system. In addition, they hypothesize that because the ground-water flow is stagnant and because the deposits lie in a discharge zone (potentiometric surfaces indicate upward flow), salinity can build up in the system, as brines move upwards into the system via diffusion or advection.

SECTION 2 - STUDY AREA

2.1 Location of Study Area

The Saginaw Lowland study area is a region of approximately 14000 square kilometers, located in the east-central Michigan basin, as shown in Figure 1.1. The Saginaw Lowland encompasses the counties of Arenac, Gladwin, Midland, Gratiot, Saginaw, Bay and western Tuscola in the state of Michigan (Figure 1.2). The study area is partially bordered by Saginaw Bay of Lake Huron.

2.2 Geology

The near-surface geologic deposits in the Saginaw Lowland are regarded as two units throughout this study. These units are referred to as "drift", corresponding to unconsolidated deposits of primarily glacial origin, and "bedrock", corresponding to the shallow bedrock formations which underlie the unconsolidated deposits or drift.

The topography of the Saginaw Lowland is characterized by level plains of lacustrine clay and gently rolling hills of ancient sand bars, beaches and moraines (Leverett and Taylor, 1915; Pringle, 1937; Vanlier, 1963).

Figure 1.1 illustrates the generalized surficial geology of the Great Lakes region. The lacustrine deposits denoted in Figure 1.1, which include the Saginaw Lowland, are known to produce saline ground water (Lane, 1899 a;

Lane, 1899 b; Twenter, 1987). The predominance of clay in regional glacial geology is illustrated in stratigraphic cross section A-A' (Figure 2.1), stratigraphic cross section B-B' (Figure 2.2) and stratigraphic cross section C-C' (Figure 2.3). The drift is primarily composed of clay-rich layers of great thicknesses. The well logs on which these cross-sections are based are provided in Appendix A. The locations of the stratigraphic cross sections are shown in Figure 2.4.

2.2.1 Geology of the Glacial Deposits

The drift has a thickness of up to 170 meters in western Gratiot County (Vanlier, 1963) but is not present in portions of northeastern Arenac County (Pringle, 1937). The drift is described as a sequence of stratigraphic units (Vanlier, 1963; Stark and McDonald, 1980; Dow Chemical Company, 1986). These units include a shallow (surficial) sand, glaciolacustrine deposits of clay and sand, a glacial till (morainal or till plain), and an aquifer (primarily sand and gravel outwash) lying in bedrock valleys. The regional stratigraphy of the drift is highly variable.

Thicker drift deposits may lie in buried erosional bedrock valleys with reliefs of 30 to 60 meters in which unconsolidated drift material has been deposited (Rhodehamel, 1951; Twenter and Cummings, 1985). The buried bedrock valleys trend northeast to northwest in Bay County

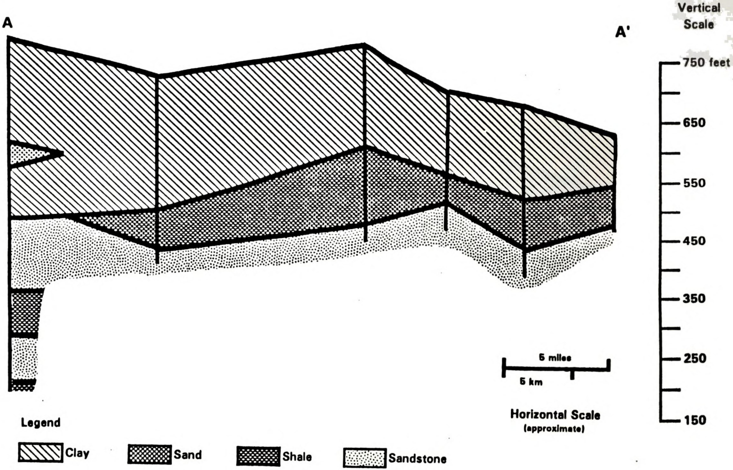


Figure 2.1 Stratigraphic cross section A-A'.

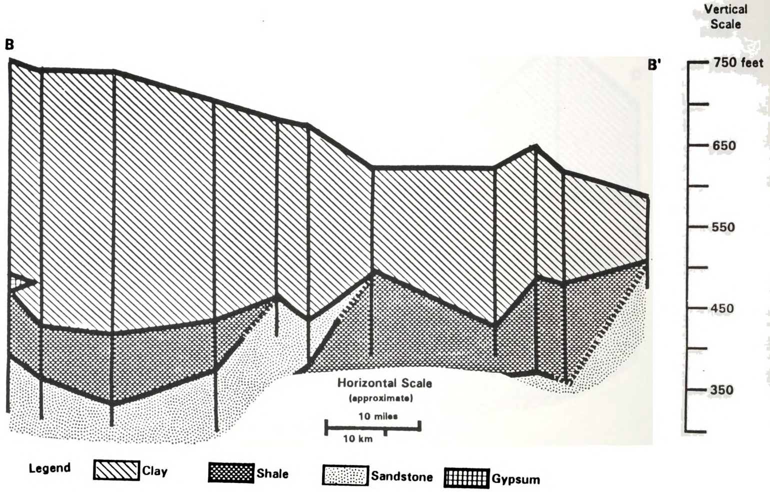


Figure 2.2 Stratigraphic cross section B-B'.

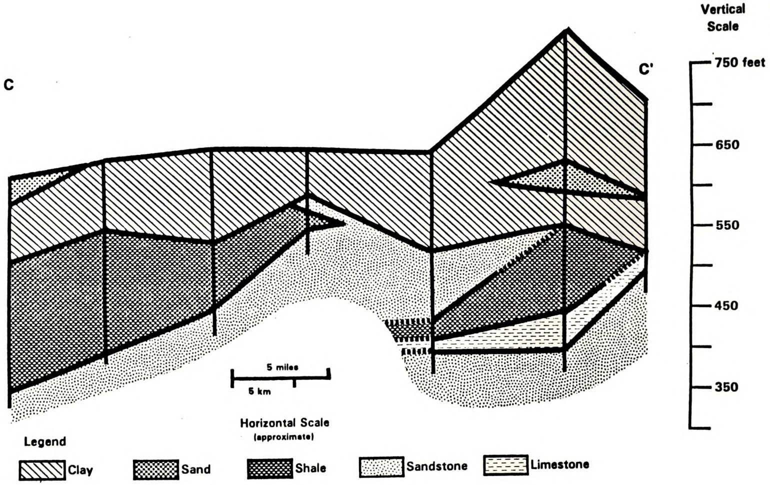


Figure 2.3 Stratigraphic cross section C-C'.

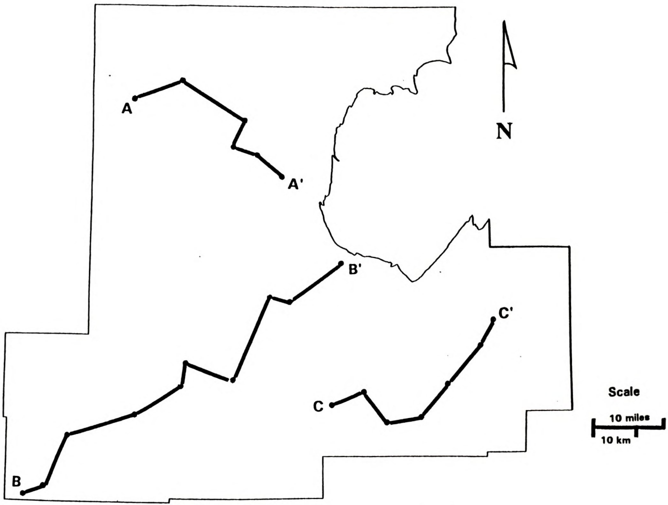


Figure 2.4 Locations of stratigraphic cross sections.

(Twenter and Cummings, 1985). In Bay County, the basal water-bearing formation, which lies below the glacial till, reaches 40 meters in thickness in bedrock valleys and is thinner where the bedrock surface is topographically high (Stark and McDonald, 1980).

The composition of the drift, although variable, is primarily composed of illite, kaolinite, chlorite, quartz, feldspar (unspecified), calcite and dolomite (Chittrayanont, 1978). In Bay County the water-bearing formations lying beneath the glacial till consist of poorly-sorted coarse sand, gravel and pebbles with some silt and clay. The sand is quartzose and the gravel consists of sandstone, carbonates, quartzite, chert, and igneous and metamorphic rocks (Stark and McDonald, 1980).

The origin of the drift deposits is primarily the result of glacial processes during the Pleistocene age (Vanlier, 1963; Stark and McDonald, 1980). The lithologic description of glacial till in the drift includes unsorted clay, silt, sand, gravel, cobbles and boulders (Dow Chemical Company, 1986). The glacial till is sometimes referred to as heavy boulder clay, according to Pringle (1937) and Vanlier (1963). Lenses of well-sorted sand and gravel, which are found in the glacial till, originated by glacial meltwater deposition. Lacustrine clays, deltaic deposits, channel deposits, and beach and dune sands are also present in the drift (Vanlier, 1963; Dow Chemical Company, 1986).

The glacial till was deposited as moraines in Arenac, Tuscola, western Gratiot and northwestern Gladwin counties. In some portions of the Saginaw Lowland, glacial till was deposited subaqueously. Some moraines have distinctive reliefs (up to 60 meters in height). Other moraines have slight relief (Leverett and Taylor, 1915; Pringle, 1937; Vanlier, 1963). The moraines were laid in belts which parallel the Saginaw Bay shoreline, as shown in the generalized map of surficial geology (Figure 1.1).

The moraines are paralleled by plains of sand and clay, which range from 15 to 30 meters in thickness (Leverett and Taylor, 1915; Pringle, 1937). The sand is typically well-rounded, sorted and quartzose, with a thickness of zero to six meters. The sand was typically deposited in a near-shore environment in proglacial lakes. The clay was typically deposited in glacial lakes and composed of mostly heavy blue clay and silt with some sand, gravel, hardpan (a clay and gravel mix) and pebbles of primarily quartzite, sandstone, siltstone, mafic igneous rocks, granite and carbonates (Pringle, 1937; Stark and McDonald, 1980).

2.2.2 Geology of the Bedrock Deposits

The drift lies on top of bedrock formations of the Michigan basin. The Michigan basin is a structural basin, consisting of layers of Paleozoic and younger sedimentary rocks, underlain by Precambrian crystalline rock (see Figure

1.2 for generalized bedrock geology). Regional dip is generally southwestward into the basin, with a northwest-southeast strike (Martin, 1958). Smaller scale folds trending northwest-southeast are found in Arenac County (Pringle, 1937) and most likely occur elsewhere in the study area. Kelly (1936) believed that a bedrock low approximately parallel to the axis of Saginaw Bay is evidenced in the Pennsylvanian Saginaw Formation. Kelly postulated that this generally supports the idea of post-Devonian folding which differs in trend from that of pre-Devonian time (Newcombe, 1932).

The Saginaw Lowland was developed primarily on the erosional surface of the underlying Pennsylvanian Saginaw Formation. Vanlier (1963) and Rhodehamel (1951) suggest that the Saginaw Lowland was base leveled due to the high resistance of the surrounding sandstone members of the Saginaw Formation and the low resistance of local shale members of the Saginaw Formation, which is predominantly shale. The neighboring bedrock uplands received thick glacial deposits due to the convergence of the Saginaw and Erie ice lobes, forming the Michigan-Saginaw and Huron-Saginaw Uplands as a result (Leverett and Taylor, 1915; Western Michigan University, 1981). Martin (1958) supports this, stating that the central lowland (which includes the Saginaw Lowland) falls between the highlands of the north-central southern peninsula and the highland extending from

the Thumb area to the south-central southern peninsula. The topography of the drift is similar to the bedrock topography on a large scale.

The youngest bedrock underlying portions the drift is referred to as "red beds", which consist of sandy gypsiferous shale and shaley sandstone with an erosional upper surface. Western Michigan University (1981) states that the red beds are of Jurassic age. The red beds have been completely removed by erosion in major pre-Pleistocene valleys (Vanlier, 1963). The red beds are found in northwestern Gladwin, western Midland and southern Gratiot Counties (Martin, 1936). The red beds are approximately ten meters thick and yield little water (Vanlier, 1963).

The major Pennsylvanian formation is the Saginaw Formation. This is the primary formation upon which the drift was deposited. The Saginaw Formation crops out in Arenac, Saginaw and Tuscola counties and underlies all of the region except northeastern Arenac County, where it is absent. The Saginaw Formation consists of lenticular beds of sandstone, shale, coal and limestone (Martin, 1936). The Saginaw Formation has a basin-wide thickness ranging from 0 to at least 163 meters with an average thickness of at least 122 meters (Kelly, 1936). In the Saginaw Lowland, the Saginaw Formation is composed primarily of shale, as shown in stratigraphic cross-sections A-A' (Figure 2.1), B-B'

(Figure 2.2) and C-C' (Figure 2.3). The locations of the stratigraphic cross sections are shown in Figure 2.4.

Within the Saginaw Lowland, the Saginaw Formation is noted for bituminous coal deposits which were mined in the region from the mid-1800's to 1950 (Cohee et al., 1950; Stark and McDonald, 1980). In Arenac County, the sandstone of the Saginaw Formation is grey and micaceous; and the shale is gray-black and carbonaceous. Marcasite and clay-iron stone concretions with sphalerite are common (Pringle, 1937). Zircon and tourmaline are found in white Saginaw sandstone of Arenac County (Kelly, 1936).

Although bedrock geology in the Saginaw Lowland is variable, Stark and McDonald (1980) define four bedrock units within the Saginaw Formation of Bay County. The deepest of these units is a fine-grained, quartzose, well-sorted and well-rounded sandstone of variable thickness, with some thin shale beds. This layer is overlain by a shale unit, consisting of thin beds of shaley quartz-rich sandstone, with some limestone. This shale unit averages 10 meters in thickness. On top of the shale unit is a coal unit of 0.5 meters average thickness. The uppermost bedrock unit is another shale unit, consisting of thin coal seams, quartzose sandstone, and mudstone and siltstone beds. The upper shale unit averages 15 meters in thickness (Stark and McDonald, 1980).

Unconformably underlying the Saginaw Formation are the Mississippian Bayport and Michigan Formations, respectively. The Bayport Formation consists of limestone, dolomite and calcareous or argillaceous sandstone. It crops out in Arenac and Saginaw Counties, and ranges in thickness from 12 to 30 meters basin-wide (Martin, 1936; Pringle, 1937).

The Michigan Formation is composed primarily of sandstone and shale with beds of gypsum and anhydrite underlain by dolomitic limestone. The formation crops out in Arenac County and has been mined for gypsum. The thickness of the Michigan Formation ranges from 0 to 152 meters basin-wide (Martin 1936; Pringle, 1937; Martin, 1958). Formations deeper than the Michigan Formation were not investigated in this study.

2.3 Hydrogeology

The drift and bedrock can each be characterized as aquitards encompassing discontinuous aquifers. The drift aquitards are composed of thick sequences of lacustrine clay and argillaceous till. The bedrock aquitards are composed of shale. Stratigraphic cross sections A-A' (Figure 2.1), B-B' (Figure 2.2) and C-C' (Figure 2.3) illustrate this. The locations of the stratigraphic cross sections are shown in Figure 2.4. In the drift, the discontinuous aquifers are composed of isolated water-bearing sand and gravel lenses within the glaciolacustrine clay and clay-rich till; and of

sand and gravel outwash deposits (found at the base of the till) (Vanlier, 1963; Chittrayanont, 1978). Although the drift and bedrock are each characterized as aquitards, there are chemical and isotopic differences between the two units. These differences will be discussed in detail in subsequent sections.

The ground water derived from the drift and bedrock in the Saginaw Lowland is noted for its salinity (Lane, 1899 a; Lane 1899 b; Vanlier, 1963; Twenter, 1987). Figure 2.5 and Figure 2.6 illustrate the regional distribution of chloride concentrations in ground water derived from these deposits. High chloride concentrations are common in ground water derived from both drift and bedrock deposits in Saginaw Lowland (see Figure 2.5 and Figure 2.6).

The Saginaw Lowland is noted for its artesian saline springs (Lane, 1899 a; Lane, 1899 b; Houghton, 1928; Martin, 1958); while the lower bedrock deposits in the region are noted for their brine content (Vanlier, 1963; Western Michigan University, 1981). Bedrock deposits located deeper within the Michigan basin produce brines concentrated to an unusually high degree (Case, 1945; Egleson and Querio, 1969; Sorenson and Segall, 1975). The deeper bedrock formations are also sources of oil and gas (Vanlier, 1963).

Regional water table elevations are shown on a contour map (Figure 2.7) which is derived from a map by Mandle

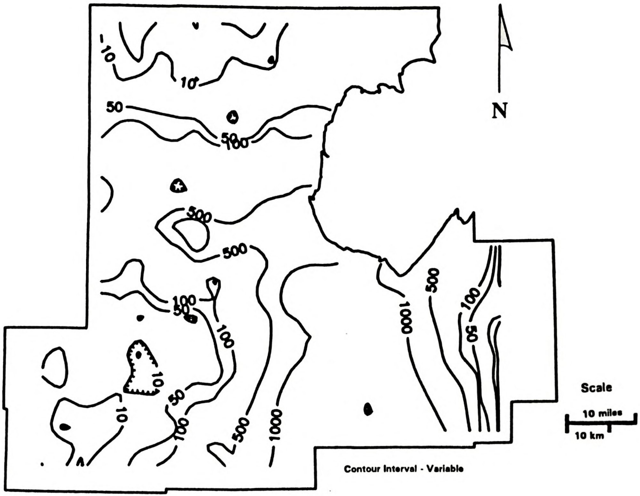


Figure 2.5 Chloride distribution in the drift deposits of the Saginaw Lowland.

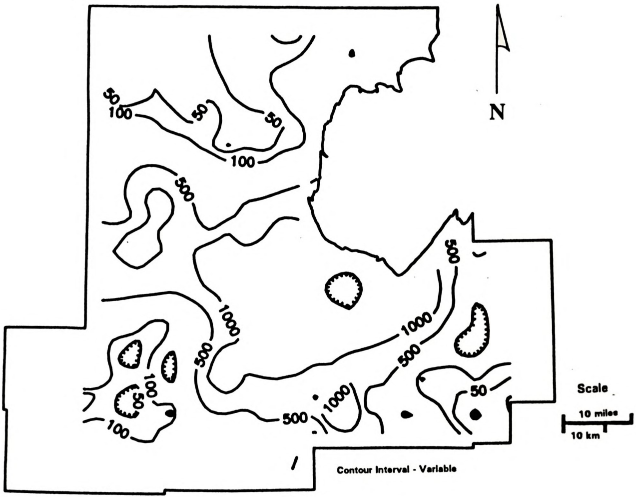


Figure 2.6 Chloride distribution in the bedrock deposits of the Saginaw Lowland.

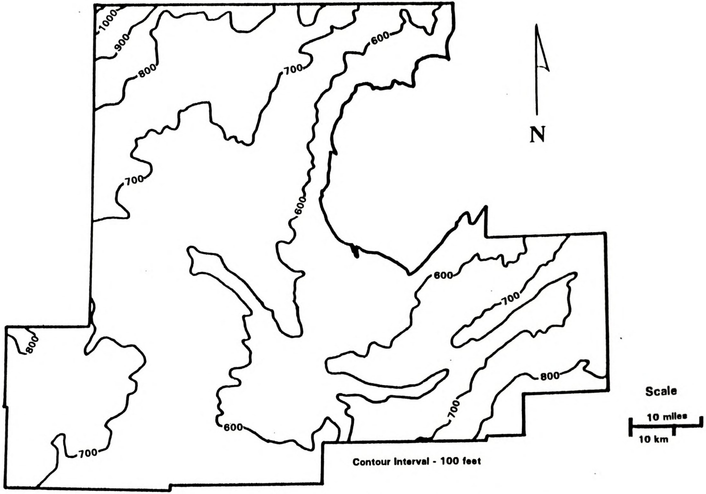


Figure 2.7 Water table elevations of the Saginaw Lowland.

(1989). Elevations are based on water level measurements taken in water wells as recorded by well drillers. The measurements are reported on well logs dated 1969 through 1975. Figure 2.7 accounts for the influence of surface-water levels from major inland lakes and streams and the Great Lakes. Additionally, Figure 2.7 reflects the influence of topography and major stream systems on the water table.

The water-bearing formations of the lower units in the drift and of the underlying bedrock are hydrologically confined (Vanlier, 1963; Stark and McDonald, 1980; Dow Chemical Company, 1986). Water levels in the confined formations average 10 meters below land surface (Stark and McDonald, 1980).

Figure 2.8 is a contour map of the potentiometric surface of the confined portions of the drift. Figure 2.9 is a contour map of the potentiometric surface of the confined portions of the bedrock. These maps are based on water level measurements as reported on well logs which have been density-corrected. Water level measurements reported on well logs for all drift wells sampled were used and are provided in Appendix B. Water level measurements reported on Well logs for all bedrock wells sampled were used and are provided in Appendix C. Water level measurements reported on additional wells logs, which were not sampled, were

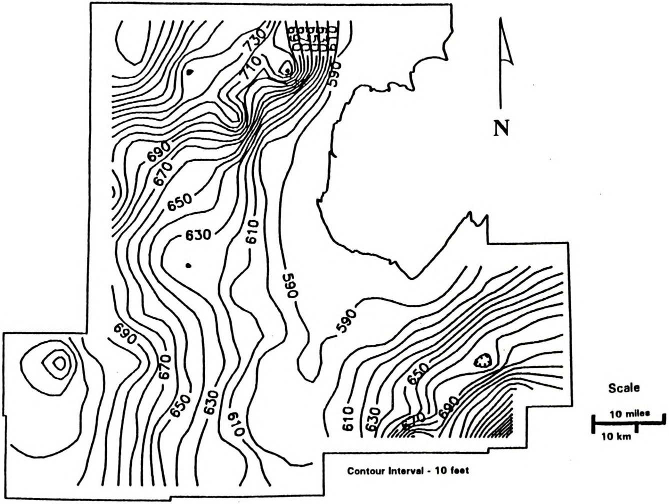


Figure 2.8 Potentiometric surface of the drift deposits of the Saginaw Lowland.

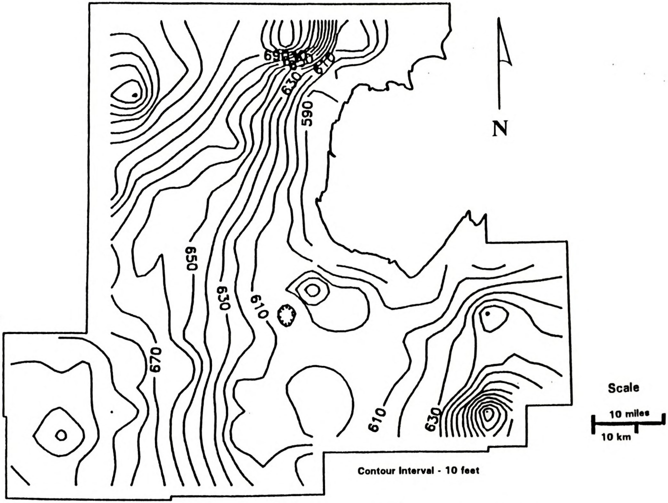


Figure 2.9 Potentiometric surface of the bedrock deposits of the Saginaw Lowland.

selected at random to increase the density of data points for construction of Figure 2.8. These well logs are provided in Appendix D.

The density of highly saline ground water in a well may affect its hydraulic head and the interpretation of piezometric potential in a well (Long et al., 1986). Because ground water in the Saginaw Lowland is highly saline, a series of equations described by Gudramovics (1981) was used to calculate water density, accounting for variability due to temperature and salinity. Water level measurements for piezometric surface interpretations in the Saginaw Lowland were then adjusted using the calculated water density.

A description of the calculations used to adjust water levels according to water density follows. At a constant temperature, the relationship between density and salinity is linear. Salinity was estimated from the chloride concentration by Equation 1 (Schopf, 1980) as follows:

$$\text{Salinity (o/oo)} = 1.80655 * (\text{Cl} \quad \text{(o/oo)}).$$

To calculate the density of water at the measured temperature in a well, the value of the y-intercept and slope was calculated. The y-intercept (density of pure water at a specified temperature) at a temperature (T) was calculated by Equation 2 (Weast, 1979) as follows:

- y-intercept = [999.83952 + (16.945176*T) - (7.9870401*10-3*T2) - (46.170461*10-6*T3) + (105.56302*10-9*T4) - (280.54253*10-12*T5)]/{[1 + (0.01687985*T)]*1000}.

The slope for the specified temperature was calculated by Equation 3 (Horne, 1969) as follows:

- slope = 8.300245*10-4 - 2.2274915*10-5 * ln T.

After calculations were completed for salinity, y-intercept and slope for a water sample at the temperature at which it was sampled, the density of the water was calculated by Equation 4 as follows:

- density = (salinity * slope) + y-intercept.

The density for each ground-water sample was calculated using Equations 1 through 4. The density was then multiplied by static water level elevations, resulting in piezometric surface elevations which were contoured as shown in Figure 2.8 and in Figure 2.9. The maps were contoured using Surfer^{TM} (Golden Software).

Each of the water level contour maps (water table, Figure 2.7; and piezometric surfaces, Figure 2.8 and Figure 2.9) indicate that within the Saginaw Lowland, the horizontal component of ground-water flow is towards Saginaw Bay.

The vertical component of ground-water flow is indicated by a residual potentiometric surface map (Figure 2.10) (see also Thorstenson and Fisher, 1979 and Long et al., 1988). The residual potentiometric surface map is the result of subtracting the potentiometric surface of the drift from the potentiometric surface of the bedrock. A positive value of residual potentiometric surface results when the potentiometric surface of the bedrock is greater than that of the drift. Figure 2.10 indicates that ground water discharges from the bedrock into the drift in much of the Saginaw Lowland. Potentiometric surfaces are generally greater (higher) in the bedrock wells than in the drift wells. Additional evidence that ground water tends to discharge from the deeper units into the shallower units is that artesian flowing bedrock wells have been reported throughout the region from as long ago as 1899 (Lane a and b) and 1906 (Cooper, 1906).

A horizontal hydraulic gradient can be estimated by observing the vertical change in water level elevation over a specific horizontal distance using Figure 2.7, Figure 2.8 and Figure 2.9. Horizontal hydraulic gradients are estimated to be 0.0001 to 0.006. The horizontal hydraulic gradient decreases in the direction of ground water flow (Chittrayanont, 1978; Stark and McDonald, 1980). Horizontal ground water flow is towards Lake Huron, and locally towards streams and drains. Stark and McDonald (1980) analyzed

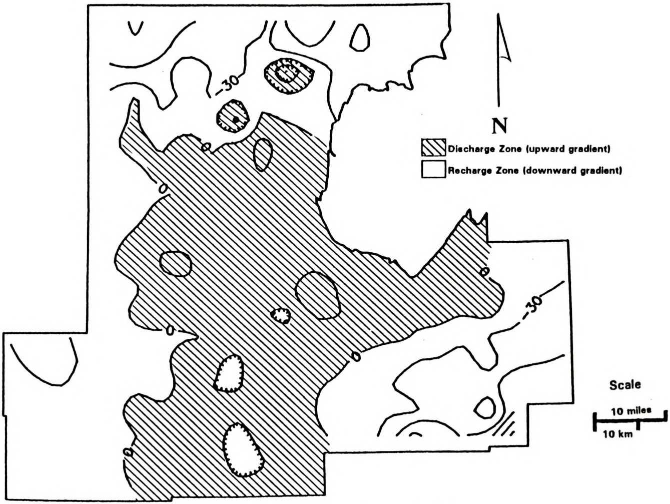


Figure 2.10 Residual potentiometric surface.

potentiometric head data from Bay County which indicated a horizontal hydraulic gradient of 0.003. The horizontal hydraulic gradient in Bay County was reported as less than 0.0005 to less than 0.002 by Long et al. (1988). These values for horizontal hydraulic gradients support the statement that the Saginaw Lowland is poorly drained (Stark and McDonald,1980). The local vertical hydraulic gradient in Bay County had a downward component of 0.03 (Stark and McDonald, 1980).

SECTION 3 - METHODOLOGY

3.1 Ground-Water Sampling Sites

Ground-water samples were collected from 96 domestic and municipal wells during the summer of 1986. Forty-one of these samples were taken from wells which derive water from drift deposits, referred to as drift wells. Fifty-five samples were obtained from wells which derive water from bedrock deposits, referred to as bedrock wells. The locations of ground-water sampling points (sampled wells) distinguished as drift or bedrock wells are shown in Figure 3.1. The locations of the ground-water sampling points distinguished by study identification number are shown in Figure 3.2. Well logs for all drift wells sampled are provided in Appendix B. Well logs for all bedrock wells sampled are provided in Appendix C.

Sample sites were selected on the basis of two primary factors: (1) type of deposit the well was screened or completed in; and (2) location of the well. A well was sampled depending on the type of deposit from which water was derived (drift or bedrock). Locations of sample sites were selected to obtain a relatively even distribution of sample points. Geochemical data from nine wells reported Long et al. (1986) for Bay County were added to the data set, with selection based on location and type of deposits from which water was derived.

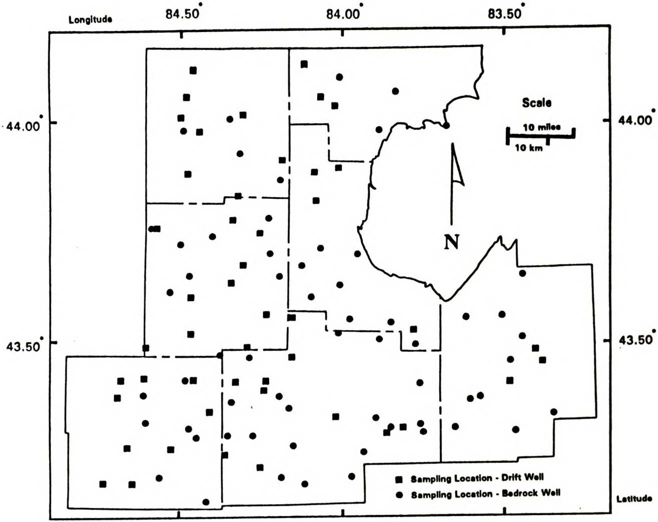


Figure 3.1 Locations of drift and bedrock ground-water sample sites.

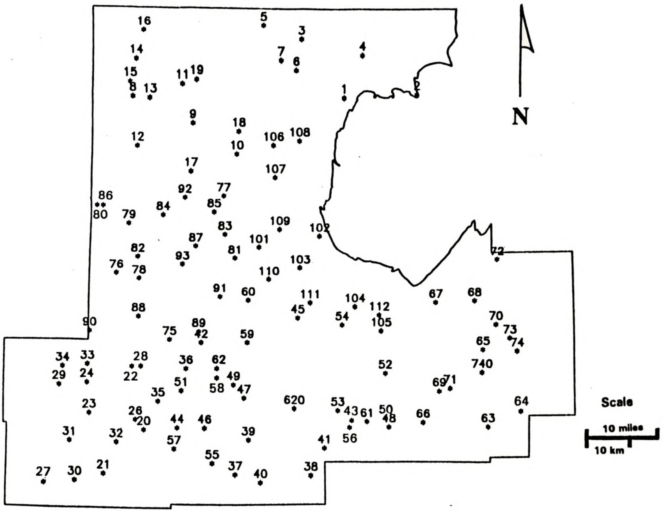


Figure 3.2 Locations of ground-water sample sites, with site numbers.

3.2 Sample Collection

Wells were pumped and field measurements and water samples were taken after constant water temperature was detected (approximately twenty minutes). Care was taken to avoid the influence of any water treatment on the samples. Field measurements and sample collection were performed according to standard techniques of the United States Geological Survey (U.S.G.S.) as described in Skougstad et al. (1985). Sample bottles were shipped on ice daily by air freight to the U.S.G.S. Laboratory in Denver, Colorado for chemical analysis.

The field measurements taken were specific conductance, temperature, pH, dissolved oxygen content and alkalinity. Specific conductance and temperature were recorded using a YSI Model 33 S-C-T meter. Specific conductance values were corrected for temperature by a correction factor equal to $1/\{1 + [.02\ (\text{temperature} - 25)]\}$. The pH was measured with a Beckman Model Φ21 pH meter.

Dissolved oxygen was measured at the sampling location with a Hach chemical kit and digital titrator, using an azide modification of the Winkler method. A sample was collected by running a hose directly into a biochemical oxygen demand (BOD) bottle. Care was taken to ensure no air bubbles came through the hose. The bottle was immersed in

water while being allowed to overflow about three times its volume. The bottle was then glass-stoppered.

A premeasured amount of manganous sulfate powder and alkaline iodide azide reagent were added to the BOD bottle. The mixture formed a flocculate precipitate. When this precipitate settled, a premeasured amount of sulfamic acid powder was added. This caused the floc to dissolve, resulting in a yellow colored solution. Two hundred milliliters of the yellow solution were measured into a beaker. Two milliliters of starch indicator solution was added to the beaker, causing a blue color to develop. A Hach digital titrator was used to titrate the blue solution with 0.200 N sodium thiosulfate. Titration was complete upon reaching a colorless solution. The dissolved oxygen value in mg/L oxygen was read directly from the Hach digital titrator, based on the strength of the sodium thiosulfate, the amount of water titrated, and the amount of sodium thiosulfate released with each rotation of the titrator.

Alkalinity was measured at the sampling location. The determination of alkalinity as calcium carbonate was performed on one hundred milliliters of unfiltered ground water which was collected in a beaker. A Hach digital titrator was used to titrate the water with 1.6 normal sulfuric acid. Titration was complete upon reaching the calcium bicarbonate titration endpoint (approximately 4.5 pH), where all solutes contributing to alkalinity had

reacted with the sulfuric acid (Hem, 1985). The alkalinity value in mg/L calcium carbonate was read directly from the Hach digital titrator, based on the strength of the sulfuric acid, the amount of water titrated, and the amount of acid released with each rotation of the titrator.

Six sample bottles were filled for laboratory analyses at each sampling site, because the various chemical constituents to be measured required different collection, preservation and analytical techniques, and large sample volumes were needed. All sample bottles were acid-washed and rinsed with distilled water. Additional sample bottles were filled for isotopic analyses, as will be discussed later.

Four of the six sample bottles collected for chemical analyses were filled with water filtered with a Geotech backflushing filter assembly. The nitrocellulose filter membrane was 142 millimeters in diameter with a pore size of 0.45 micrometers. The four sample bottle types, constituents analyzed and preservation techniques are listed below:

(1) A one-liter acid-washed white plastic high density polyethylene (HDPE) bottle was used to collect a sample for the analysis of dissolved calcium, dissolved magnesium, dissolved sodium, dissolved potassium, dissolved iron, dissolved lithium, dissolved manganese, dissolved strontium,

aluminum, arsenic, and zinc. This sample was preserved with two milliliters of nitric acid.

(2) A one-liter white plastic bottle (HDPE) was used to collect a sample for the analyses of dissolved sulfate, dissolved chloride, dissolved fluoride, dissolved solids, dissolved silica, dissolved boron, and dissolved bromide. This sample did not require preservation.

(3) A two-hundred milliliter brown plastic bottle (HDPE) was used to collect a sample for the measurement of dissolved nitrite and nitrate nitrogen. This sample was chilled on ice.

(4) A two-hundred and fifty milliliter brown plastic bottle (HDPE) was used to collect a sample for the measurement of dissolved ammonia nitrogen. This sample was preserved with 13 milligrams of mercuric chloride and chilled on ice.

At each sample location, a fifth sample bottle was filled with water which had been filtered with a Gelman stainless steel filter assembly. The 45 millimeter diameter filter paper was silver-coated. A 125 milliliter glass bottle was used to collect a sample for analysis of dissolved organic carbon content. This sample was chilled on ice.

A sixth sample collected at each sampling location was not filtered. A 250 milliliter white plastic bottle (HDPE) was used to collect a sample for analysis of total sulfide. Zinc acetate (0.5 grams) was added to each bottle as a preservative.

Additional samples for analysis of stable isotopes of oxygen, deuterium and carbon were collected at the same time as the other samples. Oxygen and deuterium isotope samples were collected, without filtering, in 125 milliliter glass bottles, and were preserved with 26 milligrams of mercuric chloride. Stable carbon isotope samples were collected, without filtering, in one-liter glass bottles, with the addition of 50 milliliters of ammoniacal strontium chloride as a preservative.

3.3 Analytic Techniques

All chemical parameters were measured according to the standard methods chemical analysis of the U.S.G.S. as described in Skougstad et al. (1985) and summarized on Table 3.1.

Oxygen and deuterium isotope samples were analyzed at the U.S.G.S. Reston Stable Isotope Laboratory in Reston, Virginia. The analytic techniques for analyses of oxygen isotopic ratios included equilibration with carbon dioxide, with a modification of the analytic technique of Epstein and Mayeda (1953). Deuterium analyses were performed with a

Table 3.1 **Parameters and methods of chemical analysis.**

Parameter	Analytic Method
Alkalinity, as $CaCO_3$	Electrometric Titration
Aluminum, Dissolved	Chelation-Extraction Atomic Absorption, Spectrometric
Arsenic, Dissolved	Hydride Atomic Absorption, Spectrometric, Automated
Boron, Dissolved	DC Plasma Atomic Emission Spectrometric
Bromide, Dissolved	Ion Exchange, Chromatographic-Electrochemical, Automated
Calcium, Dissolved	Direct Atomic Absorption, Spectrometric
Chloride, Dissolved	Ferric Thiocyanate, Colorimetric, Automated-Discrete
Fluoride, Dissolved	Ion-Selective Electrode, Electrometric, Automated
Hardness	Calculation
Hardness,Noncarbonated	Calculation
Iron, Dissolved	Direct Atomic Absorption, Spectrometric
Lithium, Dissolved	Direct Atomic Absorption, Spectrometric
Magnesium, Dissolved	Direct Atomic Absorption, Spectrometric
Manganese, Dissolved	Direct Atomic Absorption, Spectrometric
Nitrogen, Nitrite plus Nitrate, Dissolved	Cadmium Reduction-Diazotization, Colorimetric, Automated-Segmented Flow
Nitrogen, Ammonia, Dissolved	Indophenol Colorimetric, Automated
Nitrogen, Ammonia, Total	Indophenol, Colorimetric, Automated
Oxygen, Dissolved	Winkler Method, Titrimetric
pH	Glass Electrode, Electrometric
Potassium, Dissolved	Direct Atomic Absorption, Spectrometric
Silica, Dissolved	Molybdate Blue, Colorimetric, Automated
Sodium, Absorption Ratio	Calculation
Sodium, Dissolved	Direct Atomic Absorption, Spectrometric
Sodium, Percent	
Solids, Residual Dissolved	Calculation
Solids, Dissolved on Evaporation	Gravimetric, Residue on Evaporation at 180 C
Specific Conductance	Electrometric, Wheatstone Bridge
Strontium, Dissolved	Direct Atomic Absorption, Spectrometric
Sulfate, Turbidimetric Dissolved	Barium Sulfate, Turbidimetric, Automated-discrete
Sulfide, Total	Iodometric, Titrimetric
Zinc, Dissolved	Direct Atomic Absorption, Spectrometric

semi-automatic mass spectrometer after reaction with zinc according to the techniques of Kendall and Coplen (1985). Oxygen and deuterium isotopic ratio values are reported as del values, relative to values of standard mean ocean water (SMOW) (Craig, 1961 b). Analytic precision for oxygen is +0.15 o/oo and deuterium isotopic analyses are and + 2.0 o/oo, respectively.

Carbon-13 samples were analyzed at Global Geochemistry of Los Angeles, California. The analyses employed a nuclide mass spectrometer to measure the carbon-13 to carbon-12 ratio on carbon dioxide generated from a strontium carbonate precipitate, according to a modification of the technique of McCree (1950). Analytic precision for del carbon-13 values is +2.0 o/oo, relative to the PDB standard which has an assigned del carbon-13 value of 0 o/oo.

3.4 Data Reduction

The methodology for chemical data reduction included statistical, graphical and computer modeling techniques. The statistical data reduction technique of Student's t-Tests is described and the results of this technique are discussed in Section 4.1.1. The multivariate statistical data reduction techniques are described and the results of these techniques are discussed in Section 4.1.2. The graphical data reduction techniques are described and the

results are discussed in Section 4.1.3. The computer modeling techniques are described and the results are discussed in Section 4.1.4.

SECTION 4 - RESULTS AND DISCUSSION

4.1 Chemical Characterization

The results of chemical analyses of ground-water samples collected from the drift are summarized in Table 4.1. The results of chemical analyses of ground-water samples collected from the wells screened within the bedrock are summarized in Table 4.2. The techniques and results of data reduction, which included statistical (Student's t-Tests and multivariate factor analysis), graphical and computer modeling techniques, are discussed below.

4.1.1 Student's t-Tests for Comparison of Drift and Bedrock Geochemistry

Student's t-Tests were used to compare ground-water geochemistry of drift and bedrock for selected chemical parameters, to test for statistically significant differences in values between the drift and bedrock ground water. The t-tests were run with two different sets of equations, including the Cochran's Approximation to the Behrens-Fisher Student's t-Test (U.S. EPA, 1987) and Pooled Variance, which assumes that the populations have equal variances. Both sets of equations produced the same results with the Saginaw Lowland geochemical data. The population was defined as the concentrations of a chemical parameter in either drift or bedrock ground water samples. Each individual t-test for a given population was performed at

Table 4.1 - Summary of analytical results of ground-water samples collected from drift deposits in the Saginaw Lowland

Site Number	Latitude	Longitude	Del D (o/oo)	Del O1 (o/oo)	Del C13 (o/oo)	Alkalinity (CaCO3)	Al (ug/l)	As (ug/l)	B (ug/l)	Br	Ca	Dissolved Organic Carbon	Cl	F	Fe (ug/l)	Li (ug/l)	Mg	Mn (ug/l)	N	NH4
5	440738	840705	-68.5	-10.3		209	<10	13	110	0.034	57	1.9	3	0.7	680	<4	21	10	0.27	0.35
6	440214	840138	-67.5	-10.4		313	10	<1	40	0.070	95	1.2	36	0.1	6	11	22	2	0.03	0.04
7	440328	840405	-64	-9.8		195	<10	5	50	<0.010	40	6.0	1	0.6	470	8	15	18	0.23	0.30
12	435254	842847	-65	-9.5		313	<10	2	240	0.37	130	1.8	180	0.3	510	17	33	66	0.25	0.32
13	435849	842614	-71.5	-10.6		104	<10	8	290	0.026	240	1.0	7	0.4	1400	31	66	64	0.92	1.2
14	440322	842911	-67.5	-10.1		249	<10	16	80	0.020	58	1.5	1	0.6	580	9	29	9	<0.05	0.06
15	440034	843000	-66.5	-10		343	<10	2	60	0.018	82	1.2	8	0.3	46	9	31	130	0.81	1.0
16	440650	842800	-70	-10.4		214	<10	5	40	0.017	56	1.5	1	0.3	650	6	16	32	<0.05	0.06
17	434945	841928	-64.5	-10.1		141	<10	6	230	0.31	60	1.6	140	1	390	18	22	14	0.58	0.75
18	435447	841112	-61.5	-9.7		192	<10	2	280	<0.010	90	2.5	2	1.2	1000	18	28	19	0.45	0.58
19	440106	841829	-70.5	-10.35		142	<10	<1	<10	<0.010	29	2.0	2	0.2	44	5	7	27	0.06	0.08
27	431029	844346	-66	-10.1		281	<10	13	20	0.045	97	2.1	51	0.4	950	11	32	21	0.17	0.22
28	432441	842725	-63.5	-9.6	-14.00	325	<10	14	100	0.022	64	2.0	4	0.7	730	13	24	10	0.35	0.45
29	432219	844116	-65	-9.8		288	<10	4	100	0.024	110	1.2	5	0.4	1700	12	27	44	0.43	0.55
30	431032	843826	-64.5	-9.8		337	<10	14	50	0.013	65	1.2	1	0.4	530	13	26	96	0.19	0.24
31	431523	843935	-65	-9.9	-12.40	175	<10	9	180	0.027	15	3.0	3	1	41	6	10	6	0.31	0.40
32	431513	843126				173	<10	5	180	0.043	260	2.5	3	0.6	3000	31	38	67	0.50	0.64
33	432445	843628	-66	-10		227	<10	<1	170	0.12	110	1.4	51	0.4	790	20	29	54	0.42	0.54
34	432430	844045	-64.5	-9.6		315	<10	12	30	0.032	74	1.2	6	0.7	790	12	25	10	0.15	0.19
35	432022	842434	-62.0	-9.5		240	<10	4	190	<0.010	43	2.7	5	0.8	670	12	20	14	0.53	0.68
55	431252	841506	-76	-11.1		184	<10	8	420	2.0	100	1.6	560	0.5	900	30	63	20	0.83	1.1
56	431737	835141	-82.5	-11.9	-14.30	104	10	11	1100	7.1	320	0.3	3800	0.6	2400	90	100	120	3.4	4.4
57	431437	842140	-66.5	-10	-15.4	287	<10	5	180	0.038	49	2.2	9	0.8	480	13	13	19	0.44	0.57
58	432326	841436	-62.0	-9.3	-14.7	241	<10	4	130	<0.010	55	5.0	14	0.6	520	14	16	20	0.48	0.62
59	432756	840920	-71.0	-10.7		234	<10	10	240	0.16	37	2.5	130	0.7	280	9	25	8	0.52	0.67
61	431824	834845	-62.5	-9.3		392	<10	2	330	0.38	87	6.3	380	0.7	870	22	18	120	0.36	0.46
62	432437	841408	-66.9	-10		224	<10	5	230	0.081	48	1.5	42	0.6	330	21	18	13	0.31	0.40
620	431945	840108	-60.5	-8.8																
73	432857	832435	-69.5	-10.3		279		12	660	0.023	78	1.2	7	1.1	920	11	26	13	0.41	0.53
74	432724	832312	-64.5	-9.6	-13.60	263		17	330	<0.010	38	3.4	1	1.1	350	7	15	11	0.27	0.35
740	432433	832915	-68	-10.2		301						1.0								
78	433550	842806	-56.5	-8.7		365	20	<1	70	0.32	150	10	58	0.2	11	9	19	93	0.09	0.12
85	434431	841519	-82.5	-11.9		194	<10	7	290	0.17	130	3.0	12	1	960	5	39	34	1.2	1.5
86	434521	843432	-67.5	-9.9		220	<10	3	20	0.18	80	1.7	46	0.1	25	9	22	66	0.06	0.08
87	434012	841833	-72	-10.6		213	<10	<1	930	3.6	4	0.6	2100	0.5	70	70	4	<10	1.5	1.9
88	433106	842759	-76.5	-11.3		152	<10	<1	140	0.040	31	1.4	4	0.6	84	7	14	6	0.53	0.68
89	432911	841729	-60.5	-9.0	-14.20	271	<10	4	70	0.016	58	2.7	3	0.5	890	8	21	19	0.26	0.33
90	432906	843626	-65.0	-9.6		262	<10	<1	100	0.14	110	1.1	37	0.5	290	16	32	380	0.39	0.50
91	433340	841407	-66.5	-10.0		141	<10	<1	<10	<0.010	42	6.0	5	0.2	840	10	10	29	0.23	0.30
92	434619	842020	-97	-13.9		64	<10	7	330	0.18	430	1.4	47	0.8	1500	20	130	150	1.1	1.4
93	433749	842035	-98	-14		218	<10	1	180	0.018	51		6	0.9	760	14	19	11	0.52	0.67
109	434234	840405	-126.7	-17.14		162	<100	<1		<2.0	69		540	0.2	100		22	10		1.4
110	433603	840538				278	19	<1		<2.0	77		420	0.4	20		24	20		2.1
111	433306	835949				290	<100	<1		4.0	79		1500	0.3	130		33	<10		4.1
112	433140	834644	-113.8	-15.64		140	<3	5		<2.0	190		1100	0.8	40		66	90		1.4

Note: All values reported in mg/l unless otherwise noted.

Table 4.1 (cont'd).

Site Number	Latitude	Longitude	Dissolved Oxygen	pH	K	Dissolved Solids	SIO2	Na	Specific Conductance (umhos/cm)	Sr (ug/l)	SO4	S	Temperature (degrees C)	Zn (ug/l)
5	440738	840705	1.3	7.8	1.5	383	13	36	493	1400	150	<0.5	10.3	11
6	440214	840138	7.9	7.1	2.7	408	9.5	27	403	110	29	<0.5	10.7	18
7	440328	840405	1.2	7.7	1.1	208	15	16	303	580	3	<0.5	10.3	110
12	435254	842847	2.6	7.2	2.9	835	11	110	887	1400	190	<0.5	10.0	9
13	435849	842614	0.8	7.7	3.6	1420	14	53	1580	3700	790	<0.5	10.8	94
14	440322	842911	4	7.6	1.8	375	15	24	250	1100	79	<0.5	9.1	27
15	440034	843000	1.2	7.2	1.9	360	12	14	433	610	55	<0.5	10.7	36
16	440650	842800	1.2	7.6	1.1	232	11	8	373	320	19	<0.5	9.6	37
17	434945	841928	1.5	7.8	2.3	600	12	110	917	1900	160	<0.5	10.8	170
18	435447	841112	1.4	7.7	2.1	676	13	72	918	2100	360	<0.5	11.7	17
19	440106	841829	1.9	6.1	0.7	145	12	4	200	190	17	<0.5	9.1	64
27	431029	844346	1.2	7.3	1.1	470	18	20	621	230	85	<0.5	11.8	260
28	432441	842725	2.1	7.5	1.4	325	18	25	499	870	32	<0.5	16.3	50
29	432219	844116	0.01	7.4	1.7	499	16	23	716	960	150	<0.5	11.5	25
30	431032	843826	0.5	7.4	1.3	294	19	12	463	500	8	<0.5	10.6	92
31	431523	843935	1.4	8.3	1.5	194	11	45	280	450	7	<0.5	12.4	94
32	431513	843126	0.1	7.4	1.9	1310	17	57	1390	1300	740	<0.5	10.8	30
33	432445	843628	0.3	7.5	1.7	624	15	61	931	1100	240	<0.5	10.9	15
34	432430	844045	0.9	7.4	1.3		20	7	495	480	19	<0.5	11.9	19
35	432022	842434	1.2	7.7	1.8	325	16	44	461	950	59	<0.5	10.8	41
55	431252	841506	1.6	7.5	2.5	1300	13	290	1800	2900	160		11.7	110
56	431737	835141	0.6	7.5	8.8	7230	12	2100	12000	9200	420		12.5	120
57	431437	842140	1.4	7.7	1.4	312	14	44	476	740	57		10.3	44
58	432326	841436	1.3	7.8	1.8	313	17	31	472	980	55		11.0	330
59	432756	840920	2.1	7.9	1.9	448	12	94	713	1000	51		12.7	32
61	431824	834845	1.3	7.3	2.6	1060	11	280	1820	970	63	<0.5	14.3	46
62	432437	841408	0.9	7.6	2.3	460	14	67	601	530	70	<0.5	10.4	7
620	431945	840108												
73	432857	832435	0.3	7.6	2.2	471	14	44	415	2200	170	<0.5	10.3	6
74	432724	832312	1.1	7.9	1.6	220	14	24	275	740	7	<0.5	10.9	33
740	432433	832915	1.3	7.4					245			1.2	10.6	
78	433550	842806	1.2	6.9	7.7	533	9.2	19	884	710	100	<0.5	13.7	22
85	434431	841519	0.2	7.7	2.8	1030	13	110	1310	3000	610	<0.5	13.5	370
86	434521	843432	0.8	7.4	0.9	348	14	13	472	110	32	<0.5	10.3	9
87	434012	841833	1.5	7.7	6.3	3890	11	1500	4790	70	290	<0.5	11.1	20
88	433106	842759	6	8.0	0.7	286	12	48	383	890	98	<0.5	12.1	64
89	432911	841729	0.5	7.5	1.7	227	16	17	410	720	14	<0.5	11.2	13
90	432906	843626	4.3	7.4	2.0	572	17	43	846	1400	190	<0.5	10.4	68
91	433340	841407	0.9	7.7	0.7	184	19	2	259	81	21	<0.5	9.7	33
92	434619	842020	0.3	7.6	4.6	2800	11	200	2160	8800	1800	<0.5	11.8	70
93	433749	842035	0.9	7.7	1.7	395	14	39	326	1200	68	<0.5	11.3	88
109	434234	840405		7.67	4.10	4132	4.3	330	2900		96	<0.1	13.7	210
110	433603	840538		7.98	2.90	2828	5.5	300	1700		15	<0.1	14.3	200
111	433306	835949		7.76	6.20	6325	6.3	900	3500		<1	<0.1	13.9	230
112	433140	834644		7.55	5.90	4917	5.1	570	2500		340	<0.1	12.9	90

Note: All values reported in mg/l unless otherwise noted.

Table 4.2 - Summary of analytical results of ground-water samples collected from bedrock deposits in the Saginaw Lowland

Site Number	Latitude	Longitude	Del D (o/oo)	Del O1 (o/oo)	Del C13 (o/oo)	Alkalinity (CaCO3)	Al (ug/l)	As (ug/l)	B (ug/l)	Br	Ca	Dissolved Organic Carbon	Cl	F	Fe (ug/l)	Li (ug/l)	Mg	Mn (ug/l)	N	NH4
1	435900	835317	-73.5	-10.8	-13.1	191	<10	<1	3200	1.2	150	0.3	500	0.9	340	60	35	40	1.2	1.5
2	435930	834044	-72.0	-10.5		272	<10	<1	580	0.75	110	0.7	330	0.6	650	23	13	7	0.59	0.76
3	440555	840028	-65.5	-10.0		292	<10	<1	370	0.070	120	2.2	30	0.6	1900	19	23	21	0.41	0.53
4	440408	835005	-67.5	-10.0		242	<10	<1	340	0.25	150	2.1	88	0.5	890	6	28	20	0.47	0.61
8	435852	842934	-85.0	-12.3		251	<10	<1	340	0.076	110	0.9	12	0.6	500	27	23	24	0.49	0.63
9	435541	841909	-79.5	-11.7		150	<10	<1	540	0.65	150	0.8	31	0.6	770	40	40	50	1.1	1.4
10	435211	841142	-102.5	-14.4		165	<10	<1	2100	0.039	33	0.3	8	0.7	46	53	13	35	0.91	1.2
11	440028	842102	-74.0	-10.9		171	<10	<1	360	0.061	57	0.2	29	0.4	310	22	16	13	0.40	0.52
20	431649	842654	-70.5	-10.4		278	<10	<1	80	0.068	96	1.6	50	0.6	290	23	21	10	0.36	0.46
21	431126	843339	-80.0	-11.8		230	<10	<1	340	0.98	190	1.4	370	0.3	3100	50	45	60	0.46	0.59
22	432433	842859	-71.5	-10.6		195	20	<1	180	0.098	140	0.9	33	0.2	760	36	32	15	0.36	0.46
23	431849	843610				324	10	6	100	<0.010	62	3.6	10	0.6	580	13	23	21	0.35	0.45
24	432242	843633	-68.0	-10.1		581	<10	<1	130	0.33	190	3.7	280	<0.1	320	15	54	190	0.10	0.13
25	430757	842503	-83.0	-12.0																
26	431802	842810				281	<10	4	170	0.033	49	1.8	9	0.6	540	24	19	15	0.28	0.36
36	432431	841948	-65.5	-10.0		281	<10	3	80	0.091	60	1.5	49	0.4	290	21	23	14	0.15	0.19
37	431125	841115	-60.0	-9.1																
38	431130	835815	-58.5	-8.8		334	<10	<1	220	0.033	63	1.5	11	0.5	230	28	23	12	0.67	0.86
39	431542	840901	-65.0	-9.7		270	<10	2	670	0.86	70	1.2	280	0.6	480	42	12	12	0.68	0.88
40	431030	840701	-62.0	-9.2		341	<10	<1	850	0.50	36	1.1	180	0.5	140	45	10	9	0.38	0.49
41	431457	835559	-62.5	-9.2		246	<10	<1	400	0.11	34	1.8	57	0.8	110	26	10	17	1.3	1.7
42	432746	841710	-91.5	-13.0	-13.6	231	<10	<1	1700	0.27	16	0.1	220	0.5	66	50	2	8	0.36	0.46
43	431822	835111	-89.0	-12.7		185	<10	4	1600	5.0	210	0.6	2700	0.6	1100	110	59	80	2.6	3.3
44	431714	842108	-67.5	-10.0	-13.1	201	10	<1	80	0.063	180	1.7	21	0.5	960	32	29	24	0.42	0.54
45	433105	840050	-111.0	-15.7		279	<10	<1	860	3.9	76	2.1	2400	0.5	380	60	40	20	2.8	3.6
46	431714	841624	-94.0	-13.4		267	<10	<1	590	0.53	160	1.1	440	0.5	740	<10	44	50	0.57	0.73
47	432103	840956	-96.0	-13.6		312	<10	<1	2200	1.1	18	0.3	660	0.8	30	70	5	20	0.58	0.75
48	431735	834458	-66.5	-9.8		309	<10	<1	850	1.3	100	1.0	670	1	590	50	23	30	0.57	0.73
49	432240	841140	-96.5	-13.9	-7.90	288	<10	<1	4100	2.8	46	0.2	2200	1	320	150	18	20	0.98	1.3
50	431851	834531	-66.5	-9.8		312	<10	5	160	0.068	78	1.9	37	0.5	1400	18	31	23	0.76	0.98
51	432127	842026	-65.0	-9.7		268	<10	6	130	0.11	59	1.8	67	0.6	570	17	24	10	0.46	0.59
52	432425	834529	-105.0	-15.0		368	<10	<1	3900	1.2	130	1.8	610	0.8	280	90	30	50	1.1	1.4
53	431939	835342	-63.0	-9.3		247	<10	18	580	0.37	25	3.4	210	2	120	17	7	11	0.36	0.46
54	433014	835317	-111.0	-15.4		295	<10	<1	2300	2.6	64	0.3	1400	0.9	260	70	24	30	2.6	3.3
63	431751	832810	-70.5	-10.3		335		6	40	0.020	71	1.7	1	0.5	2400	5	27	99	0.16	0.21
64	432017	832113	-72.0	-10.8		348		11	30	0.023	87	1.1	9	0.8	1200	13	34	23	0.08	0.10
65	432733	832903	-74.0	-10.9		267		1	4300	<0.010	9	0.9	3	2.7	41	16	4	4	0.13	0.17
66	431823	833908	-61.5	-9.3		277		<1	240	<0.010	50	5.0	3	0.6	390	20	13	39	0.93	1.2
67	433325	833721	-115.0	-16.3		358		<1	3100	3.8	47	1.4	2600	0.7	190	80	14	30	1.3	1.7
68	433336	833049	-108.0	-15.2	-11.3	214		<1	2600	0.56	36	1.1	300	1.4	110	40	10	10	0.47	0.61
69	432208	833619	-66.5	-9.9		253	20	<1	400	0.094	30	2.9	41	1.2	78	9	10	12	1.2	1.5
70	433042	832656	-70.5	-10.4	-14.10	193	<10	3	690	0.018	41	1.7	9	1.3	200	12	20	10	0.46	0.59
71	432229	833438	-67.5	-10.2		291		<1	600	0.12	54	1.3	60	0.9	220	16	20	15	0.32	0.41
72	433913	832701	-89.5	-12.9		199	<10	<1	930	0.13	60	1.1	40	1.2	390	21	14	21	0.39	0.50
75	432758	842234	-59.5	-8.9		298	<10	1	80	<0.010	59	3.3	1	0.5	1000	12	22	14	0.36	0.46
76	433641	843142	-71.5	-10.5	-11.50	160	<10	<1	400	2.1	170	0.7	880	0.3	620	80	36	40	0.50	0.64
77	434640	841335	-89.0	-12.7		205	<10	<1	860	0.17	110	1.3	70	0.4	790	37	32	44	0.81	1.0
79	434258	842928	-77.0	-11.2		221	<10	<1	550	0.44	92	1.2	200	0.3	1600	56	18	29	0.60	0.77
80	434518	843525	-66.0	-9.8		292	<10	2	20	<0.010	72	2.3	1	0.2	1200	10	21	50	0.12	0.15
81	433843	841148	-99.5	-14.2		314	<10	<1	1200	0.019	5	0.3	2100	0.4	30	110	4	<10	1.2	1.5
82	433850	842808	-85.0	-12.2		142	10	<1	530	0.012	240	0.5	1500	0.3	1200	110	60	50	1.3	1.7
83	434152	841337	-87.0	-12.5		179	<10	<1	490	0.11	19	1.5	26	1	840	27	7	10	0.46	0.59
84	424404	842409	-67.5	-10.0		181	<10	<1	1800	2.6	180	0.2	1400	0.4	2300	160	30	50	1.5	1.9
101	434007	840633				266	<100	<1		<2	37		580	0.8	10		5.5	20		0.7
102	434146	835711				185	<100	1		2	76		910	0.4	70		20	20		1.4
103	433732	840040	-126.1	-17.9		187	17	<1		5.0	86		3000	0.6	20		27	40		1.4
104	433236	835050				399	4	2		<2	170		88	0.3	20		73	<10		<0.1
105	432936	834630				245	37	<1		3	93		2200	0.7	10		27	50		1.7
106	435301	840528				179	10	1	280	0.018	100	2.7	4	0.6	500	24	32	36		
107	434919	840508				206	10	1	440	0.31	98	2.1	100	0.3	500	39	34	22		
108	435348	840106				137	10	1	120	0.11	240	3.7	36	0.5	1700	38	68	97		

Note: All values reported in mg/l unless otherwise noted.

Table 4.2 (cont'd).

Site Number	Latitude	Longitude	Dissolved Oxygen	pH	K	Dissolved Solids	SiO2	Na	Specific Conductance (umhos/cm)	Sr (ug/l)	SO4	S	Temperature (degrees C)	Zn (ug/l)
1	435900	835317	6.7	7.3	9.5	1820	6.2	370	2220	11000	590	<0.5	10.7	50
2	435930	834044	0.6	7.3	4.2	1020	11	230	1710	1300	150	<0.5	11.6	<3
3	440555	840028	1.1	7.3	2.8	672	11	77	1100	2100	270	<0.5	10.6	11
4	440408	835005	0.9	7.2	3.5	838	12	65	1080	1900	310	<0.5	11.7	760
8	435852	842934	1.7	7.3	3.6	648	8.4	54	858	2100	320	<0.5	9.7	10
9	435541	841909	1	7.6	5.8	1820	9.5	380	2150	4300	1200	<0.5	9.8	190
10	435211	841142	2.4	7.9	5.8	788	6.6	150	820	560	290	<0.5	11.0	160
11	440028	842102	0.8	6.9	3.1	416	7.5	59	598	1400	140	<0.5	10.5	43
20	431649	842654	2.3	7.4	1.5	538	13	66	783	630	190	<0.5	11.7	320
21	431126	843339	0.7	7.9	4.0	1330	9.1	190	1910	1600	370	<0.5	11.1	40
22	432433	842859	0.9	7.4	1.9	814	12	60	1110	1800	400	<0.5	11.6	45
23	431849	843610	0.8	7.6	1.6	350	16	33	539	710	59	<0.5	12.0	26
24	432242	843633	0.3	6.8	5.1	1180	14	140	1920	820	99	<0.5	11.7	310
25	430757	842503												
26	431802	842810	0.9	7.6	1.4	338	14	50	516	520	60	<0.5	11.0	130
36	432431	841948	2.4	7.5	1.6	411	14	56	635	260	77	<0.5	13.0	210
37	431125	841115	0.01											
38	431130	835815	1.1	7.4	2.2	327	12	32	542	870	4	<0.5	11.1	110
39	431542	840901	1.2	7.7	4.0	777	8.8	190	1530	1200	84	<0.5	11.3	24
40	431030	840701	2.1	7.6	3.2	695	9.2	210	1340	1200	74	<0.5	11.6	8
41	431457	835559	4.1	7.7	2.1	298	9.9	62	508	630	8	<0.5	12.1	15
42	432746	841710	2.3	8.2	3.6	641	6.9	220	1110	610	49	<0.5	11.6	68
43	431822	835111	1.4	7.4	9.1	5230	9.5	1600	9450	4900	590	<0.5	11.4	190
44	431714	842108	1.2	7.2	1.6	959	14	61	1250	800	480	<0.5	10.2	380
45	433105	840050	2.1	7.8	8.8	4210	9.9	1600	5630	1800	25	<0.5	11.0	160
46	431714	841624	1.4	7.3	4.0	1500	10	280	2120	1400	380	<0.5	11.6	50
47	432103	840956	6.3	8.0	7.5	1630	6.3	640	2610	270	260	<0.5	13.3	70
48	431735	834458	1.4	7.2	4.4	1600	6.6	470	2640	5500	170	<0.5	10.8	50
49	432240	841140	1.1	7.8	13	3870	6.8	1600	5550	900	260	<0.5	11.5	130
50	431851	834531	1.5	7.4	2.2	454	18	39	740	1400	62	<0.5	11.1	36
51	432127	842026	1.6	7.6	1.8	448	14	67	688	650	82	<0.5	10.7	310
52	432425	834529	1.3	7.5	5.7	2370	6.4	660	2800	3100	730	<0.5	11.2	30
53	431939	835342	1.7	7.7	1.7	579	11	180	1060	690	33	<0.5	12.0	62
54	433014	835317	3.8	6.7	13	2530	6.6	880	4210	1700	15	<0.5	11.9	20
63	431751	832810	0.6	7.3	1.2	270	15	5	426	240	13	<0.5	10.3	5
64	432017	832113	0.1	7.3	1.5	375	17	6	343	230	54	<0.5	9.9	10
65	432733	832903	0.3	8.5	1.3	339	7.4	120	418	240	16	<0.5	10.9	22
66	431823	833908	0.6	7.5	2.2	218	12	17	312	790	2	<0.5	10.3	16
67	433325	833721	0.3	7.7	9.4	4400	6.2	1700	6600	1500	170	<0.5	11.0	90
68	433336	833049	0.4	7.8	3.7	1370	6.6	440	2060	650	450	<0.5	11.3	30
69	432208	833619	1	8.0	1.7	339	13	88	393	800	13	<0.5	11.5	28
70	433042	832656	2.9	7.7	2.4	372	12	57	454	1300	120	<0.5	10.4	98
71	432229	833438	1.4	7.3	2.4	410	9.7	65	615	1100	48	<0.5	10.5	5
72	433913	832701	1.1	7.6	3.4	527	7.6	86	765	2400	210	<0.5	10.5	5
75	432758	842234	1.5	7.5	1.5	286	16	22	459	740	9	<0.5	10.6	90
76	433641	843142	3.8	7.2	5.7	2140	7.3	500	2950	3700	370	<0.5	11.3	170
77	434640	841335	1.5	7.6	6.8	1060	7.1	180	1340	2000	540	<0.5	11.9	270
79	434258	842928	0.01	7.6	4.1	894	11	190	1130	950	270	<0.5	10.8	11
80	434518	843525	1.1	7.5	1.0	282	17	5	419	150	4	<0.5	12.0	31
81	433843	841148	1	7.7	8.8		7.6	1600	4660	60	250	<0.5	11.3	90
82	433850	842808	1	7.3	8.2	3250	8.4	880	4360	3900	750	0.5	11.4	90
83	434152	841337	1.6	8.5	2.7	640	8.8	150	706	360	210	<0.5	10.8	10
84	424404	842409	1.1	7.5	14	3450	6.2	800	3000	4600	280	<0.5	10.3	210
101	434007	840633		7.93	6.20	4392	3.0	560	2600		330	<0.1	12.9	100
102	434146	835711		7.00	10.00	5309	3.0	680	3100		320	<0.1	10.0	20
103	433732	840040		8.61	14.00	13115	3.3	1900	7800		90	<0.1	15.5	360
104	433236	835050		7.17	1.90	2319	8.4	26	1300		250	<0.1	14.8	80
105	432936	834630		7.27	14.00	11350	4.0	1700	6600		460	<0.1	17.3	600
106	435301	840528	0.37	7.73	2.7	682	11	50	928	2400	370		11.5	460
107	434919	840508	0.01	7.64	4.4	739	7.8	92	1093	1400	290		12.9	380
108	435348	840106	0.01	7.6	2.9	1530	13	85	1781	4200	920		11.5	290

Note: All values reported in mg/l unless otherwise noted.

the 90 percent confidence level. When multiple t-tests are compared, the combined confidence level is less than 90 percent.

The Student's t-Tests compared the null hypothesis to an alternate hypothesis to determine if the data supplied significant evidence to reject the null hypothesis in favor of the alternate hypothesis. The null hypothesis, H_o, states that the average value of the parameter in the ground water in the drift was equal to the average value in the ground water in the bedrock. The alternate hypothesis, H_1, states that the average value of the parameter in the ground water in the drift was not equal to the average value in the ground water in the bedrock.

The results of this comparison are summarized in Table 4.3, along with the average values of the chemical parameters. The Student's t-Tests were run on log-normalized data. The data were found to be log-normally distributed as illustrated by frequency histograms of concentrations (Figure 4.1 through Figure 4.15).

As shown on Table 4.3, the results of the Student's t-Tests indicate no significant difference between the average values of calcium and magnesium concentrations, and the average values of alkalinity, pH, and temperature for the drift and bedrock. Significant differences occur, however, between average concentrations of sodium, potassium,

Table 4.3 Comparison of Saginaw Lowland and Bay County drift and bedrock ground-water chemistries via the Student's t-Test. Test was conducted at the 90% confidence level, with the null hypothesis:H_o: difference = 0.

Variable[1]	Average Value Drift Deposits	Average Value Bedrock Deposits	Significant Difference?	Average Value Greater in Drift?[2]
Ca	99.3	93.2	NO	
Mg	30.86	25.64	NO	
Na	194.0	404.7	YES	NO
K	2.63	4.92	YES	NO
SO_4	191.24	260.19	YES	NO
Cl	282.9	537.2	YES	NO
Alkalinity[3]	232.2	256.1	NO	
pH	7.55	7.55	NO	
Temp.(·C)	11.47	11.45	NO	
Si	13.15	9.67	YES	YES
Dissolved Solids	1189.7	1744.1	YES	NO
Deuterium (del)	-63.50	-77.57	YES	YES
Oxygen-18 (del)	-10.65	-11.70	YES	YES

[1] All components reported in mg/l unless otherwise noted.

[2] When the t-Test indicates no significant difference, then the difference in average values is not significant.

[3] Reported as $CaCO_3$.

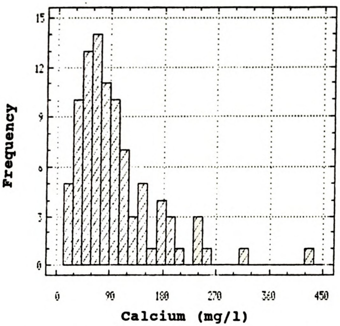


Figure 4.1 Frequency histogram of calcium concentrations.

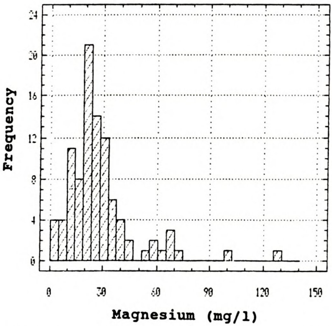


Figure 4.2 Frequency histogram of magnesium concentrations.

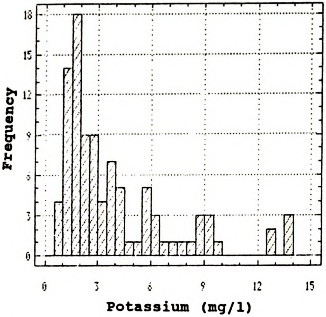


Figure 4.3 Frequency histogram of potassium concentrations.

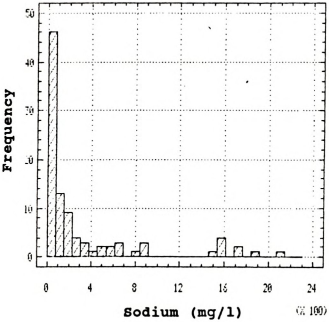


Figure 4.4 Frequency histogram of sodium concentrations.

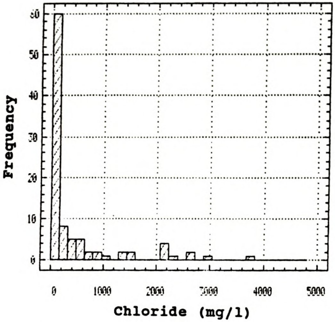


Figure 4.5 Frequency histogram of chloride concentrations.

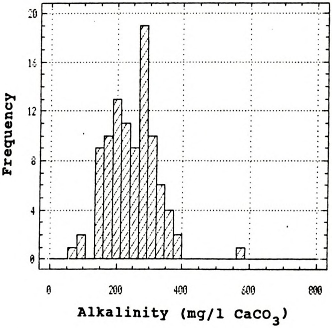


Figure 4.6 Frequency histogram of alkalinity values.

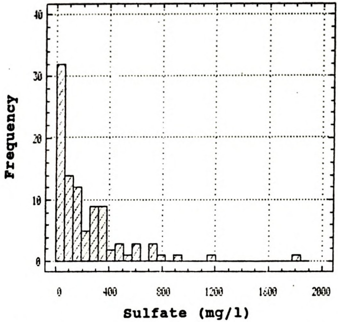


Figure 4.7 Frequency histogram of sulfate concentrations.

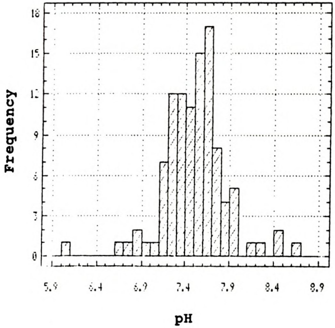


Figure 4.8 Frequency histogram of pH values.

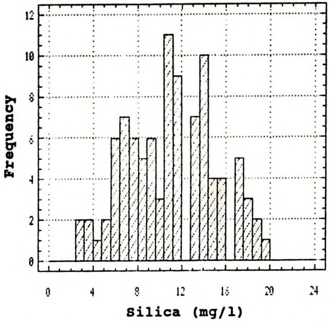


Figure 4.9 Frequency histogram of silica concentrations.

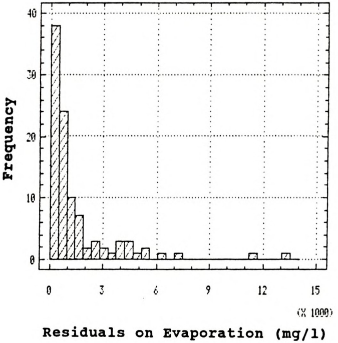


Figure 4.10 Frequency histogram of residuals on evaporation values.

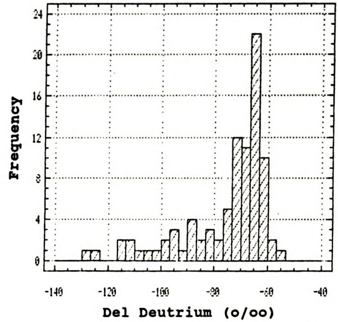


Figure 4.11 Frequency histogram of deuterium concentrations.

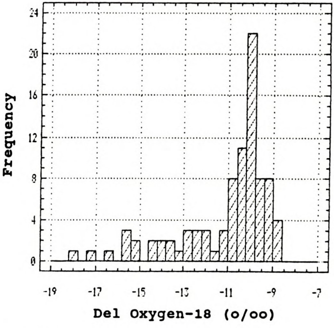


Figure 4.12 Frequency histogram of oxygen-18 concentrations.

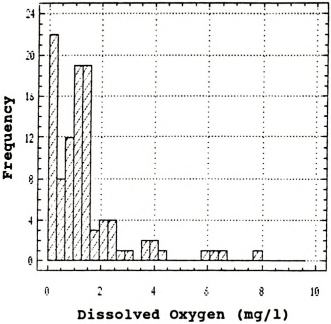


Figure 4.13 Frequency histogram of dissolved oxygen concentrations.

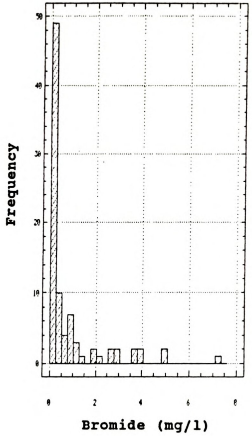


Figure 4.14 Frequency histogram of bromide concentrations.

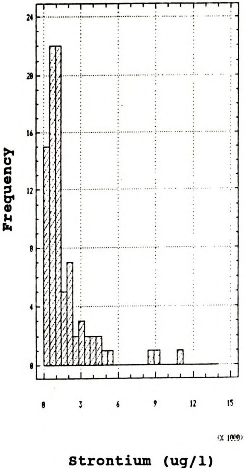


Figure 4.15 Frequency histogram of strontium concentrations.

sulfate, chloride, and dissolved solids for the ground water samples collected from the drift and from the bedrock. Each of the chemical parameters has statistically greater values in the bedrock. Significant differences also occur for average concentrations of silica, deuterium and oxygen-18 concentrations, but the concentrations of these parameters are significantly greater in ground water from the drift than from the bedrock.

Student's t-Tests were also performed by Long et al. (1986) with the Bay County data set. These t-tests were performed at the 95 percent confidence level, but those done for this study were performed at the 90 percent confidence level for each t-test (for a combined confidence level of less than 90 percent). Despite the different confidence levels, the Bay County t-tests indicate similar trends between drift and bedrock ground-water chemistry as the Saginaw Lowland t-tests, with the exception of sulfate concentrations. Sulfate concentrations are significantly different between drift and bedrock sources in the Saginaw Lowland, but are not significantly different in Bay County.

4.1.2 Multivariate Factor Analysis of the Geochemical Data Set

The statistical technique of multivariate factor analysis was used to examine the structure in the geochemical data set as a means of defining the number and sulfate, chloride,

samples collected

of the

as

types of water masses represented in the data set, and the controlling geochemical processes affecting the ground-water system. Multivariate factor analysis was used to redefine the variables of this data set into a smaller number of variables. A description of factor analysis methodology and usage is discussed by Klovan (1975), Joreskog et al, (1976), Davis (1986) and Kim and Mueller (1978). Multivariate factor analysis has been applied to geochemical data sets by Hitchon et al. (1971); Bopp and Biggs (1981); Hull (1984); Davis (1986) and Long et al. (1988).

The factors which result from factor analysis applied to geochemical data sets are interpreted as an indication of different water masses (Q-mode) or as specific processes affecting the ground water (R-mode). Q-mode factor analysis is a test of the homogeneity of a data set. Q-mode compares relationships among samples in terms of chemical variables. R-Mode compares relationships among chemical variables in terms of samples. R-mode attempts to find structure in geochemical data by grouping elements with similar chemical behaviors together into factors which represent simpler relations among fewer variables.

The geochemical data set for the Saginaw Lowland study consists of 19 chemical parameters and 105 ground-water samples. The data were found to be log-normally distributed as illustrated by frequency histograms of concentrations (Figure 4.1 through Figure 4.15). Because factor analysis

assumes that data are normally distributed (Hitchon et al., 1971), log transformation of the geochemical data (except pH) was done prior to factor analysis. Only chemical parameters were included in the analysis, with the exception of specific conductance which has a strong linear correlation with dissolved solids and thus distinguishes water of similar ionic ratios, but with different ionic concentrations (Hitchon et al., 1971). The parameters included dissolved calcium, dissolved magnesium, dissolved sodium, dissolved potassium, dissolved strontium, dissolved lithium, dissolved chloride, dissolved sulfate, alkalinity, dissolved ammonia nitrogen, dissolved bromide, dissolved fluoride, dissolved silica, dissolved boron, dissolved manganese, dissolved iron, zinc, specific conductance and pH.

Q-mode analysis was performed on the data set with the use of a main frame computer. The data was rotated according to Promax rotation. Q-mode revealed that one factor explains more than 90 percent of the variance in the data set, and almost 96 percent of the variance is explained by two factors. Homogeneity in the data set is indicated because one factor explains more than 90 percent of the variance in the data set. There is one major "population" or water mass in the data set (Hitchon et al., 1971; Bopp and Biggs, 1981; Davis, 1986; Long et al., 1988). Therefore, the data set can be treated as one geochemical

system. R-mode factor analysis, which requires a homogeneous data set, was then performed.

R-mode factor analysis was applied with Promax rotation, which was found by Long et al. (1986) to be the most meaningful manner of rotation with this type of data. The application of R-mode factor analysis resulted in five geochemical factors which account for 97 percent of the variance in the data set. R-mode factor analysis was also performed by Long et al. (1986) on the Bay County data set. The analysis resulted in three geochemical factors.

Figure 4.16 is a diagram which shows the factor loadings of the five factors resulting from Promax rotation. The factor loading of a variable (chemical parameter in this case) indicates the relative significance of the variable in defining a factor. The greater the factor loading (positive or negative) for a parameter, the more significance the parameter has on the factor. A factor loading near zero indicates that the parameter is of little significance to the factor. As a convention, parameters falling between +0.250 and -0.250 are considered to be of little significance to the factor's meaning (Long et al., 1986).

The R-mode factors for the Saginaw Lowland data set are interpreted as follows. Factor One, which accounts for 42 percent of the variance in the data, has large positive loadings for chloride, sodium, bromide, potassium, specific

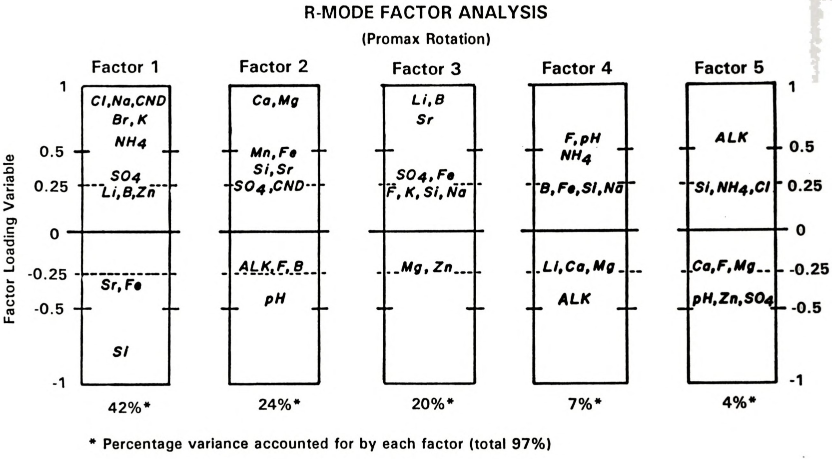


Figure 4.16 Diagram of R-mode factor loadings.

conductance and ammonia. Strontium, iron and silica have large negative loadings. Factor One is interpreted as a salinity factor. The chemical parameters with large loadings are common dissolved constituents in water of high salinity. The large loadings on bromide, potassium, ammonia and strontium are not consistent with the dissolution of salt, as only sodium and chloride would have large loadings. These parameters suggest a brine influence on water chemistry. Factor One is similar to Factor One of the same statistical technique performed on the Bay County data set by Long et al. (1986).

Factor Two, which accounts for 24 percent of the variance, has large positive loadings for calcium, magnesium, manganese, iron, silica, strontium and a large negative loading on pH. Factor Two is interpreted to represent water-rock interaction, such as carbonate mineral equilibria. Calcium, magnesium, manganese, iron and strontium are cations which often form carbonate minerals. The buffering affect of carbonate on pH is perhaps causing the inverse loading of calcium and magnesium to pH. Factor Two is similar to Factor Two of the same statistical technique performed on the Bay County data set by Long et al. (1986).

Factor Three accounted for an additional 20 percent of the variance in the data set. Factor Three has large positive loadings on lithium, boron, strontium, iron and

sulfate. Factor Four, accounting for an additional 7 percent of the total variance, has large positive loadings on fluoride, pH, ammonia and a large negative loading on alkalinity. No factors similar to Factors Three and Four were found in the Bay County data set during R-mode multivariate factor analysis. The geochemical significance of Factors Three and Four is unclear.

Factor Five accounts for 4 percent of the variance in the data set. Alkalinity has a large positive loading; whereas pH, zinc and sulfate have large negative loadings. The large but opposite loadings for alkalinity and sulfate suggest the possibility of sulfate reduction occurring in the system. Factor Five is similar to Factor Three of the same statistical technique performed on the Bay County data set by Long et al. (1986).

Ground-water samples collected in Bay County exhibited a decrease in sulfate values corresponding to an increase in del sulfur-34 values (Long et al., 1988). This correlation suggested that sulfate reduction is affecting the system in Bay County. Sulfate reduction is a bacterial process in which bacteria consume sulfate ions. The sulfate ions are assimilated via chemical reduction. Alkalinity is increased. Selective bacterial assimilation of the sulfur-32 isotope results ground-water enrichment in the sulfur-34 isotope, as was observed by Long et al, (1988).

The relatively small variance explained by Factor Five indicates that the process (or processes) represented by Factor Five (possibly sulfate reduction) has less significance in controlling the geochemistry of Saginaw Lowland ground water than other factors. As discussed in Section 4.1.1, sulfate concentrations in the Saginaw Lowland are significantly greater in ground water from the bedrock than the drift, but are not significantly different between the bedrock and drift in Bay County. This suggests that sulfate reduction is affecting the system in Bay County, and has no strong affect on the regional system.

The existence of two additional factors in the Saginaw Lowland ground-water geochemical data is a result of differences in the Saginaw Lowland and Bay County data sets, and reflects the presence of a transition zone from saline ground water within the Saginaw Lowland to fresher meteoric ground water at the outer limits of the Saginaw Lowland.

4.1.3 Graphical Analyses

Graphical analyses of the geochemical data set were used to chemically classify the ground-water system and to determine processes controlling ground-water geochemistry. One of the graphical techniques used is the ternary diagram, which aids in the geochemical characterization of waters (Fritz and Frape, 1982; Hull, 1984; Frape et al., 1984; and Henderson, 1985). Ternary diagrams can be used to detect

trends in major ion ground-water chemistry, such as mixing between water masses of different chemistries. Mixing which is conservative for all parameters results in a trend on the diagram in which all of the "mixtures" plot along a tie-line between the end-member waters (Freeze and Cherry, 1979; Hem, 1985).

Diagrams can be constructed for cations (calcium, magnesium, sodium and potassium) and anions (chloride, sulfate, carbonate and bicarbonate). The data (cations and anions) are plotted as percentages of total equivalents per unit volume dissolved constituents. A limitation of the ternary plots is that plotted points do not reflect concentrations of dissolved solids. Points representing different samples of having different salinities may plot at the same location on the ternary diagram. The ternary diagrams are useful in understanding trends in the data set.

Figure 4.17 is a ternary diagram of chemical analyses of ground-water samples from the drift. Figure 4.18 is a ternary diagram of chemical analyses of ground-water samples from the bedrock. Also plotted for comparative purposes are the chemical compositions of Michigan Basin formation brines (Dundee, Berea and Marshall formations) (Long et al., 1986), local surface waters (Long et al., 1986), and typical Michigan rain water (National Atmospheric Deposition Program, 1981).

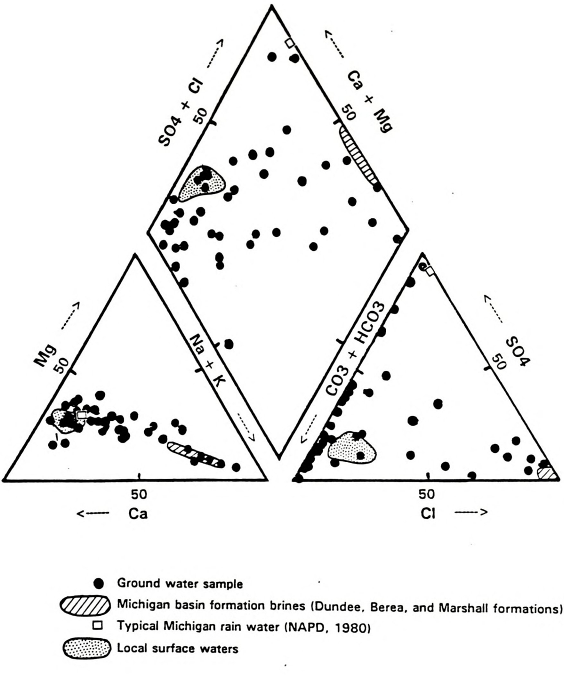


Figure 4.17 Ternary diagram of ground-water chemistry in drift deposits.

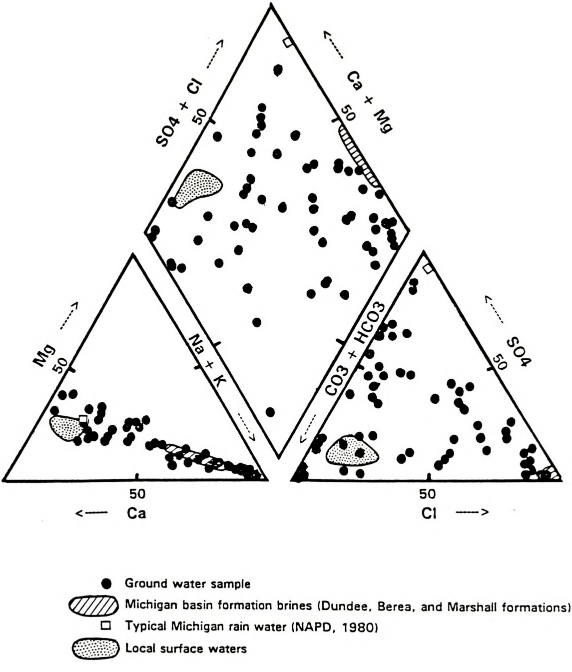


Figure 4.18 Ternary diagram of ground-water chemistry in bedrock deposits.

The cation-anion data for the drift ground-water samples are plotted on Figure 4.17. There is a linear trend in the cation triangle between the brine and surface water end-members which suggests mixing between brine and surface water. The linear trend shows water compositions ranging from approximately 60 percent calcium, 30 percent magnesium and 10 percent sodium-potassium to a composition of almost 100 percent sodium-potassium. There are two linear trends in the anion triangle. The first linear trend is between surface water composition (approximately 15 percent chloride, 70 percent carbonate-bicarbonate and 15 percent sulfate) and the brine composition (almost 100 percent chloride). The other trend is between a composition of approximately 10 percent chloride, 50 percent carbonate-bicarbonate and 40 percent sulfate and the brine composition. In the upper diamond, there is a linear trend between the surface water and brine end-members which strongly suggests mixing between meteoric and saline water masses. This distinctive linear trend in the diamond is not evident in similar ternary plots for the Bay County data by Long et al. (1988).

The cation-anion data for the bedrock ground-water samples are plotted on Figure 4.18. There is a linear trend in the cation triangle between the brine and surface water end-members which suggests mixing between brine and surface water. This trend is much like the trend in Figure 4.17 for

drift samples. The anion triangle exhibits a linear trend between a composition of approximately 10 percent chloride, 30 percent carbonate-bicarbonate and 60 percent sulfate and the brine composition. In addition, the anion triangle shows the two linear trends found in Figure 4.17, with. There is a wide range of carbonate-bicarbonate values, as in Figure 4.17. There is a large amount of scatter in the points in the anion triangle compared to Figure 4.17. In the upper diamond of Figure 4.18, there is a linear trend between the surface water and brine end-members, though not as marked as the trend in Figure 4.17. This trend again suggests mixing between meteoric and saline water masses.

The distinctive linear trend in the diamond in Figure 4.17 and in Figure 4.18 is not evident in ternary plots for the Bay County ground-water data by Long et al. (1988). The linear trend in the cation triangle is also found in similar ternary plots for Bay County data by Long et al. (1988), but this trend is more distinct in Figure 4.17 and Figure 4.18. These differences in ternary diagrams between Saginaw Lowland and Bay County support the hypothesis that the Saginaw Lowland is a transition zone between (1) the surface water and brine compositions; and (2) the occurrence or lack of sulfate reduction in the system. The regional (Saginaw Lowland) ground-water system is influenced by meteoric and brine end-members; more so than the Bay County system which is appears to be influenced more strongly by brines.

Another graphical techniques used is the frequency histogram, which shows the distribution of concentrations of a chemical parameter within a group of samples. Frequency histograms have been used to geochemically characterize waters (Hull, 1984). These graphs can indicate whether a parameter is normally or log-normally distributed. Figure 4.1 through Figure 4.15 (see Section 4.1.2) are frequency histograms of chemical and physical parameters for all ground-water samples collected. The chemical parameters exhibit log-normal distribution.

Graphical representation of the geochemical data also includes x-y plots and histograms of concentration ratios. These types of graphs aid in interpretation of geochemical data (Frape and Fritz, 1982; Hull, 1984; and Frape et al., 1984). Figure 4.19 is a histogram of the chloride to bromide concentration ratios (in mg/l) for all ground water samples. Also plotted is the range of chloride to bromide values found in local oilfield brines (400 to 600) (Long et al., 1986) and for a typical solution formed from halite dissolution (3025) (Wilson and Long, 1984). The ground-water samples range from 50 to 1150, except one sample which plots at 2700. This range is similar to the range of brines and of Bay County ground-water samples (Long et al., 1986). A brine influence on the ground water is clearly suggested. However, halite dissolution is also suggested by the larger chloride to bromide ratio values of some samples.

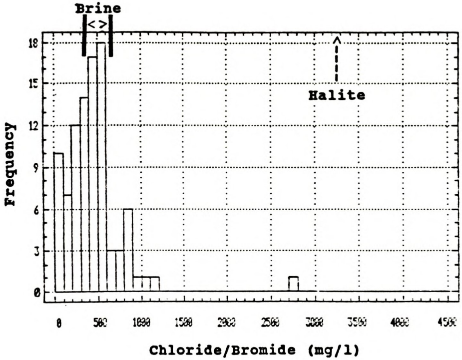


Figure 4.19 Histogram of chloride to bromide concentration ratios.

Halite dissolution is also suggested by the one-to-one relationship between sodium and chloride (Figure 4.20) in the plot of sodium versus chloride molar concentrations. Figure 4.20 indicates that dissolution of halite has provided sodium and chloride to the system. A brine would show a correlation of sodium to chloride other than one to one, because chloride would be complexed with additional cations such as calcium, potassium and magnesium.

Figure 4.19 and Figure 4.20 suggest that the movement of deep basin brines upwards into the system and the process of halite dissolution both influence the ground-water geochemistry. These two processes have not yet been adequately explained and incorporated in a model of the ground-water system in the Saginaw Lowland.

Figure 4.21 is an x-y plot of log chloride concentrations versus del oxygen-18 values for the drift ground-water samples. At low chloride values, del oxygen-18 values range between -11 and -9. As chloride values increase, some del oxygen-18 values become lighter. This is particularly evident in bedrock ground-water samples (Figure 4.22). The trends suggest that water of greater salinity is more likely to be isotopically lighter.

4.1.4 Chemical Modeling

Chemical modeling is a tool used to determine the origin of geochemical characteristics of ground water.

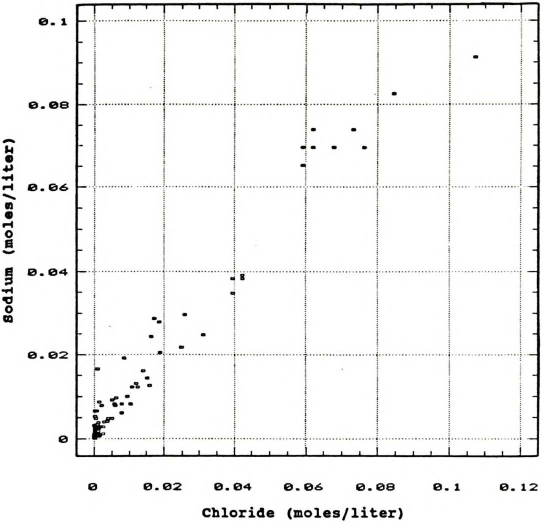


Figure 4.20 Sodium versus chloride molar concentrations.

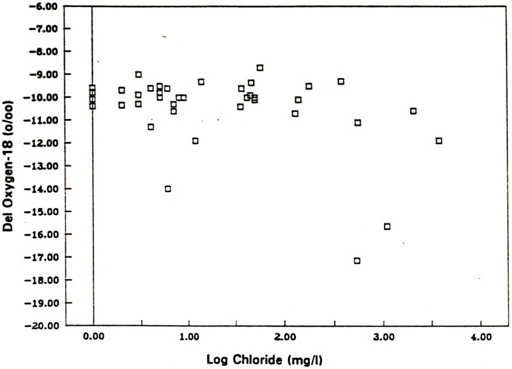


Figure 4.21 Log chloride concentration versus oxygen-18 concentration in the drift deposits.

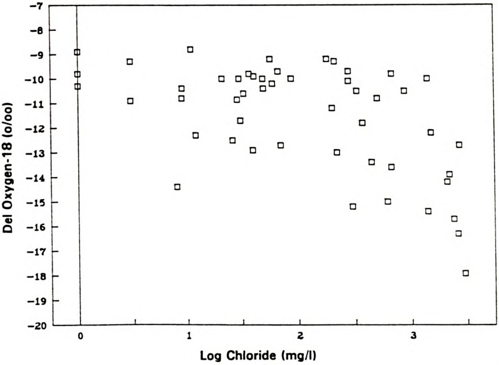


Figure 4.22 Log chloride concentration versus oxygen-18 concentration in the bedrock deposits.

Chemical modeling is used to identify reactive minerals in an aquifer which are controlling the chemistry of ground water by describing the thermodynamic state of solutions (Jenne, 1980). Chemical modeling can also aid in the interpretation of origin and chemical evolution along a flow path. Chemical modeling has been used in ground-water studies by Schwartz (1974); Hull (1984); Henderson (1985); Long et al. (1986); Wood and Low (1986); Long et al. (1988); Rose and Long (1989); Stoessel et al. (1989); Hendry and Schwartz (1990); and Kehew and Passero (1990).

A chemical model computer program uses analytical data of natural waters to calculate chemical equilibria. The chemical model calculates the thermodynamic speciation of inorganic ions and complex species in solution. WATEQF (Plummer et al, 1984), a FORTRAN IV version of WATEQ, was the computer program used to calculate chemical equilibria in the ground water samples from the Saginaw Lowland.

Histograms of mineral saturation index (SI) values for selected compounds are one result of chemical modeling on the Saginaw Lowland data set. The selected minerals are representative regional drift and bedrock mineralogy as discussed in Sections 2.2.1 and 2.2.2. These minerals include calcite, aragonite, dolomite, gypsum, halite, quartz and chalcedony. The SI of a mineral is equal to the log of the ratio of the ion-activity product to the solubility

product. The SIs were calculated with the chemical modeling program.

SIs have been plotted as frequency histograms for calcite (Figure 4.23), aragonite (Figure 4.24), dolomite (Figure 4.25), gypsum (Figure 4.26), halite (Figure 4.27), quartz (Figure 4.28) and chalcedony (Figure 4.29). A SI of zero represents thermodynamic equilibrium between the solid and dissolved phases of a mineral. A SI greater then zero represents theoretical supersaturation with respect to the dissolved phase, and a SI less than zero represents a theoretically undersaturated solution. SI values at or just above zero for calcite (Figure 4.23) suggest that ground water is in equilibrium or slightly supersaturated with respect to calcite. SI values just below zero for aragonite (Figure 4.24) and dolomite (Figure 4.25) suggest that ground water is slightly undersaturated with respect to these two minerals. SI values much less than zero for gypsum (Figure 4.26) and halite (Figure 4.27) suggest that ground water is undersaturated with respect to these two minerals. SI values greater than zero for quartz (Figure 4.28) suggest that ground water is supersaturated with respect to quartz. Figure 4.29 shows that ground water is at equilibrium with respect to chalcedony, because the SIs are at zero.

The stability relationships of aluminosilicate minerals is commonly studied with activity-activity diagrams (Hull, 1984; Henderson, 1985; Long et al., 1986; Wood and Low,

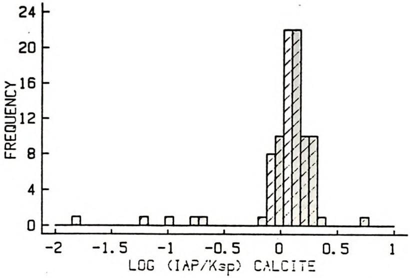


Figure 4.23 Frequency histogram of calcite saturation indices.

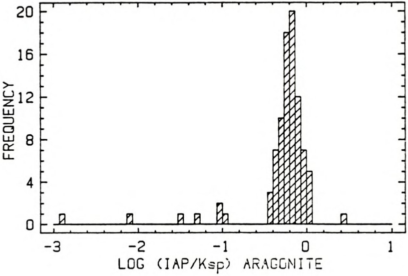


Figure 4.24 Frequency histogram of aragonite saturation indices.

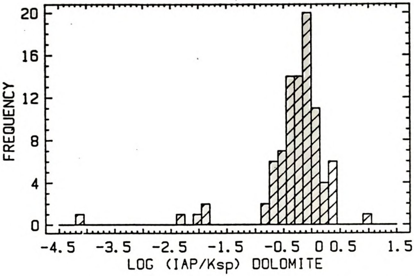


Figure 4.25 **Frequency histogram of dolomite saturation indices.**

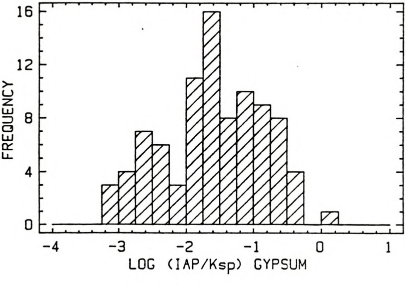


Figure 4.26 **Frequency histogram of gypsum saturation indices.**

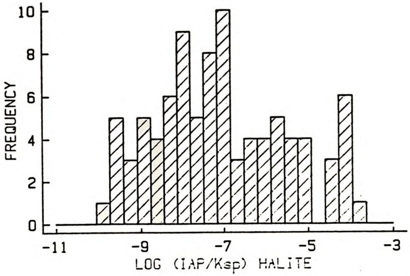


Figure 4.27 Frequency histogram of halite saturation indices.

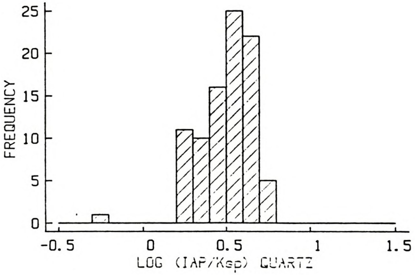


Figure 4.28 Frequency histogram of quartz saturation indices.

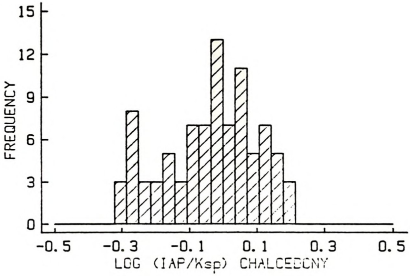


Figure 4.29 **Frequency histogram of chalcedony saturation indices.**

1986; Long et al., 1988; and Rose and Long, 1989). These diagrams are based on activities calculated with chemical modeling and on thermodynamic stability fields.

Using the results of chemical modeling on the ground water data, an activity-activity diagram of potassium aluminosilicate minerals is presented as Figure 4.30. The mineral stability fields in the diagram are based on Velbel (1992). The diagram was constructed from the data of Robie et al. (1979). The placement and extent of the illite stability field in Figure 4.30 is based on an idealized illite-surrogate as defined by Grim (1968). The idealization of the illite stability field is intended to simulate the approximate placement and extent of the illite stability field in relation to the placement of the ground water sampling points.

The ground-water sample data in Figure 4.30 plot within the illite and kaolinite stability fields, straddling the illite/kaolinite stability field boundary. This indicates thermodynamic equilibrium of the ground water with respect to illite and kaolinite, which are present in the drift deposits in the Saginaw Lowland (Chittrayanont, 1978).

Using the results of chemical modeling on the ground water data and mineral stability fields based on Drever (1982), an activity-activity diagram of sodium aluminosilicate minerals is presented as Figure 4.31. The

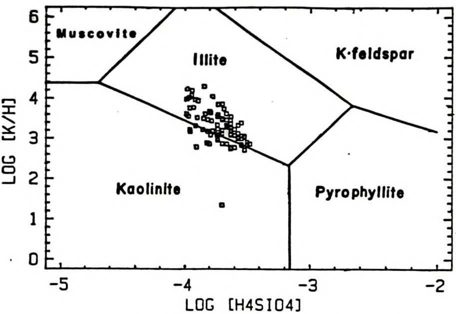


Figure 4.30 Mineral stability diagram of potassium aluminosilicate minerals.

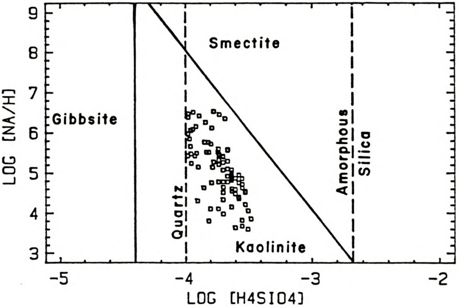


Figure 4.31 Mineral stability diagram of sodium aluminosilicate minerals.

ground-water sample data plot within the kaolinite stability field. This also indicates thermodynamic equilibrium of the ground water with respect to kaolinite.

4.2 Oxygen and Deuterium Isotopes

Concentrations of the stable isotopes of oxygen and deuterium in ground water are used to indicate the origin and evolution of ground water. Isotopic ratios in the water reflect physical processes which have affected it. In low salinity ground water, del oxygen-18 and del deuterium values are conservative; they are unaffected by physical, chemical or geological processes. In the hydrosphere, del oxygen-18 and del deuterium values are not conservative (Frape and Fritz, 1982). A plot of del oxygen-18 values versus del deuterium values for ground-water and surface-water samples can be used to demonstrate that ground water is derived from local precipitation (Wood and Low, 1986).

Oxygen-18 and deuterium concentrations were measured in the Saginaw Lowland ground-water samples. The results of the isotopic analyses are summarized in Table 4.1 for drift samples and Table 4.2 for bedrock samples. The concentrations of oxygen-18 and deuterium are reported according to the standard of Craig (1961 b), as del (ratios) values relative to values of standard mean ocean water (SMOW). Samples were collected as described in Section 3.2 and analyzed as described in Section 3.3. Figure 4.32 is a

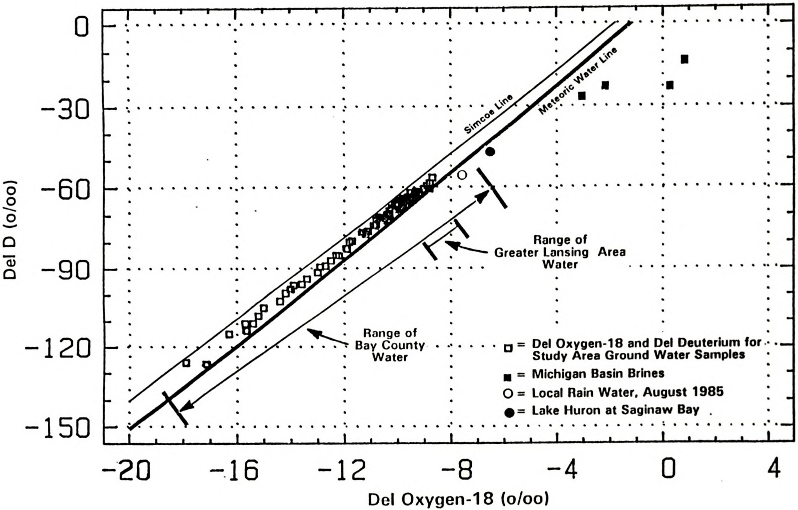
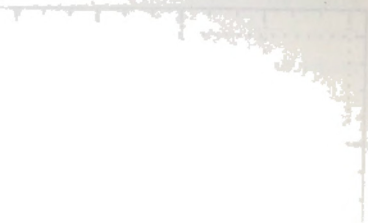


Figure 4.32 Deuterium concentration versus oxygen-18 concentration.



plot of del oxygen-18 vs. del deuterium for all ground-water samples from the Saginaw Lowland. Also plotted on Figure 4.32 are the following: (1) the meteoric water line (MWL) established by Craig (1961 a) as the relationship between oxygen-18 and deuterium concentrations in meteoric waters which have not undergone large amounts of evaporation; (2) the line resulting from oxygen versus deuterium concentrations for rain-water samples collected near Simcoe, Ontario (see Figure 1.1 for location of Simcoe study site) by Desaulniers et al. (1981); (3) the isotopic compositions of samples of Michigan basin formation brines (Wilson and Long, 1986); (4) the isotopic compositions of local rain water and Lake Huron at Saginaw Bay (Long et al., 1986); (5) the range of isotopic values from Bay County ground waters (Long et al., 1988); and (6) the range of isotopic values of ground water from the greater Lansing area (GLA) of Michigan (see Figure 1.1 for location) (Slayton, 1982; Long and Larson, 1981).

The ground-water samples have del oxygen-18 isotopic values which range from -17.91 to -8.70 o/oo and del deuterium isotopic values which range from -126.7 to -56.5 o/oo. The ground-water samples plot along a line of slope 7.8 and y-intercept 10.86. This is similar to the MWL of Craig (1961 a) with a slope of 8 and y-intercept of 10. Figure 4.32 suggests that meteoric water (modern-day and

ancient) is the source of both drift and bedrock ground water in the Saginaw Lowland, because samples plot along the MWL.

The linear relationship of the Saginaw Lowland ground-water samples is similar to the line resulting from isotopic values of rain-water collected at Simcoe, Ontario, located in a region geographically and hydrogeologically similar to the Saginaw Lowland (Desaulniers et al., 1981). The Simcoe line has a slope of 7.5 and y-intercept of 12.6. This line also falls close to the MWL. The similarity of the Simcoe line to the Saginaw Lowland line suggests that modern-day precipitation is one of the sources of ground water in the Saginaw Lowland.

The formation brine samples on Figure 4.32 have del oxygen-18 values ranging from -3.02 to +1.10 o/oo and del deuterium values ranging from -28.6 to -10.7 o/oo. The ground-water isotopic data does not indicate mixing of Michigan basin formation brines with meteoric water. The mixing of brine and meteoric water would result in a linear relationship between the two end-members on a del oxygen-18 versus del deuterium plot (Frape and Fritz, 1982). Samples from the interface of brine and fresher shallow ground water would allow better understanding of the role brines play in the near-surface hydrogeologic system. Long et al. (1988)

did not collect ground-water samples from depths great enough to detect the interface of brine and fresher shallow ground water.

The isotopic values of ground-water samples from Bay County (Long et al., 1988) plot along the MWL. The samples range from -7.0 to -18.5 o/oo for del oxygen-18 and from -56 to -137 o/oo for del deuterium. Figure 4.32 illustrates the range of these samples, but it does not illustrate their actual position along the MWL. The Saginaw Lowland samples plot densely in the region of heavier isotopic values, while the Bay County samples tend to be more isotopically depleted. A meteoric source for Bay County ground water is indicated by oxygen and deuterium isotopic data (Long et al., 1988).

Del oxygen-18 and del deuterium values for the GLA ground water plot within a small range of values on the MWL (Figure 4.32). The GLA ground water is believed to be modern-day meteoric water (Long et al., 1988). The range of the GLA samples is similar to the heaviest values found in the ground water of the Saginaw Lowland, suggesting that modern-day meteoric water is one end-member of the ground water in the Saginaw Lowland.

Isotopic values for the Saginaw Lowland samples range from isotopic depletion to values similar to modern-day precipitation. This wide range of values suggests either

the mixing of isotopically-depleted glacial meltwater with modern-day meteoric recharge, or the isotopic variability in annual precipitation. Long et al. (1988) investigated these possibilities for the Bay County samples and concluded that large isotopic variability in annual precipitation is unlikely. Yearly average isotopic values for local precipitation were estimated at -7.34 and -8.55 o/oo del oxygen-18; and -50.59 and -60.44 o/oo del deuterium. Lake Huron water has del oxygen-18 and del deuterium values of -7.45 o/oo and -55.22 o/oo respectively, similar to calculated yearly average isotopic values for precipitation. These approximate isotopic values of regional annual precipitation are heavier than measured ground-water isotopic values.

The distribution of del oxygen-18 values for drift ground-water samples is shown in Figure 4.33. The distribution of del oxygen-18 values for bedrock ground-water samples is shown in Figure 4.34. The bedrock aquifer is slightly depleted isotopically relative to the drift (average del oxygen-18 value of -11.70 o/oo for bedrock and -10.65 o/oo for drift). The distribution of del oxygen-18 values is similar in the drift and bedrock systems (Figure 4.33 and Figure 4.34), in that isotopic values are depleted near the center of the Saginaw Lowland, and become more enriched towards the perimeter of the study area. This pattern indicates that the Saginaw Lowland encompasses two

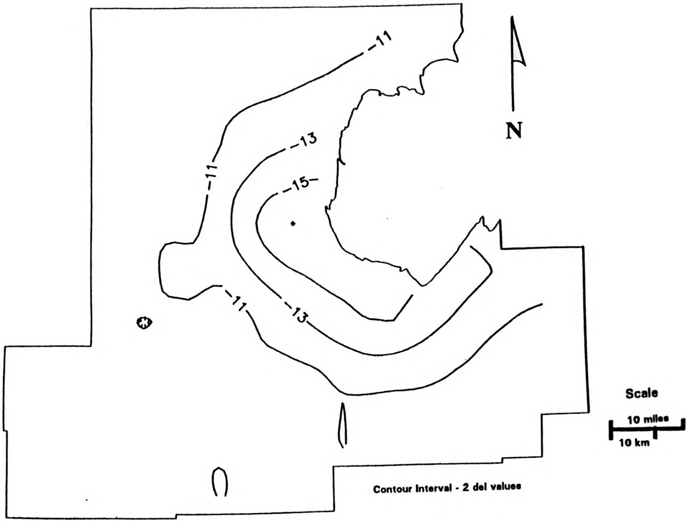


Figure 4.33 Distribution of oxygen-18 concentrations in the drift deposits.

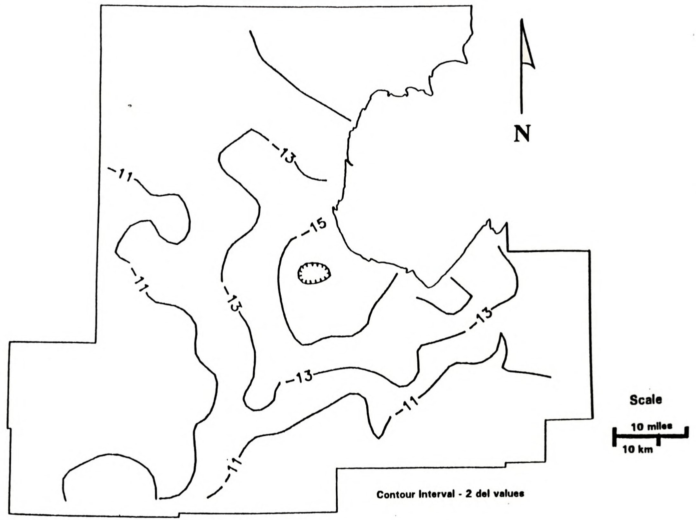


Figure 4.34 Distribution of oxygen-18 concentrations in the bedrock deposits.

zones: (1) a region of isotopically-depleted water and (2) a transition zone from isotopic depletion to isotopic enrichment as in modern-day precipitation.

Isotopic depletion indicates formation of water at cooler temperatures than present day (Dansgaard, 1964; Mook, 1972; Payne; 1972 Siegenthaler, 1979; Gat, 1981). Isotopic depletion in ground water has been attributed to glacial meltwater recharge in aquifers by Clayton et al. (1966); Fritz et al. (1974); Perry et al. (1982); and Siegel and Mandle, (1984). The extremely low isotopic values of the Saginaw Lowland ground water represent retention of glacial meltwater by aquitards, which can have considerably different geochemical and hydrologic properties than aquifers (Back, 1986).

Desaulniers et al. (1981) investigated ground-water geochemistry of argillaceous Quaternary deposits (aquitards) in southwestern Ontario (location shown in Figure 1.1) which have a geologic setting similar to that of the Saginaw Lowland. They concluded that the pore water in the deposits is a mixture of late Pleistocene-aged and modern-day recharge water. Bradbury (1984) performed a similar investigation in argillaceous deposits of northwestern Wisconsin, and concluded that ground water was original pore water from time of till deposition 9,500-10,000 years BP.

Isotopic evidence suggests that Saginaw Lowland ground water is a mixture of modern-day precipitation and glacial meltwater from approximately 10,000 years before present (BP). This is the most likely time of the most recent glacial meltwater recharge in the east-central Michigan basin (Fritz et al., 1974) based on documented climatic changes in the Great Lakes region. There is no isotopic evidence that other physical or chemical processes such as mixing with brine or intense evaporation have affected the ground water (Craig, 1961 a; Dansgaard, 1964; Hitchon and Friedman, 1969; Gat, 1981).

4.3 Carbon Isotopes

The concentration of the stable carbon isotopes in ground water is used to indicate the origin and evolution of ground water. The carbon isotopic signature is the result of exchange of ground water with various sources of carbon (coal, carbon dioxide gas in soil zones, carbonate minerals, other carbon-bearing minerals, methane gas, plant material) each of which has a distinct range of del carbon-13 values (Curtis et al., 1972; Mook, 1972; Payne, 1972; Rightmire and Hanshaw, 1973; Long et al., 1988). Sources of dissolved carbon and microbiological processes affecting the ground water can be determined from studies of the carbon-13 isotope. Stable carbon isotope values in ground water can be used to characterize the origin of ground water (Plummer,

1977; Thorstensen and Fisher, 1979; Desaulniers et al., 1981; Wood and Low, 1986; Chapelle et al., 1988; and McMahon et al., 1990).

Carbon-13 concentrations were measured in the Saginaw Lowland ground water on seven samples from drift deposits and seven samples from bedrock deposits. The results of isotopic analyses are summarized in Table 4.1 for drift samples and Table 4.2 for bedrock samples. The concentration of carbon-13 is reported as a del (ratio) value relative to the PDB standard. Samples were collected as described in Section 3.2 and analyzed as described in Section 3.3. Figure 4.35 is a histogram of ground-water del carbon-13 values. Also plotted on Figure 4.35 are local rain water (-8.27 o/oo) and Saginaw Bay, Lake Huron, water (-9.93 o/oo) (Long et al., 1988).

The ground-water samples have del carbon-13 values which range from -15.4 o/oo to -7.9 o/oo, with an average of -13.08 o/oo. The Bay County ground-water samples exhibited a wide range of del carbon-13 values (-21.38 o/oo to -8.14 o/oo), with an average of -13.8 o/oo (Long et al., 1988). The del carbon-13 values of ground water in the Saginaw Lowland fall within this range. A much greater number of Bay County ground water samples were analyzed for carbon-13 than for Saginaw Lowland. Long et al. (1988) found no systematic distribution of del carbon-13 in the Bay County ground-water system.

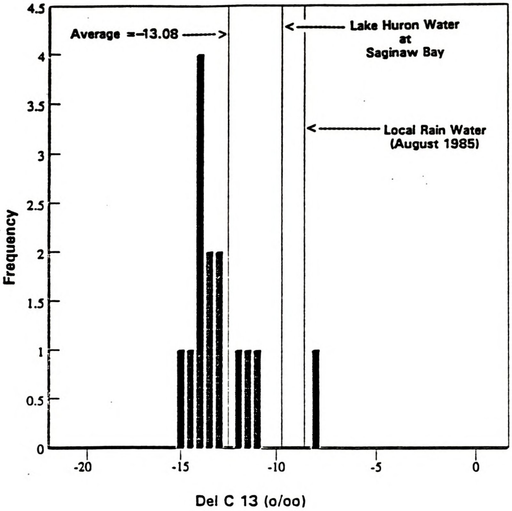


Figure 4.35 Histogram of carbon-13 concentrations.

A slight correlation between del carbon-13 values and depth of sample is suggested by Figure 4.36. Points on the graph represent the values of del carbon-13 plotted at the midpoint depth of the well screens from which samples were withdrawn. Drift wells were screened in sand and/or gravel. Bedrock wells were screened in combinations of shale, sandstone and/or limestone. Based on the small number of samples analyzed, Figure 4.36 suggests that ground water becomes more enriched in carbon-13 at depth. The process which would result in this vertical distribution of carbon-13 values is unclear.

Photosynthesis causes preferential uptake of carbon-12 in plants, producing depletion of carbon-13 in plant matter. As a result, marine organic carbon and recent marine sediments have del carbon-13 values of about -20 o/oo. Similarly, land organic carbon and recent freshwater deposits have del carbon-13 values of about -25 o/oo. (Stumm and Morgan, 1981). The amount of carbon-13 in dissolved carbon reflects the relative amounts of several carbon sources (Wigley et al., 1978). For example, a combined source of carbon consisting of lignitic material (-25 o/oo) and carbonate minerals (0 o/oo) results in an actual average value of dissolved carbon-13 content in ground water of -12.1 o/oo (Thorstenson and Fisher, 1979).

The average del carbon-13 values in Saginaw Lowland ground water of -13.08 o/oo may represent the combined

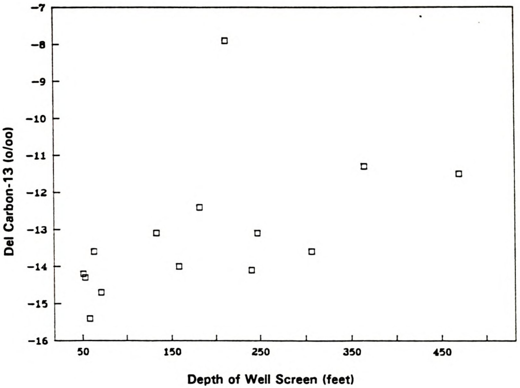


Figure 4.36 Carbon-13 concentration versus depth.

influence on dissolved carbon of lignitic material derived from local coal deposits (-25 o/oo) and of carbonate minerals such as calcite, aragonite and dolomite, found in local drift and bedrock deposits. The more enriched values of Saginaw Lowland del carbon-13 values (-7.9 o/oo) indicate a meteoric source.

SECTION 5 - SUMMARY AND CONCLUSIONS

5.1 Summary

The following is a summary of the many results of the study and an evaluation of the several hypotheses proposed in the Introduction. Hypothesis 1, that the ground water system contains isotopically-depleted meteoric water that recharged the system when the climate was much cooler (perhaps glacial meltwater of the Pleistocene Epoch), was investigated with the use of stable isotopic data, as described in Section 4.3 and Section 4.4. These data indicated that the isotopic geochemistry of the ground water is influenced by mixing of modern-day meteoric recharge water with meteoric water formed at cooler temperatures bearing isotopic depletion. The data suggest that the isotopically-depleted water was derived from glacial meltwater recharge during the late Pleistocene epoch, when the climate was much cooler than present day (Emiliani, 1971).

Hypothesis 2, that the ground water system contains saline water derived from brines deep in the Michigan basin, was investigated with the use of chemical characterization, as described in Section 4.1. The chemical data suggest that salinity is a dominant factor of the ground-water geochemistry. The salinity is the result of both the diffusion or advection of highly concentrated Michigan basin

brines upward into the near-surface deposits of the Saginaw Lowlands and the dissolution of halite. The brine input is suggested by factor analysis, chloride to bromide concentration ratios and ternary diagrams of major ion chemistry. The halite input is suggested by a plot of molar sodium concentrations versus molar chloride concentrations. The chemical characterization also suggests geochemical interactions between ground water and surrounding geologic deposits, including calcium carbonate thermodynamic equilibrium.

Hypothesis 3, that the isotopically-depleted water and saline water are retained in the ground water system through the combined affects of aquitards, low regional horizontal hydraulic gradients, and a regional ground-water discharge zone, was investigated with the use of geologic maps and water level and lithologic data for each well sampled, as described in Section 2.2 and Section 2.3. The maps and these data suggest that the Saginaw Lowland ground-water system has a low horizontal hydraulic gradient and regional ground-water discharge. The system is dominated by thick aquitards. The combined affects of these three characteristics are believed to result in salinity buildup, retention of isotopically-depleted ground water and retention of upwardly migrating basin brines. The different water types identified mix within the system under the influence of these characteristics.

This study also attempted to verify that the additional processes identified by Long et al. (1986, 1988) in the Bay County ground water system are also affecting the Saginaw Lowland system. Verification of the additional processes was evaluated by analyzing the ground water samples for similar chemical and isotopic constituents and by evaluating the geochemical data in a similar manner as in the Bay County study. The additional processes include water-rock interactions including calcium carbonate equilibrium and stability with potassium aluminosilicate minerals; and the biological reduction of sulfate.

Evidence for water-rock interactions was provided by chemical modeling with WATEQF. Chemical modeling indicates that ground water is in equilibrium or slightly supersaturated with respect to calcite and is slightly undersaturated with respect to aragonite and dolomite. Activity-activity diagrams show that the ground-water data plot primarily within the illite and kaolinite stability fields, indicating thermodynamic equilibrium of the ground water with respect to illite and kaolinite.

Evidence for the occurrence of the biological reduction of sulfate in Bay County was provided by trends in sulfate and bicarbonate concentrations and del carbon-13 and del sulfur-34 analyses (Long et al., 1988). Based on the results of factor analysis, the process of microbiological reduction of sulfate does not appear to be occurring to a

great extent in Saginaw Lowland. The process may be a phenomenon localized in Bay County. Further investigation including sulfur and carbon isotope analyses would be necessary to better characterize the process of microbiological reduction of sulfate in the Saginaw Lowland ground-water system.

The study was also used to estimate whether the data reduction techniques used in the Bay County study (Long et al., 1986, 1988), would produce interpretable results on more widely-spaced data points. The statistical data reduction techniques used are the Student's t-Test and multivariate factor analysis. The graphical data reduction techniques include ternary diagrams, frequency histograms, and x-y plots. The computer modeling technique used is chemical modeling with WATEQF.

The data reduction techniques produced similar and/or complimentary results for the Saginaw Lowland and Bay County studies, despite large differences of scale with regards to sampling sites. The Saginaw Lowland study used a total of 105 sampling sites over an area of about 14000 square kilometers. The Bay County study used a total of almost 400 sites over an area of about 800 square kilometers. The data reduction techniques have proven useful in data interpretation in a large scale ground-water study.

Despite the different confidence levels in the Student's t-Tests of this study and of the Bay County study, as discussed in Section 4.1.1, the t-tests indicated similar trends between drift and bedrock ground-water chemistry as the Saginaw Lowland t-tests, with the exception of sulfate concentrations. Sulfate concentrations were significantly different between drift and bedrock sources in the Saginaw Lowland, but were not significantly different in Bay County.

R-mode multivariate factor analysis resulted in three factors representing processes affecting ground water in the Saginaw Lowland. These factors corresponded to three R-mode factors for the geochemical data from Bay County ground water of Long et al. (1986). However, a total of five factors were required to account for the same amount of variance in the Saginaw Lowland data as were only 3 factors in the data of the Bay County study. More factors are required to describe the many processes affecting the ground-water system on a regional scale. For example, the study area encompasses not only "Bay County-like" ground water, but also fresher, younger water on the perimeter of the study area.

Ternary diagrams revealed stronger evidence for mixing between surface water and brine endmember waters than was found in the Bay County data (Long et al., 1986). This supports the hypothesis that the ground water of the Saginaw

Lowland occurs in a transition zone between surface water and brine compositions.

The histogram of chloride to bromide concentration ratios (in mg/l) for all ground water samples illustrated a range of brines similar to that of Bay County ground-water samples (Long et al., 1986). A brine influence on the ground water is clearly suggested.

Halite dissolution is also suggested by the plot of sodium versus chloride molar concentrations which indicated that dissolution of halite provided sodium and chloride to the system. This is similar to the findings of Long et al. (1986). These findings suggest that the movement of deep basin brines upwards into the system and the process of halite dissolution both influence the ground-water geochemistry. These two processes have not yet been adequately explained and incorporated in a model of the ground-water system in the Saginaw Lowland.

5.2 Conclusions

The goal of this study was to examine the extent of isotopically-depleted ground water in the Saginaw Lowland of the Michigan basin and investigate several hypotheses based primarily on the previous work of Long et al. (1986, 1988) in Bay County of the Saginaw Lowland. The occurrence of isotopically-depleted ground water was compared to regional

lithology and ground-water geochemistry in order to test the hypotheses.

As summarized in Section 5, the results supported the hypotheses. Isotopic evidence is lacking for brine influence on the ground water system, but geochemical evidence suggests a brine influence on the system. This is consistent with the model of the system, because diffusion of brines into the system would have little affect on isotopic signatures in low concentrations, yet low concentrations of brines diffusing into the system will have strong impacts on geochemical signatures, due to the extremely high concentrations of ions in brines. Collection of ground-water samples from depths great enough to detect the interface of brine and fresher shallow ground water would allow for better understanding of the role brines play in the near-surface hydrogeologic system.

This study found a correspondence in geographic distribution of low del oxygen-18 and del deuterium values (Figure 4.33 and Figure 4.34), high chloride concentrations (Figure 2.5 and Figure 2.6), surficial lacustrine and morainal clay deposits (Figure 1.1, Figure 2.1, Figure 2.2 and Figure 2.3), and the residual potentiometric surface (Figure 2.10). The isotopically-depleted, saline water occurs where argillaceous deposits are thick, in the central portion of the study area near Saginaw Bay.

The ground water system has not flushed out the isotopically-depleted meteoric water formed when the climate was much cooler than the present, nor the salinity in the system. The dynamics of the ground water flow system are subject to further interpretations of the past and present hydrodynamics of the system.

APPENDIX

APPENDIX

ALUMINUM SPECIATION INVESTIGATION

Aluminum is commonly analyzed as total dissolved aluminum. For example, the analytical data for the 1986 sampling for this study of ground water geochemistry in the Saginaw Lowland included total dissolved aluminum. In order to determine to determine the equilbria of aluminosilicate minerals via chemical modeling, concentrations of aluminum species are required. The equilibria of aluminosilicate minerals via chemical modeling was investigated during the ground water study in the Saginaw Lowland. In order to determine the concentrations of aluminum species, resampling of selected wells, based on preliminary chemical modeling, was done in the summer of 1987. Twenty-five wells were resampled and analyzed in the Geochemistry Laboratory at Michigan State University.

Collection and analysis of the samples for aluminum speciation was done according to the methods described below. The laboratory analytical data (total dissolved aluminum, monomeric and polymeric aluminum species, and major ions) resulting from this investigation of aluminum speciation is provided in Table A.1. The concentrations of

Table A.1 - Laboratory Analytical Results of 1987 Ground Water Sampling for Aluminum Speciation Investigation

Site Number	Ca	Mg	Na	K	Cl	SO4	Alkalinity (CaCO3)	Alkalinity (HCO3)
Drift Deposit Wells:								
5	56	23	36	1.5	6.5	273.4	183	223.131
13	240	72	54	3.5	11.1	803.3	103	125.587
14	59	32	24	1.5	5.7	83.45	287	349.939
18	100	30	74	2.0	5.7	377.3	136	165.824
35	44	21	45	1.9	8.8	64.75	257	313.360
55	110	66	280	2.6	500	159.1	195	237.763
56	310	102	2300	9.7	3800	408.5	123	149.973
57	48	14	42	1.4	7.1	52.28	225	274.342
58	53	17	31	1.7	11	55.39	276	336.526
62	49	20	70	2.1	46	73.06	311	379.202
87	1.2	0.6	1700	6.4	2000	387.7	183	223.131
Bedrock Deposit Wells:								
3	150	26	123	3.0	29	377.3	252	307.263
4	170	31	69	3.4	90	335.7	203	247.517
9	170	47	410	6.0	340	698.2	163	198.745
21	180	44	200	4.0	340	377.3	192	234.105
37	35	9.0	160	3.4	46	32.53	350	426.755
38	62	26	33	2.3	12	5.52	332	404.807
39	69	14	280	4.1	270	77.21	299	364.570
40	34	9.6	250	3.4	190	81.37	343	418.219
41	33	11	63	2.0	58	16.95	258	314.579
43	230	66	2000	9.2	2500	834.5	156	190.210
69	31	11	89	1.7	45	7.60	288	351.158
71	54	21	64	2.4	51	48.12	258	314.579
82	240	69	1100	8.5	1500	626.7	219	267.026
83	18	6.9	220	2.5	30	242.2	184	224.351

Note: All concentrations reported in mg/l, unless otherwise noted.

Table A.1 (cont'd).

Site Number	Sr	Si	pH	Dissolved Oxygen	S	Ferrous Fe	Total Fe	Ferric Fe
Drift Deposit Wells:								
5	1.6	8.2	8.14	0.00	0.02	0.56	0.79	0.23
13	4.0	9.6	7.92	0.00	0.02	1.57	1.70	0.13
14	1.2	10.3	7.89	0.42	0.03	0.55	0.64	0.09
18	2.2	8.9	7.98	0.26	0.01	0.55	0.79	0.24
35	0.93	11.2	7.87	0.06	0.03	0.60	0.76	0.16
55	3.0	8.9	7.91	0.00	0.01	0.86	0.92	0.06
56	9.4	8.4	7.64	0.00	0.00	3.16	3.45	0.29
57	0.75	9.4	7.87	0.46	0.09	0.33	0.43	0.10
58	0.98	12.0	8.00	0.77	0.08	0.38	0.47	0.09
62	0.61	9.2	7.84	0.05	0.01	0.32	0.37	0.05
87	0.06	7.9	7.75	0.00	0.03	0.06	0.23	0.16
Bedrock Deposit Wells:								
3	2.6	7.3	7.69	0.00	0.09	1.20	2.44	1.24
4	2.1	7.8	7.60	0.00	0.00	1.21	2.40	1.19
9	4.6	5.2	7.87	1.03	0.01	0.57	0.77	0.20
21	1.5	5.9	8.30	0.00	0.03	2.90	7.63	4.73
37	1.3	6.4	7.89	0.70	0.03	0.30	0.32	0.02
38	0.89	8.2	7.74	0.48	0.00	0.26	0.26	0.00
39	1.3	6.3	7.83	0.40	0.00	0.50	0.58	0.08
40	1.2	6.1	7.92	0.83	0.01	0.10	0.14	0.04
41	0.66	6.8	7.70	0.62	0.00	0.08	0.12	0.04
43	5.4	7.1	7.68	0.26	0.00	1.18	1.34	0.16
69	0.77	8.5	8.12	0.08	0.00	0.08	0.11	0.03
71	1.3	7.1	7.19	2.08	0.04	0.22	0.25	0.03
82	4.3	4.6	7.54	0.00	0.00	1.29	1.75	0.46
83	0.35	5.8	8.61	0.65	0.00	0.20	0.69	0.49

Note: All concentrations reported in mg/l, unless otherwise noted.

Table A.1 (cont'd).

Site Number	Specific Conductance (umhos/cm)	Temperature (degrees C)	Monomeric Al (ug/l)	Reactive Al (ug/l)	Total Al (ug/l)
Drift Deposit Wells:					
5	546	11.6	3.78	2.17	3.64
13	1674	11.8	0.00	0.24	2.20
14	558	9.5	1.98	1.45	3.64
18	909	11.5	0.93	0.62	3.86
35	515	11.2	0.70	2.22	3.28
55	2190	12.1	0.00	0.00	2.81
56	11700	13.3	0.00	2.35	5.53
57	474	11.3	3.16	0.43	2.12
58	492	10.7	0.61	0.87	3.37
62	692	11.0	1.83	0.00	2.12
87	6664	13.7	0.00	1.03	2.89
Bedrock Deposit Wells:					
3	1162	10.6	0.00	0.98	3.31
4	1164	12.5	0.94	1.87	4.85
9	2474	10.7	0.61	1.22	1.26
21	1882	12.3	0.00	0.15	4.75
37	680	11.3	0.43	0.43	4.89
38	600	12.5	0.69	7.18	1.57
39	1546	11.6	0.00	0.15	3.97
40	1292	11.6	2.00	0.43	2.25
41	551	12.1	0.51	0.51	2.64
43	8235	15.9	0.00	0.00	2.80
69	607	11.2	1.83	1.13	3.36
71	675	10.6	1.91	1.74	3.09
82	5706	12.0	0.00	0.00	2.68
83	878	11.4	1.91	1.27	4.23

Note: All concentrations reported in mg/l, unless otherwise noted.

monomeric aluminum and major ions were chemically modeled using WATEQF (Plummer et al, 1984), a FORTRAN IV version of WATEQ. Saturation indicies for various aluminosilicate minerals calculated by chemical modeling are provided in Table A.2.

Analyses for aluminum species were conducted on a Perkin-Elmer atomic adsorption unit equipped with a graphite furnace and an autosampler. Analyses for major ions were conducted according to standard U. S. Geological Survey techniques (Skougstad et al, 1985).

A ten-second extraction was performed in the field on the twenty-five ground water samples. The resulting extract contained monomeric aluminum species. The ten-second extraction sample was prepared by filtering the sample through a 0.2 micrometer pore size polycarbonate Nuclepore filter which had been acid rinsed, soaked in distilled deionized water and rinsed thoroughly with the sample water before use. A Nuclepore 0.47 millimeter diameter filtration apparatus was attached to an acid-rinsed 200 milliliter Erlenmeyer flask and a peristaltic pump was used to provide reverse pressure for filtration.

Fifty milliliters of the filtrate was then carefully pipetted out and dispensed into a 200 milliliter acid-rinsed beaker. Distilled deionized water was added to produce a final volume of approximately 100 milliliter. Immediately

Table A.2 - Saturation Indicies for Various Aluminosilicate Minerals, 1987 Aluminum Speciation Investigation

Site Number	Adularia	Beidel-lite	Gibbsite	Kaolinite	K-Mica	Pyro-phyllite	Quartz	SiO2
Drift Deposit Wells:								
5	-0.017	2.811	0.906	2.909	9.042	5.043	0.422	-0.952
13	1.047	6.17	2.402	5.886	13.096	7.931	0.419	-0.958
14	0.83	4.851	1.64	4.584	11.355	6.761	0.535	-0.847
18	0.974	5.76	2.117	5.429	12.45	7.314	0.49	-0.899
35	0.434	4.778	1.964	4.832	11.609	6.878	0.32	-1.05
55	0.047	2.948	1.017	3.024	9.334	5.275	0.356	-1.009
56	-0.639	2.26	0.893	2.666	8.392	4.403	0.323	-1.059
57	0.923	5.59	2.157	5.383	12.481	7.371	0.415	-0.964
58	-0.243	2.743	0.919	2.863	8.842	4.971	0.384	-0.988
62	-0.132	2.721	1.004	2.918	9.127	5.15	0.314	-1.049
87	0.75	4.943	1.743	4.723	11.481	6.907	0.497	-0.881
Bedrock Deposit Wells:								
3	0.149	3.632	1.66	3.906	10.713	5.365	0.176	-1.205
4	-0.349	1.857	0.789	2.235	8.475	4.005	0.199	-1.173
9	0.7	5.05	2.203	5.109	12.352	6.82	0.227	-1.149
21	0.076	3.539	1.531	3.812	10.384	5.524	0.253	-1.125
37	-0.909	1.791	0.975	2.421	8.289	3.959	0.107	-1.266
38	-0.14	3.862	1.67	4.128	10.446	5.998	0.266	-1.107
39	0.046	5.068	2.193	5.241	11.676	6.953	0.311	-1.071
40	0.886	4.484	1.919	4.413	11.97	6.105	0.199	-1.177
41	0.952	5.398	2.106	5.205	12.409	7.147	0.376	-1.003
43	-0.553	2.105	0.919	2.57	8.531	4.311	0.242	-1.134
69	0.669	4.877	1.854	4.739	11.622	6.764	0.392	-0.984
71	1.168	6.097	2.423	5.802	13.26	7.766	0.353	-1.022
82	0.331	4.537	1.811	4.564	11.199	6.651	0.34	-1.03
83	-0.171	2.713	1.075	2.938	9.233	5.372	0.236	-1.113

Note: Concentrations of mononuclear aluminum were used in chemical modeling.

after this step, 2 milliliters of 8-hydroxyquinoline solution was added by repipette. The 8-hydroxyquinoline solution was prepared according to Barnes, 1975. The preparation technique is also described below. "Metal free" ammonium hydroxide was added dropwise to adjust the pH to 8.3. The ammonium hydroxide was prepared according to Barnes, 1975. The pH probe had been standardized with pH buffers 7 and 10, which were at ambient temperature. Five milliliters of buffer solution were then added with a repipette to keep the pH at 8.3. The buffer solution was prepared according to Barnes, 1975. The preparation technique is also described below.

The mixture was poured into an acid-rinsed 250 milliliter volumetric flask. Ten milliliters of methyl isobutyl ketone (MIBK) were then added by pipette and swirled for 10 seconds. The layer of MIBK was allowed to separate out. The volumetric flask was carefully filled with water. Using an Eppendorf pipette, the MIBK extract (approximately 6 milliliter) was removed and stored in 30 milliliter high-density polyethylene (HDPE) bottles, which had been acid rinsed and soaked in distilled water.

In addition to the ten-second extraction, a thirty-minute extraction was performed in the field on a freshly obtained ground water sample. The resulting extract contained polymeric aluminum species. The thirty-minute extraction was conducted in the same manner as the 10 second

extraction, except that the volumetric flask was shaken by hand for 30 minutes before the MIBK was added. The extract was then removed, in the same manner as for the 10 second extract.

Several reagents were prepared for use in this laboratory work. The 8-hydroxyquinoline solution was prepared in the following manner. Two grams of 8-hydroxyquinoline were dissolved in 5 milliliters of distilled glacial acetic acid and diluted to 200 milliliters with distilled deionized water (Turner 1969; May et al., 1979; Okura et al., 1962; James et al. 1983; Bloom et al. 1978; Barnes 1975).

The buffer solution was prepared by adding 223 milliliters of 10 M "metal free" ammonium hydroxide and 115 milliliters of distilled glacial acetic acid to 500 milliliters of distilled deionized water. The pH was then adjusted to 8.3 with 10 molar ammonium hydroxide and acetic acid. The solution was then diluted to one liter with distilled deionized water (Barnes, 1975).

To collect samples for analysis of total aluminum concentration in the field, sample water was filtered with the same filtration equipment as the extractions, except that a 0.4 micrometer pore size polycarbonate Nuclepore filter was used. Two hundred and fifty (250) milliliters of filtered sample was poured into 250 milliliter HDPE bottles, which had been acid rinsed and soaked in distilled water prior to use. The sample was then acidified to pH 2 with

0.5 milliliter double distilled Ultrex* nitric acid. The acidified sample was left undisturbed for at least two weeks prior to analysis, in order to allow larger polynuclear aluminum species and colloidal suspended material to convert to a more reactive form of aluminum (Barnes, 1975).

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