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A SPATIAL ANALYSIS OF THE AQUEOUS GEOCHEMISRY OF THE NEAR SURFACE GROUNDWATERS OF THE MICHIGAN BASIN AQUIFER SYSTEM

By

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ABSTRACT

A SPATIAL ANALYSIS OF THE AQUEOUS GEOCHEMISTRY OF THE NEAR SURFACE GROUNDWATERS OF THE MICHIGAN BASIN AQUIFER SYSTEM

By

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In the Michigan Basin Aquifer System brine is actively advecting or diffusing, thereby interacting with fresh groundwaters, especially in the Saginaw Bay Area. This study investigates the water mass interactions through the analysis of distribution diagrams constructed for the major and minor ions and saturation indices of minerals for different aquifers and depth intervals. The GIS IDRISI program constructs these diagrams which regionally demonstrate the geochemical evolution of the groundwater in light of the system's hydrogeology. Through spatial analyses, the brine is shown to increase the ions' concentrations and control the saturation states of gypsum and quartz but not calcite and dolomite in relevant brine-freshwater interaction areas. Ionic spatial variations observed may be explained through additional chemical mechanisms, namely mineral-rock interactions, microbial activity, and anthropogenic sources.

ACKNOWLEDGEMENTS

I wish to experess my appreciation to the members of my advisory committee, Dr. David T. Long, Dr. Duncan Sibley, and Dr. Stuart Gage for their advice and suggestions, and critical review of the manuscript. A project of this scope could not have been completed without their help.

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INTRODUCTION

Nature of Problem

Groundwater from the aquifer systems in the Lower Peninsula of Michigan has become an increasingly important source for water (USGS MI-RASA, 1996). The aquifer systems supply a major source of freshwater to municipalities throughout the state. Population growth, irrigation, and industrial development place a demand on these groundwater resources as well (Mandle, 1986). Therefore, a necessity arises to protect and manage these resources. The feasibility of these imperatives can be attained through the knowledge of the aqueous chemistry of the aquifers as well as the processes controlling the aqueous chemistry.

The purpose of this research is to examine the spatial chemistries of chloride, sodium, calcium, magnesium, potassium, barium, strontium, sulfate, and bicarbonate concentrations and selected saturation states of minerals in the near surface aquifer groundwaters in the Michigan Basin. The spatial distribution of these variables are studied in light of the hypotheses of brine-freshwater interactions and other chemical processes occurring within the Michigan Basin, especially the Saginaw Bay Area (SBA) (Wahrer et. al, 1996; Ging et. al, 1996; Meissner et. al, 1996). This study will better define the geochemical evolution of the near-surface groundwater thereby establishing a framework of background information and providing a regional assessment of groundwater resources (USGS MI-RASA, 1996).

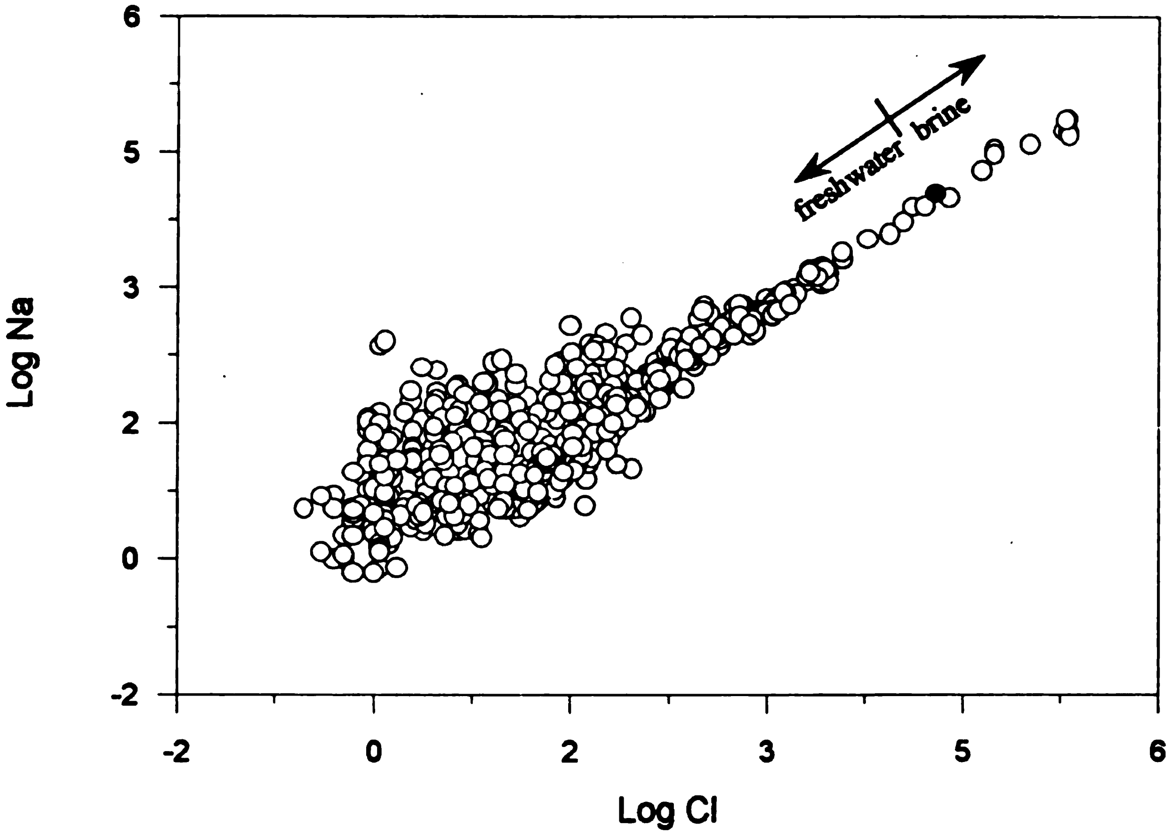
Background

Houghton initially recognized the existence of concentrated fluids underlying freshwater in the Lower Peninsula of Michigan in 1838 (USGS MI-RASA, 1996). In the late 1800's, saline, near-surface groundwater (<100 m) was identified in argillaceous glacial sediment and underlying bedrock in eastern and east-central Michigan including the Saginaw Bay Area (SBA) (Lane, 1899). Cohee and others (1950) hypothesized that coal mining activity in the SBA has produced these saline waters through the unplugging of bore holes and dewatering of coal mines allowing salt-water encroachment to occur. However, this can only be considered under localized conditions thereby excluding these anthropogenic sources as the sole cause of the large scale SBA saline water distribution. Subsequent analysis found these groundwaters to be enriched in calcium, magnesium, sodium, and chloride (Handy, 1982; Twenter and Cummings, 1985), but the source of the salinity and cause of its distribution was not investigated.

Long and others (1988) proposed the source of these saline groundwaters to be an Upper Mississippian-Pennsylvanian brine advecting or diffusing upward into the near-surface meteoric water. The cause of the salinity distribution is controlled by the slow flushing of water in the argillaceous sediments by recent meteoric water. The brine advection or diffusion hypothesis was additionally supported by isotopic studies of the groundwaters (Long et. al, 1988). In 1996, the U.S. Geological Survey (USGS) completed a the Michigan-Regional Aquifer Systems Analysis (MI-RASA) describing the hydrogeology, geochemistry, and regional ground-water flow of the glacial and bedrock aquifers in the Michigan Basin, which included the results of the study by Long and others (1988).

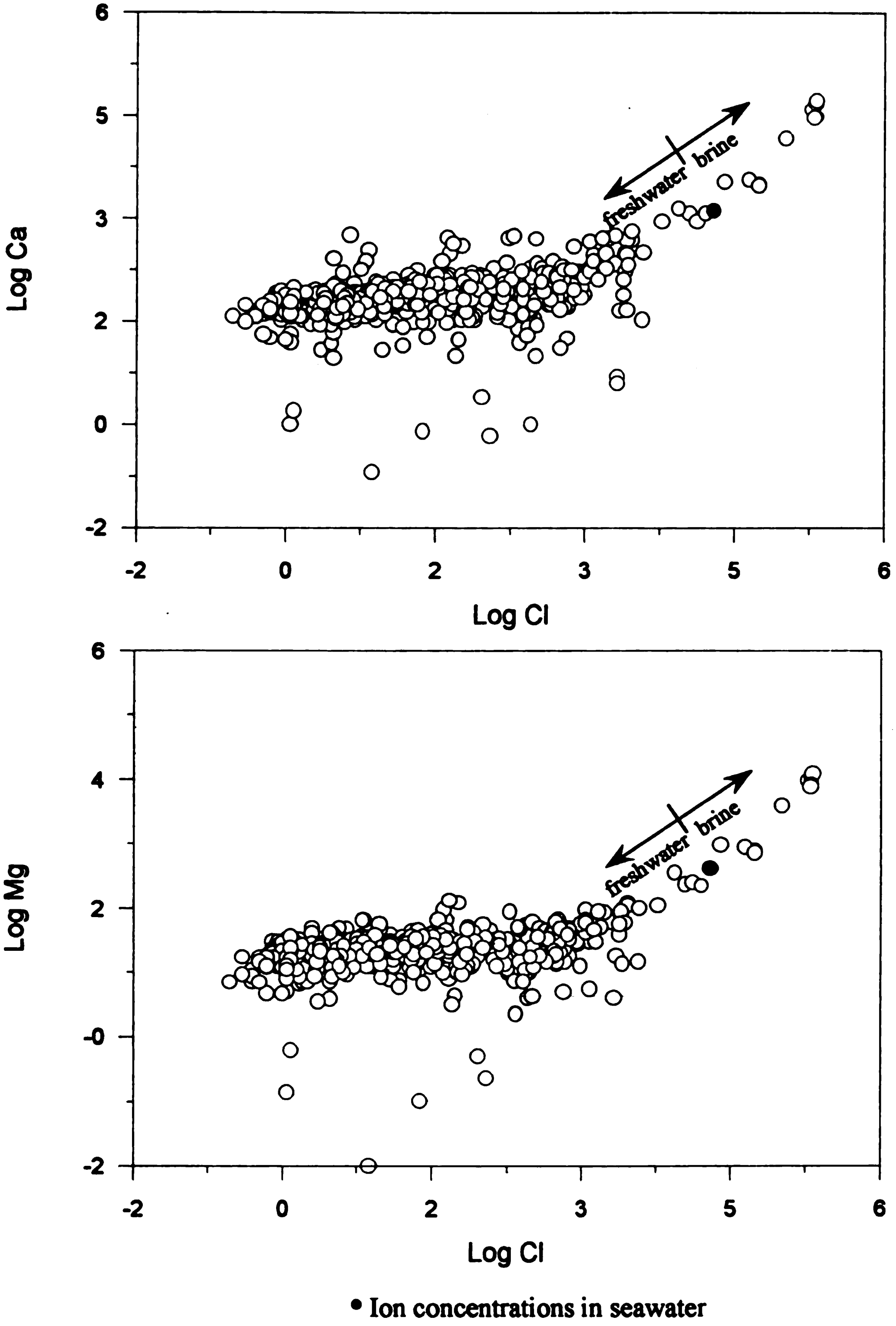
The MI-RASA report constructed spatial distribution maps of chloride, sulfate, and total dissolved solids concentrations and $\delta^{18}O$ values for waters in the aquifer systems. In the SBA, chloride, sulfate, and total dissolved solids were shown to be relatively high in concentration with respect to the near-surface groundwaters in the rest of the Michigan Basin, thereby determining the SBA waters to be anomalous. These distribution maps better defined the geochemical and isotopic nature of the SBA as well. Beyond the special consideration of the SBA, the MI-RASA report provided a preliminary analysis of the geochemical evolution of the groundwaters in the Michigan Basin through these spatial distribution maps, solute-solute diagrams, and end-member mixing models.

The solute-solute diagrams found that the relative concentrations of chloride, sulfate, sodium, calcium, magnesium, bicarbonate, and potassium were affected by a brine-freshwater interaction (Figures 1, 2, 3, and 4) (modified from the MI-RASA, 1996). The study concluded



• Ion concentrations in seawater

Figure 1. Solute-solute concentration plots of Log Cl vs. Log Na (modified from USGS MI-RASA, 1996)



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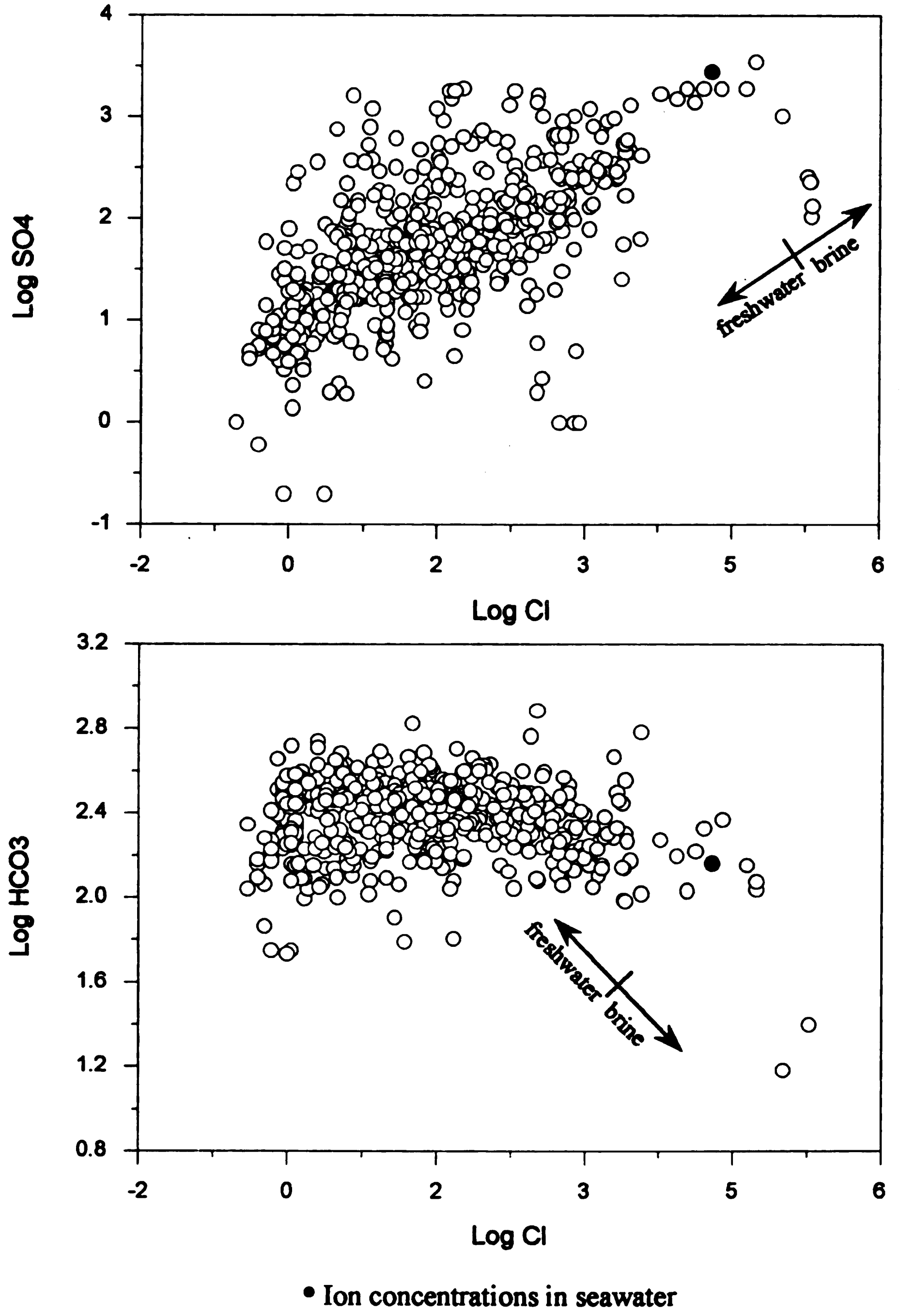

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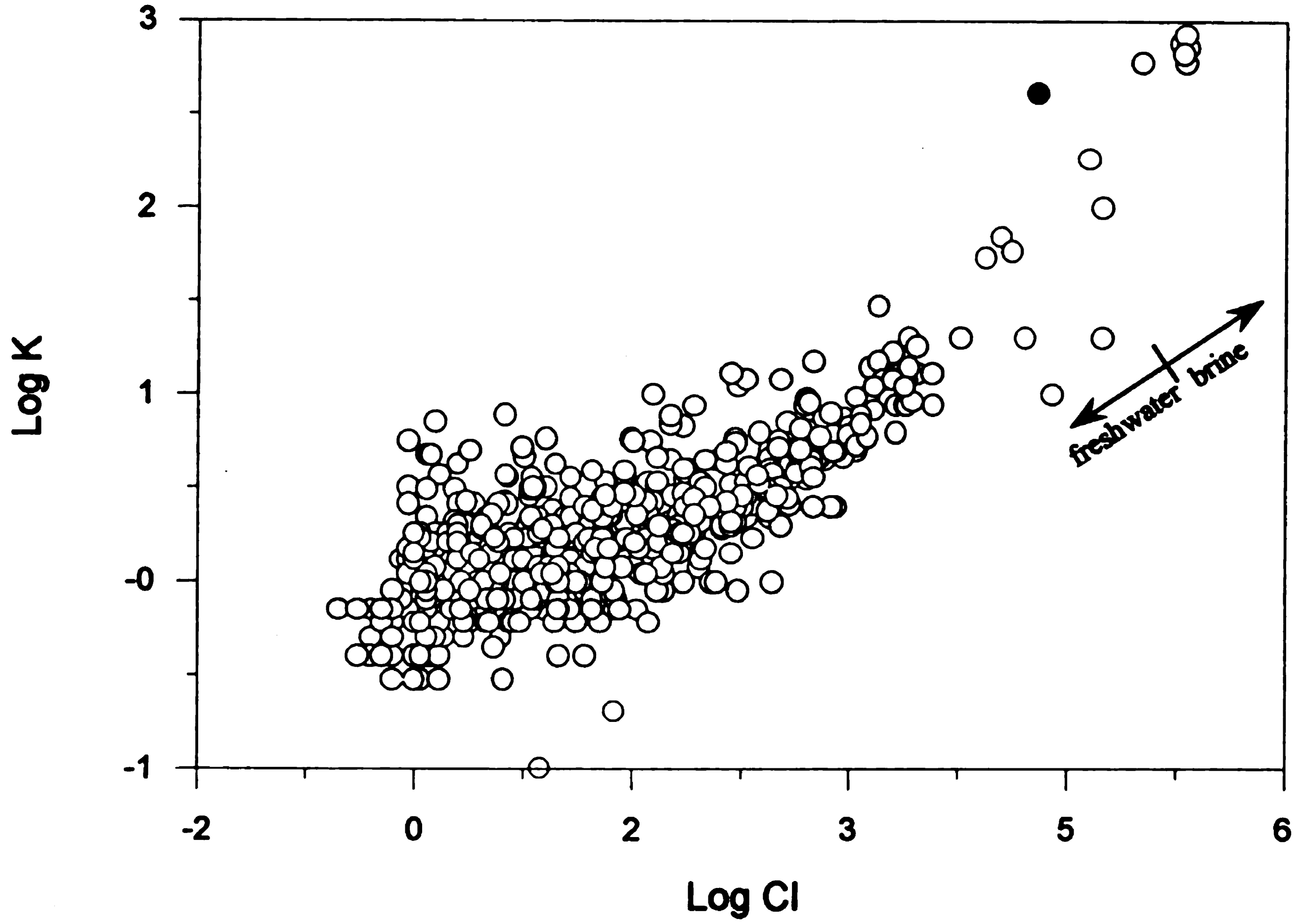


● Ion concentrations in seawater

Figure 4. Solute-solute concentration plots of Log Cl vs. Log K (modified from USGS MI-RASA, 1996)

that brine has formed from the evaporation of seawater giving the residual solution a specific solute geochemical character. The results showed that ion concentrations increase in the residual water through an evaporation sequence to form the brine but uniformly decrease in concentrations once mixed with an end-member of fresh water. However, concentration plots of sulfate and bicarbonate were seen scattered around the brine end-member, which alluded to alternate mechanisms controlling their concentrations, especially microbial reactions (Figure 3). Scattered data arrays of all the ions' concentrations near the freshwater end-member were also seen, which may be explained by alternative geochemical mechanisms (Figure 1, 2, 3, and 4).

The MI-RASA end-member mixing model was performed with calcite and dolomite in constant equilibrium. This model verified the that sodium, calcium, magnesium, potassium, sulfate, and bicarbonate were affected by the interaction between brine and freshwaters through the concentration data arrays that formed along the mixing trajectories. Around the groundwater end-members, the concentrations of these ions fell off the modeled trajectory supporting the idea that different processes were having an impact the groundwater ion concentrations. Therefore, the brine-freshwater mixing is a dominant, but not the only, geochemical mechanism occurring that has an impact on the ions' concentrations. In light of these results, the spatial distributions of these elements were never represented. Distribution diagrams of these ion concentrations could show regional variations of the ion concentraions and therefore areas of major or minimal brine-freshwater interaction along with areas where other mechanisms may be impacting solute concentrations.

From the geochemical modeling of the solutes, the MI-RASA demonstrated that the calcite-dolomite-gypsum system involved three of the most important solution-mineral reactions that are occurring or have occurred. These reactions have been important in controlling the freshwater and brine end-members as modeled in the RASA report. From the analyses of the groundwater samples collected for the MI-RASA, frequency histograms were constructed for the saturation indices (SIs) of a number of minerals (MI-RASA, 1996). Upon examination of the SI frequency histograms, results showed that calcite and dolomite were in equilibrium, gypsum was undersaturated, and quartz was supersaturated for the majority of the water samples (both freshwater and brine) in the aquifer systems. (A mineral saturation index is defined by the formula, $SI=IAP/K_{sp}$, where IAP is the ion activity product, and K_{sp} is the stability constant of the mineral.) The spatial distributions of the level of disequilibrium with respect to these minerals are unclear. For example, the results from the RASA report did not study the SIs of the minerals on a regional scale and if the brine impact causes an SI SBA anomaly as seen with the constructed chloride and sulfate maps.

Overall, a regional geochemical/hydrogeolgic model of the Michigan Basin was developed in the MI-RASA. The isotopic data (chloride and $\delta^{18}O$) suggested the interaction of three water masses in the aquifer systems. These include modern meteoric water, meteoric water recharged to the systems during cooler glacial time periods, and the underlying formation brine. Major recharge of modern meteoric water occurs in the highland areas of the Michigan Basin, in the south and northwest, while major discharge occurs in lower areas in the Michigan Lowlands and the anomalous SBA. Meteoric water is also known to be incorporated into the Michigan stream system discharging into Lake Michigan, Lake Huron, or Lake Erie, therefore having little interaction with the groundwater system studied. The older glacial groundwater is trapped in the clay, glacial till, and lacustrine sediments in the SBA thereby giving an isotopic signature to the older water in the SBA. These two water masses acquire their geochemical character (solute chemistry) mostly through water-rock interactions; they are essentially geochemically indistinguishable in this respect.

The third water mass is brine, deriving its geochemical character through an evaporation sequence, which is advecting or diffusing upward towards the SBA due to hydrological gradients (Long et. al, 1988). Two major brines are formed, one in the Marshall aquifer and one at the Upper Mississippian-Pennsylvanian boudary. The Marshall brine advects or diffuses towards the SBA but not as readily into the shallower geologic units due to the overlying Michigan Confining

Unit. The Upper Mississipian-Pennsylvian brine is able to advect or diffuse upward into the shallower units and towards the SBA due to more permeable sediments. Due to the sedimentology of the SBA, the modern meteoric water and/or the brine are not able to efficiently flush the older freshwaters out of the system into the Saginaw Bay, and this process causes a buildup of interacting waters. Overall, the three water masses are interacting and mixing to a certain degree in the aquifer system thereby giving different geochemical characters to the regional groundwaters in respect to solute concentrations.

In light of this model and previous studies, a further look into the spatial water chemistry and processes controlling the water chemistry in the Michigan Basin including the anomalous SBA is conducted in this study. It is this study's hypothesis that the geochemical nature of the groundwaters affected by the interaction of the water masses will be seen to alter spatially throughout the Michigan Basin. More specifically, the solute-solute diagrams composed in respect to chloride were similar to each other due to the mixing between brine and freshwater. Chloride concentrations known to be affected by this water mass mixing were shown to have characteristic distribution patterns in the aquifer systems (Ging et. al, 1996 Meissner et. al, 1996; Wahrer et. al, 1996). Considering the similar trends in the ion concentrations with respect to the brine-freshwater interactions, the spatial distributions of the ion concentrations should be similar to chloride concentrations and to one another. Therefore, the relative concentrations of chloride, sodium, calcium, magnesium, potassium, and sulfate will be high in brine-freshwater contact zones in the Michigan Basin, while the inverse relationship will be seen in respect to bicarbonate. In light of the chloride distribution maps for the aquifer units, high concentrations of the ions will be found in the middle of the Marshall aquifer and in the anomalous SBA in all three aquifer units, except for bicarbonate in which an inverse relationship and lower concentrations will be seen.

Areas within the basin of minimal brine impact, where older groundwaters and occurring meteoric recharge are the dominant water source, other chemical mechanisms acting within the system will pose a greater control on the ions' concentrations. The most probable physical-chemical processes are biological activity (sulfate reduction and methanogenesis), mineralogical controls, cation-exchange reactions, adsorption-desorption reactions, and anthropogenic inputs (USGS MI-RASA, 1996). These freshwater zones will be seen in the spatial distributions of the ion concentrations along with the variations in the distributions possibly caused by other geochemical mechanisms.

Considering the mineralogical reactions in the systems and the results from the SI histograms constructed in the RASA, most of the Michigan Basin will be saturated with respect to calcite and dolomite, undersaturated with respect to gypsum, and supersaturated with respect to quartz. It is this study's hypothesis that no variation in calcite and dolomite SIs will be seen in regards to brine-freshwater interaction zones. This hypothesis is based on the results of the MI-RASA mixing model that kept calcite and dolomite in equilibrium; the same trends were seen in this mixing model that were seen in the solute-solute diagrams regarding ion concentrations. Gypsum SIs will be affected relative to brine-freshwater mixing areas due to the scatter of sulfate concentration data seen in the mixing model when gypsum was kept in equilibrium. Sulfate concentrations would cluster along the mixing trajectory if the brine-freshwater interaction was not controlling gypsum saturation states. Likewise, a silica-chloride diagram was constructed and resulted in a scattered data array for silica concentrations and no linear trend with respect to the brine-freshwater mixing (Figure 5). Therefore, quartz SIs will be affected relative to brine-freshwater interaction zones in the aquifer systems.

To test this study's hypotheses, spatial distribution diagrams for the aquifer systems are constructed through the use of previously collected data (USGS MI-RASA, 1996; Dannemiller and Baltusis, 1990; Wahrer et. al, 1996; Ging et. al, 1996; Meissner et. al, 1996), which includes cation and anion concentrations of groundwaters. In this study, spatial diagrams are made for the dissolved ion concentrations of chloride, sodium, calcium, magnesium, sodium, potassium, strontium, barium, bicarbonate, and sulfate. These diagrams will demonstrate the prominence of

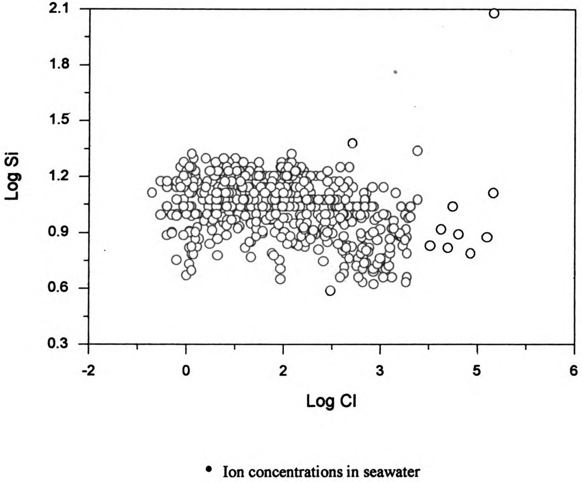


Figure 5. Solute-solute concentration plots of Log Cl vs. Log Si (modified from USGS MI-RASA, 1996)

individual suites of ions in each aquifer unit (Glaciofluvial, Pennsylvanian, and Marshall aquifers), which directly relates to a characteristic water chemistry. The construction of the diagrams and spatial analyses between them are done by the Geological Information Systems (GIS) computer program IDRISI (Eastman, 1995). To provide ground truth to the IDRISI diagrams, the IDRISI spatial diagrams for chloride and sulfate are compared to the MI-RASA images for the same components. As with the ions, distribution diagrams for the saturation indices (SIs) of calcite, dolomite, gypsum, and quartz are composed for the aquifers in order to gain further insight into the geochemical nature of the groundwaters in the aquifer systems. Upon completion of the diagrams, interpretations will made in light of the hypothesized overall geochemical/hydrological model for the evolution of the near surface groundwaters in the Michigan basin.

Distribution maps are also constructed and analyzed at various sampling depth intervals within the system to support the initial aquifer analyses (Appendix A). The need to construct the slice maps is due to the irregular contact boundaries between the aquifer units mostly due to erosion of the units' surfaces when exposed. The undulating topography of these boundaries could result in the same well sampling depth being derived from two different aquifer units. Along the same line, the concave nature of the Michigan Basin may produce this same result. These slice maps create a more integrative and continuous vertical trend for an individual variable's concentration and thus shows how the water chemistry is evolving, moving in a vertical direction in different locales within the Michigan Basin. Nine depth interval maps are composed for each variable corresponding to the depths of greater than 801 feet, 601 to 800 feet, 551 to 600 feet, 501 to 550 feet, 451 to 500 feet, 401 to 450 feet, 301 to 400 feet, 201 to 300 feet, less than 200 feet above sea level. Interpretations can then be made considering the slice maps and the geochemical/hydrological model of the system.

Hydrogeologic Framework of the Michigan Basin Aquifer System

The Michigan Basin regional aquifer system covers nearly 22,000 $mi.^2$ of the Lower Peninsula of Michigan (Figure 11) (Wahrer et. al, 1996). The boundary of the system's area is defined by the contact between the Mississippian Marshall Sandstone and the Mississippian Coldwater Shale. Above these units are Pennsylvanian and Pleistocene glacial deposits which are sedimentary rocks and unconsolidated material in nature. The chemistries of the groundwaters within the specified aquifer units are heterogeneous and regionally dependent. Three major aquifer units are considered in the analysis of the near surface groundwaters in the Michigan Basin aquifer system: the Glaciofluvial aquifer, the Pennsylvanian aquifer, and the Marshall aquifer. These units are listed in descending order from the surface to the confining Mississippian Coldwater Shale unit. Figure 12 demonstrates this sequence and the entire chronostratigraphy of the system of the aquifer (Wahrer et. al, 1996).

The Pleistocene deposited Glacial Drift consists of a glacial lacustrine confining unit (0 to 100 feet thick), the Glaciofluvial aquifer (0 to 900 feet thick), and a glacial till confining unit (50 to 175 feet thick) listed in descending order (Wahrer et. al, 1996). The Glaciofluvial aquifer unit predominates in the northwestern parts of the aquifer and is composed of coarse to gravel grained bar, lag, and channel deposits. Some coarse grained till deposits, also acting as part of the aquifer, are seen in this area. This combination unit provides sufficient supply and flow of groundwater regionally. In the Saginaw Lowland Area (SLA), which extends east from the outer edge of the Port Huron Morainal System to the Saginaw Bay, consists mostly of basil till and clay sized glaciolacustrine deposits (Long, 1993). These units act as confining units excluding the flow of groundwater. The mineralogy of the glacial drift entails illite, kaolinite, chlorite, quartz, feldspars, calcite, and dolomite (Chittrayanont, 1978).

The hydrogeology of the Glaciofluvial Aquifer is seen to take two courses (Figure 13) (Wahrer et. al, 1996). Most water, generally meteoric in origin, discharge into local stream

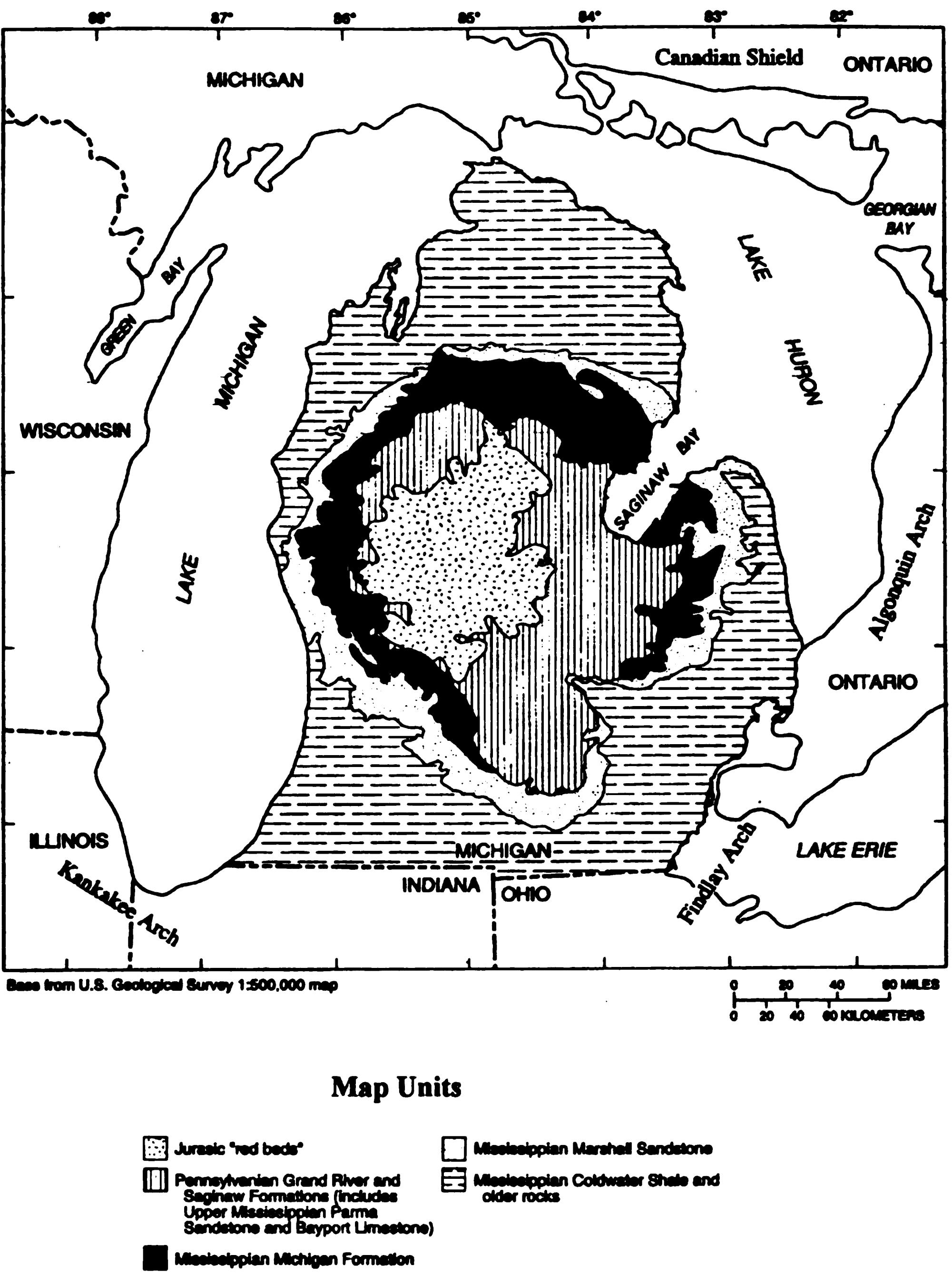
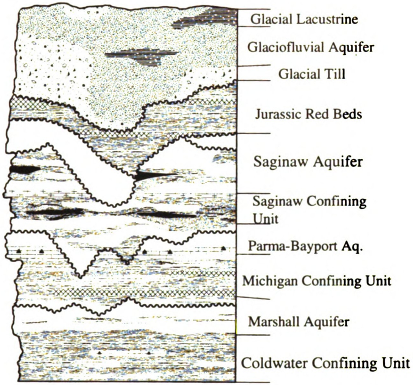


Figure 6. Study area and bedrock geology of the Lower Peninsula of Michigan (modified from USGS MI-RASA, 1996)



Lithology and stratigraphy of Michigan Basin

Figure 7. Relation between stratigrpahic and hydrologic units in the Lower Peninsula of Michigan (modified from USGS MI-RASA, 1996)

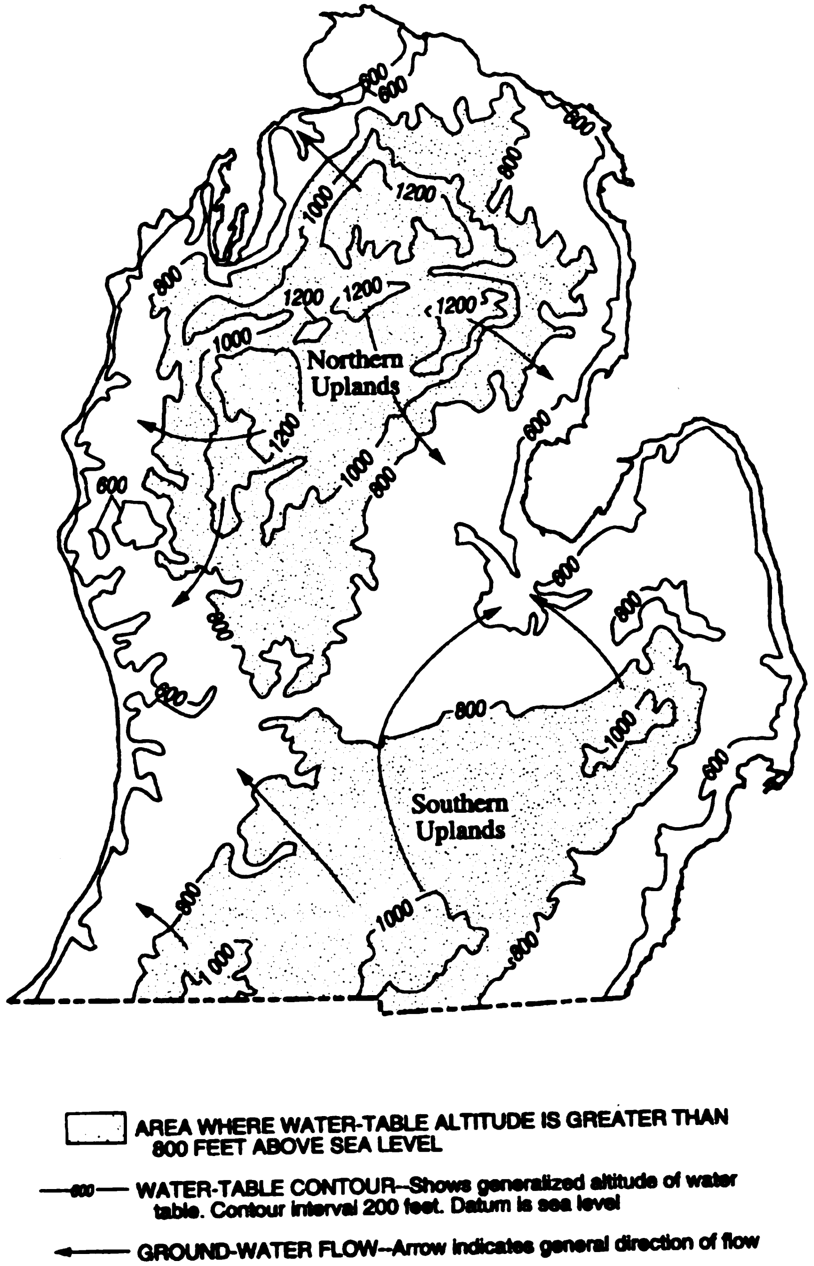


Figure 8. General groundwater flow directions in the Glaciogluvial aquifer (modified from Wahrer et. al, 1996)

systems and move along flow paths concordant to the regional streams into Lake Michigan, Lake Erie, or Lake Huron. Some water infiltrates deeper into the aquifer unit and moves along intermediate flow paths toward the Saginaw Bay Area or Michigan Lowland Area where it is discharged (Mandle and Westjohn, 1989). This intermediate and regional flow path of groundwaters follows the general trend of flux from upland areas downgradient toward lowland areas.

Below the glacial drift is the Jurassic Red Beds which also serve as a confining unit. This unit predominates in the west-central part of the aquifer and is usually between 50 to 200 feet in thickness (Long, 1993). The red beds are composed of red clay, mudstone, siltstone, sandstone, gray-green shale, and gypsum (Shaffer, 1969). Clays and mudstones predominate owing to its confining nature.

Underneath the Jurassic Red Beds are the Pennsylvanian deposits which include the Saginaw aquifer and the Saginaw confining units. The Saginaw aquifer unit is considered a bedrock aquifer composed of consolidated material. The sedimentology of this unit consists of lenticular beds of sandstone, shale, coal, and limestone (Martin, 1936). Quartz, micas, dolomite, calcite, and plagioclases are the dominant minerals in this zone. Where the Pennsylvanian deposits are the thickest (600 feet), the aquifer is between 300 and 400 feet thick but taper to a thickness of 200 feet in thinner Pennsylvanian deposits. Underlying this aquifer unit are impermeable shale beds (Saginaw confining unit) which are 100 to 300 feet thick in the thicker parts of the Pennsylvanian deposits and 50 to 100 feet thick in the thinner Pennsylvanian deposits. Groundwater flow in this aquifer unit is not well understood but considered to migrate and discharge in the Saginaw Bay Area (Figure 14) (Meissner et. al, 1996)).

Below the Saginaw formation is the Parma Sandstone and Bayport Limestone aquifer units which begin the Misssissippian deposits. These units are considered together as the Parma-Bayport aquifer (Meissner et. al, 1996). The high porosity and connectiveness in this aquifer provide very adequate groundwater storage and flow for public utilization. The Parma Sandstone

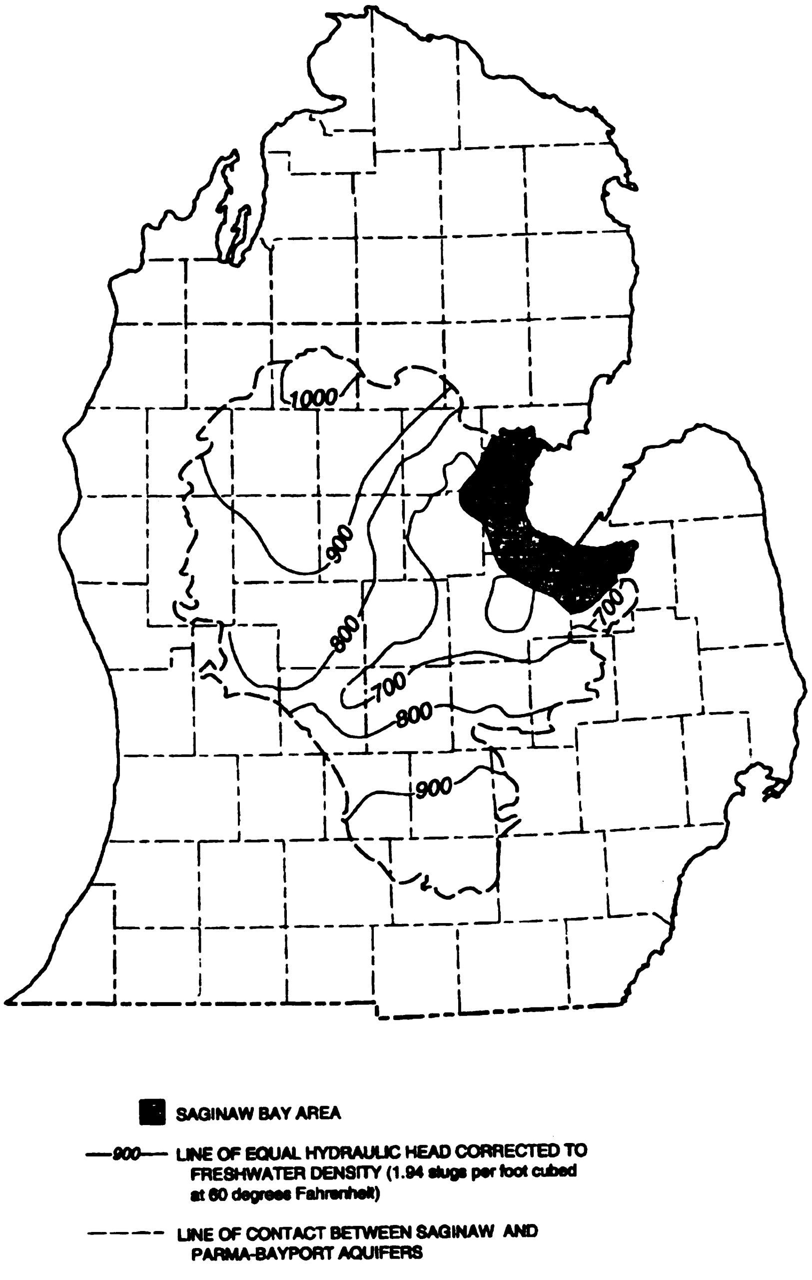


Figure 9. Simulated predevelopment equivalent freshwater head in the Saginaw aquifer and location of the Saginaw Bay Area (modified from Meissner et. al, 1996)

is over 100 feet thick and is composed of sandstone, shale, siltstone, and thin lenses of limestone (Cohee, 1965). The mineralogy of this top subunit of the aquifer consists of quartz, micas, dolomite, calcite, and plagioclases. Below this subunit is the Bayport subunit consisting of sparsely fossiliferous to very fossiliferous limestone, dolostone, sandy limestone, cherty limestone, and sandstone (Cohee et al., 1951). This subunit is less than 50 feet thick and has a mineralogy of calcite, quartz, and dolomite.

The last unit in the aquifer system sequence involves the Mississippian deposited Michigan Formation. This formation entails the Michigan confining units (250 to 400 feet thick) and the basal Marshall aquifer unit (75 to 175 feet thick) (Ging et. al, 1996). The Michigan confining units are composed of shale with beds of gypsum and anhydrite underlain by dolomitic limestone. The Marshall aquifer is mostly a medium grained calcerous and quartz sandstone with medium grade hydroconductivity. The hydrologic pathways seen in the Marshall aquifer (Figure 15) follow those of the Glaciofluvial and Saginaw Aquifers in which the water discharges in the Saginaw Bay Area or the Michigan Lowland (Mandle and Westjohn, 1989).

Capping the Michigan Basin aquifer system at the base is the Coldwater shale. This unit also has some local occurrences of limestones, dolomites, and sandstones and ranges in thickness from 500 feet in the eastern part of the aquifer to 1,100 feet in the western part of the aquifer. Another shale unit of Devonian origin lies below the Coldwater shale: the Devonian confining unit. This unit is about 1,320 feet thick (Ging et. al, 1996).

The last group to consider in the system analysis is the Traverse Group of Middle Devonian Age. The upper Traverse Formation is approximately 830 feet thick and is composed of bio-calcarenite limestone, anhydrite, dolomite, and shale. Dolomite is observed in the southern and western parts of the aquifer and limestone in the eastern parts of the aquifer. The other member of the Traverse Group is the Bell confining unit, which is between 0 and 80 feet thick (Ging et. al, 1996).

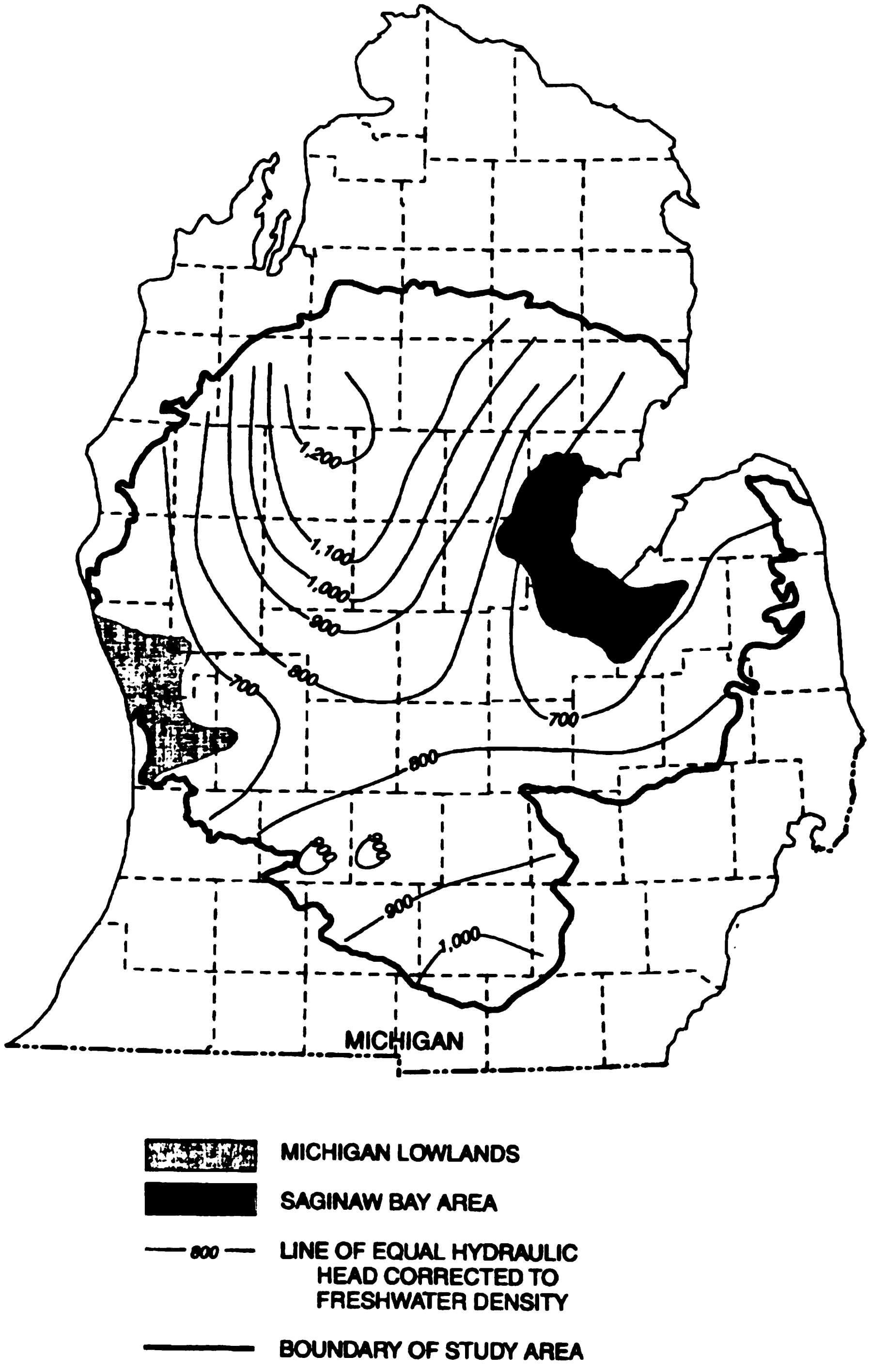


Figure 10. Predevelopment equivalent freshwater heads in the Marshall aquifer and location of the Saginaw Bay Area (modified from Ging et. al, 1996)

METHODS AND MATERIALS

The analysis done in this study was mainly performed through the use of the Geographical Information Systems raster spatial analysis computer program: IDRISI for Windows (Eastman, 1995). IDRISI for Windows consists of a main interface program and a collection of over 100 program modules that provide facilities for the input, display, and analysis of geographic data. These geographic data are described in the form of map layers. Because geographic data may be of different types, IDRISI for Windows incorporates two basic forms of map layers: raster image layers and vector layers (Eastman, 1995).

Image layers describe a region of space by means of a fine matrix of cells. These cells each contain numeric values that express the nature of the land at that location. In this case, the numeric values were associated with the ion concentrations and mineral SIs to produce spatial distribution diagrams. Vector layers, on the other hand, are useful for describing distinct features in the landscape. These included features such as the study boundaries for the Marshall and Glaciofluvial Aquifers, slice intervals, the Pennsylvanian Aquifer, and the SBA which were overlain upon the image maps (Eastman, 1995).

The variables analyzed were chloride, sodium, calcium, magnesium, potassium, sulfate, bicarbonate, strontium, barium and the SIs of calcite, dolomite, gypsum, and quartz. The ionic concentrations, temperature, and pH data used in the calculation of the mineral SIs of groundwater samples were collected from numerous databases (Ging et. al, 1996; Meissner et. al, 1996; Wahrer et. al, 1996; Dannemiller et. al, 1990). Groundwater samples are associated with varying depths within each aquifer at different locations and are represented by x and y coordinates and latitude and longitude coordinates in the cumulative database. At every particular depth and location within the aquifer systems, a water sample has a concentration for each of the ions (in mg/L), pH, temperature, and numerous other geochemical attributes associated with it.

To format the spatial variabilities of the water samples for the IDRISI program the location of each water sample originally in latitude and longitude measurements were converted into Universal Transverse Mercator (UTM) coordinates. This conversion was performed through the CRSTM.EXE computer program (Gage Personal Communication, 1996). The sample depths were then converted into feet above sea level basing the depths and depth intervals on a common datum.

Once all the variables were associated with the same planar and coordinate format, they were entered into the IDRISI program as a vector file. An interpolation of the vector points was then done to convert the points and their associated values into an image layer. The INTERPOL module interpolates an areal surface from the point data. This procedure is an inverse squared, distance-weighted average (Eastman, 1995).

The distance weight exponent used in this study is two (the default setting) yielding a weight equal to the reciprocal of the distance squared. In this interpolation process, a 6-point search radius about each point was used. This process provides an image layer. The image layer displays various colors correlating to a palette (Eastman, 1995). For each ion concentration, the palette intervals were defined and reclassed to associate a color with a concentration range interval. These concentration range levels were determined by separating the area of a histogram curve of the ion's concentrations into equal intervals. The RECLASS module was utilized to associate the value ranges to an integer category. For each ion, sixteen integer categories were made spanning the entire range of data. Subsequently, these integer values were associated with a palette file displaying sixteen colors where each color corresponds to an integer category and therefore a specific concentration interval for a noted ion.

This process was repeated for each ion for the different aquifer units. The imported data used to construct the image layers were segregated by means of the unit depths for the aquifer units. This data set comprises 304 samples from the Glaciofluvial aquifer, 154 samples from the Pennsylvanian aquifer, and 130 to 243 samples depending on the ion from the Marshall aquifer.

Along the same lines, distribution diagrams were constructed for the saturation indices of calcite, dolomite, gypsum, and quartz. The values for the SIs were determined through the WATEQ4F speciation program (Ball and Nordstrom, 1991). WATEQ4F calculates the equilibrium distribution of inorganic aqueous species of major and important minor elements in natural waters using the geochemical data and in situ measurements of temperature and pH found in the cumulative database. Therefore, through the data entered into the program and set parameters, the saturation indices of the minerals were calculated (Ball and Nordstrom, 1991). Once these values were determined, the spatial distribution diagrams were constructed for the different minerals in the noted aquifer units. Areas of supersaturation, saturation (equilibrium), and undersaturation were then presented. Mineral saturation indices that fell within the range of $\pm0.5\{\log_{10}K_{sp}\}$ of a mineral are considered to be in equilibrium with the water (Jenne et. al, 1980). This method suggests that a five-percent error of the log dissolution constant (K_{sp}) encompasses the true value. A similar approach in the study of mineral SIs was used by Long and others (1988) and Wood and Low (1988). Through a histogram of the saturation index data, degrees of undersaturation ($SI<-0.5\{\log_{10}K_{sp}\}$) and supersaturation ($SI>+0.5\{\log_{10}K_{sp}\}$) were categorized into five intervals. Using a great number of intervals was not viable due to the error of the WATEQ4F determination of the SIs and using less than five intervals would have overgeneralized the results. The five established intervals were then constructed in the RECLASS module.

The images produced were modified depending on the spatial availability of data. In the aquifer and slice distribution maps, the range of data do not always cover the entire aquifer. Therefore, the areas where no value is present were edited and shown as "cross-hatched" areas. During the interpolation process from a vector into an image layer, each vector point's value is ascertained a weight exponent to produce a spatial distribution with respect to neighboring points (six-point search radius). This poses the issue of how true the spatial distributions determined form the data are. A lone vector point at a great distance from neighboring points has less influence on the spatial distribution due to the "unknown" true values of areas surrounding the singular point. Therefore, the resulting distribution will only appear as an isolated "spot" in the image layer. Points found in clusters have greater influence on the distribution of the points' values due to the greater degree of information regarding the cluster area; thus, the distribution surrounding the cluster of points is "truer" than the distribution surrounding the lone point.

Therefore, to determine which areas represented true data and distributions, numerous maps were constructed for the same set of data using different weight exponents (one, two, four, and eight). The different weight exponents gave a point or group of points varying amounts of influence on the spatial distribution around them determined through an interpolation of the points. Using one as the weight exponent increases the influence of a lone point or group of points, whereas four and eight decrease the influence. Viewing all the maps made for a single set of data at different weight exponents, it was estimated how far from a point or group of points one could consider the spatial distribution to be true. Once an estimated distance of the influence of point distributions was attained, the aquifer was edited discounting areas where no data was available.

Additionally, three other issues did arise in the construction of the distribution maps for different variables in aquifer units and depth intervals. From the Marshall aquifer, the latitude and longitude coordinates found in the MI-RASA data base were not provided in respect to the data needed for the construction of the maps. These latitude and longitude coordinates were needed for input into the CRSTM.EXE program to convert these coordinates into UTM coordinates used in this study. The database only supplied an X-Y coordinate system for the allotted data, which was established by the MI-RASA (1996). To amend the noncorresponding coordinate systems, vector files were made in accordance to the X-Y system, and the RESAMPLE module in IDRISI was then utilized.

RESAMPLE registers the data in one grid system to a different grid system covering the same area. The process uses polynomial equations to establish a rubber sheet transformation, as if one of the grids were placed on rubber and warped to make it correspond to the other. The actual process is one in which a new grid is constructed and a set of polynomial equations is developed to describe the spatial mapping of data from the old grid into the new one. The new grid is then filled with data values by resampling the old grid and estimating, if necessary, the new vector value. Once the new vector files for the Marshall aquifer were made, the interpolation process was performed to provide an image file relevant to the new coordinate system.

Another issue entailed the distribution of the concentration values of chloride, sodium, calcium, and strontium with respect to the Marshall aquifer, the 200 feet and less depth interval, and the 201 to 300 feet depth interval. A difficulty was presented when the INTERPOL module tried to compose a map from the vector files of these variables. The module can not process data that have maximums and minimums values spatially adjacent to each other. For example, chloride values in the Marshall aquifer are between less than 1 and greater than 180,000 mg/L; values at these extremes often were found relatively close to each other. The interpolation could not assimilate the proximal data, and an interpolation pass would not establish a valid contour in between the two ends using the default nearest neighbor, six-point search radius procedure. To address this problem, the raw data was input into the function: $1 + (\log_{10}(\text{data})\} * 100$. Adding one to the values and multiplying by 100 separated the values, which allowed the data set to be expressed and analyzed more easily.

The multiplication of the values by 100 was necessary to address the final issue. The RECLASS module is based on an integer scale. When trying to reclass real values into intervals, such as assigning an integer category to numbers between 0.50 and 0.75, the reclassification scheme would automatically round the values to an integer. Therefore, after logging the data and adding one, the set reclassification intervals would have to contend with all real numbers, which would automatically be rounded to the nearest integer. This flaw made reclassification obsolete. Multiplication of the values by 100 bypassed this problem and dissociated the values into operable interval ranges. The original classification intervals were then altered by the same formula $(\{1 + \log_{10}(x)\} * 100)$ to correlate to the new data set. Saturation indices were also multiplied by 100 to surpass the same problem due to the fact that WATEQ4F produced real number SI values. The new values and classifications for both the ion concentrations and saturation indices sustained the integrity of the database and therefore, the distribution diagrams processed through the new data.

An examination of the spatial distributions was performed after all the maps were made for the ion concentrations and mineral saturation index distributions. This examination involved a description of the spatial distribution of the high and low concentrations of each ion for every aquifer unit. In the aquifer examinations is the comparative analysis between the chloride and sulfate aquifer maps constructed in the IDRISI program and the hand contoured maps produced in the MI-RASA report to assess the ground truth of the IDRISI diagrams.

A subsequent integrated analysis is made to establish a normalized trend or pattern developed between all the ions. This examination involves the correlation of highs and lows relative to the ions. After a collective analysis of the ionic components in the system, more detailed discussions of the individual components and comparative analyses between certain ion pairs were investigated. These individual ion distribution maps were discussed in light of the overall geochemical/hydrological model of the system. The function of the comparative analyses was to associate between relative highs and lows of the distribution maps of specific ion suites. In consideration of ionic pairs, sodium and chloride are compared due to the fact that their geochemical behaviors and sources are similar. Calcium and magnesium are also compared due to their similar chemical character, behavior, and sources. A third and final ionic pair comparison is made between bicarbonate and sulfate. These two elements are compared due to the effects that microbial activity has on their residual concentrations.

In these comparative analyses, the CROSSTAB module of the IDRISI program was used. The significant operation that CROSSTAB offers is cross-classification, which produces a new image that shows the locations of all combinations of the categories (concentration intervals) in the original images. A legend is automatically produced showing these combinations between the two images. Most importantly, this function relates to the relative ratio of concentrations between two or more species as associated by a palette color. This module was only utilized to locate areas of great difference between the compared variables. The areas of relative similarity or dissimilarity formulated, an investigation of the chemical mechanisms potentially controlling the different variables' associated magnitudes were discussed.

After considering the ion distribution maps, the SI distribution maps of calcite, dolomite, gypsum, and quartz for the aquifers were examined individually. This investigation considers the developed overall geochemical/hydrological model of the system. This analysis of the mineral SI distribution maps especially considers the effect the brine-freshwater reactions have upon the saturation states of these minerals and if any pattern could be derived from the brine migration. Comparative analyses were also given between the saturation indices of the different minerals and their ion components. This investigation examined the effect that precipitation and dissolution reactions may have on the present spatial distributions of the ion components. This part of the study addressed the effect of the saturation stabilities of: 1) calcite on calcium and bicarbonate concentrations, 2) dolomite on calcium, magnesium, and bicarbonate concentrations, and 3) gypsum on calcium and sulfate concentrations.

These same methods used in the aquifer analyses were employed in the analyses of the slice distributions for both ion concentrations and mineral SIs (Appendix A). An overall comparison was then made between the aquifer and slice distribution maps. This discussion entailed whether the normalized spatial trends found in the cumulative analyses for all the ions for both methods were similar to each other. This part of the study was used as support for the analysis done for the aquifers and the results derived from this analysis. It also provided a look into and reasons for variations and discrepancies seen between the different approaches.

DISTRIBUTION OF DISSOLVED ION CONCENTRATIONS IN GROUNDWATER FROM THE GLACIOFLUVIAL, PENNSYLVANIAN, AND MARSHALL AQUIFERS

Dissolved Chloride

In the Marshall aquifer the chloride distribution has a range of less than 1 to greater than 180,000 mg/L (Figure 11a). The highest concentrations (greater than 180,000 mg/L) are found in middle region of the basin including much of the central section of the SBA anomaly. These concentrations decrease very towards the boundaries of the basin to values less than 4 mg/L. The majority of the far northeastern part of the aquifer has higher concentrations with some zones reaching values of 3,000 to 20,000 mg/L. A western and northern zone also have relatively high concentrations of 1,500 to 20,000 mg/L.

The same basic pattern is seen in the MI-RASA chloride distribution map for chloride in the Marshall aquifer (Figure 12) (modified from Ging et. al, 1996). Discrepancies are seen in the extent of the higher concentrations in the north and west. Here, the IDRISI image has higher concentrations in these boundary areas (1,500 to 3,000 in the west and 3,000 to 20,000 mg/L in the north), while the RASA map has levels of 100 to 1,000 mg/L in both areas. Regions in the southeast (just south of the SBA) have variations also, in which slightly higher concentrations (100 to 1,000 mg/L) are seen in the RASA map compared to the distribution map constructed in this study (less than 1 mg/L). These variations may be accounted for with respect to the different methods used in countouring the data. RASA used hand contouring methods, whereas this study used the GIS IDRISI modeling program. The hand contouring methods may not use outlying data that is askew form surrounding spatial data distributions. IDRISI uses all the available data, and if outlying spatial data is amidst a different data range distribution, IDRISI will skew the results to a medium between the two extremes.

In the Pennsylvanian aquifer concentrations of chloride range from 1 to 60,000 mg/L (Figure 11b). The highest concentrations of chloride between 20,000 and 60,000 mg/L are found in the southeast, while the western portion of the SBA and areas to the south and northwest of the

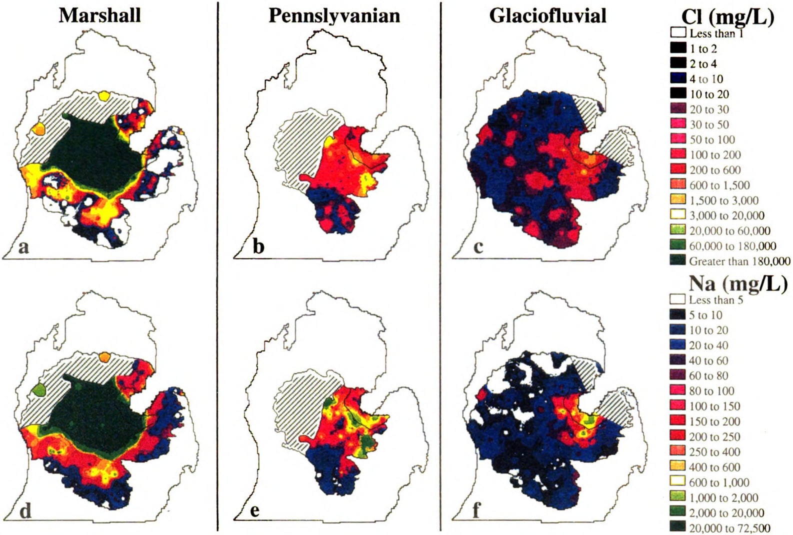


Figure 11 a-c Distribution of dissolved chloride in the Marshall, Pennsylvanian, and Glaciofluvial aquifers
d-f Distribution of dissolved sodium in the Marshall, Pennsylvanian, and Glaciofluvial aquifers

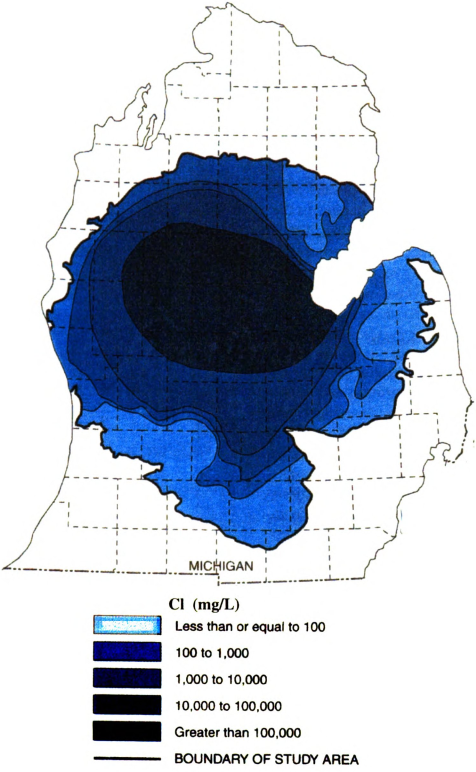


Figure 12. Distribution of dissolved chloride in the Marshall aquifer (modified from Ging et. al, 1996)

SBA have relatively high concentrations of 3,000 to 20,000 mg/L. Lower concentrations are seen in most of the southern part of the aquifer with levels less than 10 mg/L. The middle of the aquifer unit has intermediate chloride levels of 100 to 200 mg/L.

Again compared to the RASA chloride distribution map for the Pennsylvanian aquifer, the two maps correlate well with one another (Figure 13) (modified from Meissner et. al, 1996). Higher concentrations are seen in the eastern part of the SBA and just south of the SBA in the IDRISI image compared to the RASA map. This discrepancy may be due to the different contour intervals used where the RASA sets the interval above 1,000 mg/L, and IDRISI uses more definitive contour intervals and defines the area between 3,000 and 20,000 mg/L. A variation does originate on the southern boundary of the aquifer where the RASA map has concentrations well above 1,000 mg/L, while the IDRISI image has values ranging between 50 and 100 mg/L. The variations between the maps may also be due to the number of chloride measurements used in the construction of the spatial maps. The RASA study used 427 samples, and this study used 154 samples.

The Glaciofluvial aquifer has a range of less than 1 to 20,000 mg/L (Figure 11c). Levels less than 20 mg/L are seen throughout the aquifer except for the SBA, a small zone just west of the SBA, and a small zone just south of the SBA. These areas reach concentrations of 200 to 3,000 mg/L. Most of the SBA, areas surrounding the SBA, a zone in the middle of the aquifer, and a zone in the northwestern part of the aquifer have relatively high values also of 200 to 600 mg/L. A small midsouthern zone in the SBA and a small area just west of the SBA reach a high of 1,500 to 3,000 mg/L, while the highest concentration zone is just south of the SBA (3,000 to 20,000 mg/L).

When comparing the IDRISI image of chloride in the Glaciofluvial aquifer and the RASA image of chloride in the Glaciofluvial aquifer (Figure 14), the same distribution patterns are seen around the SBA and in most of the basin (Modified from Wahrer et. al, 1996). However, there are major variations between the two maps in the middle and the west. The RASA map has

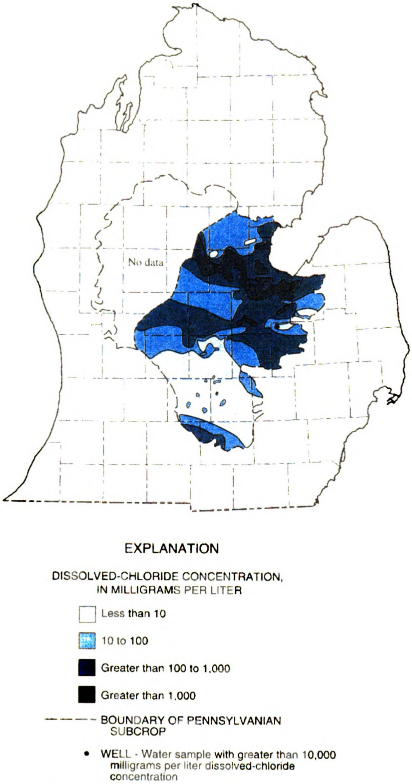


Figure 13. Distribution of dissolved chloride in the Pennsylvanian aquifer (modified from Meissner et. al, 1996)

a relatively high zone of 100 to 1,000 mg/L in the far midwest of the aquifer, while the IDRISI image indicates the area with a range between 4 and 10 mg/L. Two areas, one in the middle and one on the northwest border, show a concentration range of 200 to 600 mg/L for the IDRISI image. These same areas correspond to values of 10 to 100 mg/L for the RASA report. The different number of samples used in constructing the maps may produce the differences found. The RASA study only used 279 samples, whereas this study used 304 samples.

Overall, in the comparison of the dissolved chloride distribution maps for the three aquifers between the RASA report and this study, the same general distributions are seen. A great variation is found in the northern and western parts of the Marshall aquifer in which the IDRISI image is seen to have much higher concentrations than the RASA image (Figure 11a and Figure 12). The reverse is true in which the southern part of the Pennsylvanian aquifer has much higher values for the RASA map than for the IDRISI image (Figure 11b and Figure 13). As a whole, few discrepancies are found in the three aquifers in the comparative analyses. These variations can be due to the different methods used in the construction of the distribution maps and contouring intervals. In the RASA map construction, the hand contouring methods employed may not use outlying data that is askew form surrounding spatial data. IDRISI uses all the available data, and if outlying spatial data is amidst a very different data range distribution, IDRISI will skew the results to a medium between the two extremes. The number of samples used in constructing the maps was also different in respect to the Pennsylvanian and Glaciofluvial aquifers which could cause variations.

Dissolved Sodium

In the Marshall aquifer, the sodium concentrations range from values of less than 5 to 72,500 mg/L (Figure 11d). The highest concentrations are seen in the middle of the aquifer and the central SBA with concentrations between 20,000 and 72,500 mg/L. These concentrations decrease concentrically away from the center of the basin and SBA to levels of less than 1,000 mg/L in the outer fringe of the aquifer. The southern boundary of the aquifer has the lowest

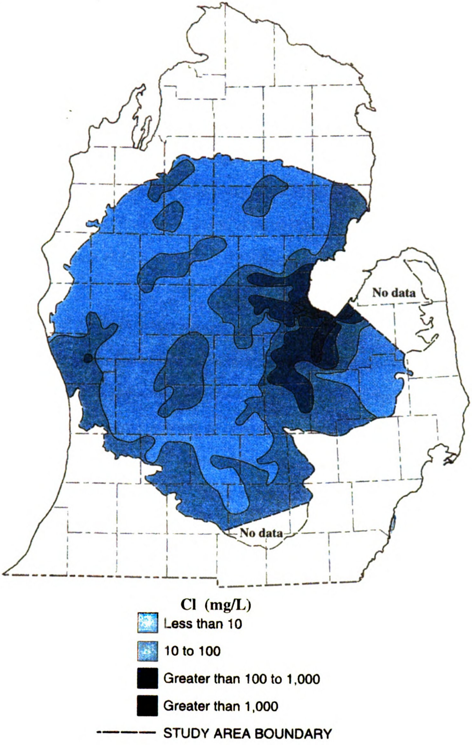


Figure 14. Distribution of dissolved chloride in the Glaciofluvial aquifer modified from Wahrer et. al, 1996)

levels between less than 5 and 30 mg/L. The northeast has slightly higher concentrations with some zones having concentrations between 600 and 1,000 mg/L. Relatively high levels of sodium are also found in a western (600 to 1,000 mg/L) and northern zone (250 to 600 mg/L).

The Pennsylvanian aquifer has a range of less than 5 to 20,000 mg/L of dissolved sodium (Figure 11e). The western SBA and areas just to the northwest and south of the SBA have the highest sodium levels of 2,000 to 20,000 mg/L. The western SBA has values between 1,000 and 2,000 mg/L, while the northern SBA has lower values of 100 to 200 mg/L. Areas just southwest and west of the SBA and towards the middle of the aquifer have relatively high values of 200 to 250 mg/L also. Most of the southern half of the aquifer has lower concentrations less than 20 mg/L.

Levels of dissolved sodium are seen in the Glaciofluvial aquifer with values between less than 5 and 2,000 mg/L. Generally, concentrations of less than 40 mg/L are found in the aquifer unit except for the SBA and surrounding areas (Figure 11f). Around the SBA, concentrations are 150 to 250 mg/L. These concentrations decrease towards the boundaries of the aquifer to the lower levels (less than 40 mg/L). The southeastern SBA and areas just south and west of the SBA have the highest concentrations of 1,000 to 2,000 mg/L.

Dissolved Calcium

Calcium concentrations in the Marshall aquifer range from less than 20 to greater than 40,000 mg/L (Figure 15a). The highest concentrations are found in the center of the aquifer (greater than 40,000 mg/L); these concentrations decrease concentrically to slightly lower values in the southeast (4,000 to 40,000 mg/L). This latter range includes the majority of the SBA with the western boundary of the anomaly having the highest values of 20,000 to 40,000 mg/L. These concentrations decrease even more towards the boundaries of the aquifer to values averaging between 70 and 105 mg/L. Very low areas of less than 20 mg/L are found in the southeastern SBA, just north of the SBA, and the southwest. The west has relatively high concentrations of 600 to 4,000 mg/L, as does a northern zone (160 to 200 mg/L).

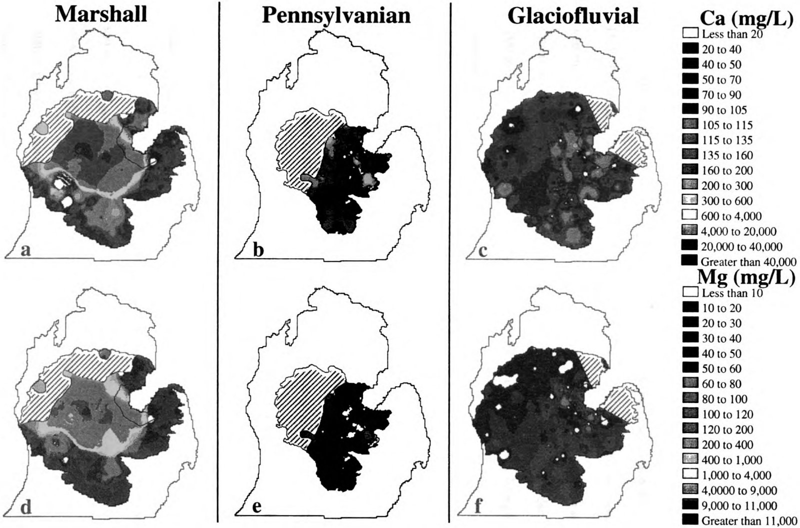


Figure 15 a-c Dissolved calcium distribution in the Marshall, Pennsylvanian, and Glaciofluvial aquifers
d-f Dissolved magnesium distribution in the Marshall, Pennsylvanian, and Glaciofluvial aquifers

The Pennsylvanian aquifer has a range of less than 20 to 4,000 mg/L (Figure 15b). This aquifer has high concentrations of 600 to 4,000 mg/L in the western SBA and areas just south and northwest of the SBA. A region just off the western boundary of the aquifer has relatively high concentrations of 300 to 600 mg/L. Levels less than 90 mg/L are seen southwest of the SBA to the southern boundary of the aquifer. The majority of the middle region of the basin has concentrations between 135 and 160 mg/L.

The Glaciofluvial aquifer has concentrations between less than 20 and 600 mg/L (Figure 15c). The three highest zones of calcium concentrations (300 to 600 mg/L) are found in the western SBA and just west and south of the SBA. Relatively high concentrations are also seen in a small zone just southwest of the SBA and a small western zone just off the border of the aquifer (200 to 300 mg/L). The rest of the basin has concentrations between 50 and 70 mg/L.

Dissolved Magnesium

In the Marshall aquifer a range of less than 10 to greater than 11,000 mg/L is seen (Figure 15d). High concentrations are found in the center of the aquifer (greater than 11,000 mg/L); these concentrations decrease concentrically towards the boundaries of the aquifer. Most of the SBA has slightly lower concentrations of 4,000 to 9,000 mg/L. Lower values are found on the southern fringe and in the northeastern region of the aquifer ranging between 20 and 40 mg/L. The far eastern part of the SBA has extremely low concentrations of less than 10 mg/L. A zone north of the SBA and two zones in the southwest also have concentrations of less than 10 mg/L. A northern zone has relatively low concentrations of 40 to 60 mg/L, while a western zone has relatively high concentrations (400 to 1,000 mg/L).

The Pennsylvanian aquifer distribution map of magnesium has a range of less than 10 to 400 mg/L (Figure 15e). High points of 200 to 400 mg/L are found just south and west of the SBA. A small zone on the western edge of the SBA including a large western zone also has relatively high magnesium levels of 80 to 120 mg/L. Numerous zones of 50 to 60 mg/L are found in the northeast and northwest. The rest of the basin is at levels of less than 40 mg/L including most of the SBA anomaly.

The Glaciofluvial aquifer has a concentration range of less than 10 to 120 mg/L of magnesium (Figure 15f). Very low concentrations (less than 30 mg/L) are seen for most of the north, west, and south. Higher concentrations are found in the SBA where certain areas have levels of 80 to 120 mg/L just off the western border and south of the SBA. The SBA has a small zone in the south that has higher values of 60 to 80 mg/L, while the rest of the SBA has slightly lower values of 20 to 30 mg/L.

Dissolved Sulfate

In the Marshall aquifer, values of dissolved sulfate range from less than 10 to 3,500 mg/L (Figure 16a). Concentrations of 1,000 to 3,500 mg/L are seen in a number of areas throughout the west, southeast including the southern part of the SBA, and southwest. Most of the west-southwest, southeast, and SBA have concentrations between 400 to 1,000 mg/L. These concentrations decrease towards the middle, southern fringe, and northeastern regions of the aquifer. Lower levels between 20 and 70 mg/L are located just off the southern border of the aquifer. The middle of the aquifer has relatively low concentrations (100 to 150 mg/L). The remainder of the northeast and much of the midsouth have a concentration range of 80 to 150 mg/L.

Like the initial comparison of the chloride maps for the RASA and this study, the sulfate distribution images correlate well with each other for the Marshall aquifer (Figure 17) (Modified from Ging et. al, 1996). The only differences are seen in the "horse shoe" shaped pattern found in the RASA. This "horse shoe" is a belt of higher concentrations that begins in the northwestern part of the aquifer, extends due south, turns east, then north connecting with the SBA. The RASA "horse shoe" has high concentrations of sulfate (greater than 1,000 mg/L). In this same distribution pattern, the IDRISI image has lower concentrations levels of (400 to 1,000 mg/L) throughout the southwest and even goes as low as 200 to 300 mg/L in the southernmost area of the "horse shoe". Limited data used in this study may cause the variations seen regarding the two

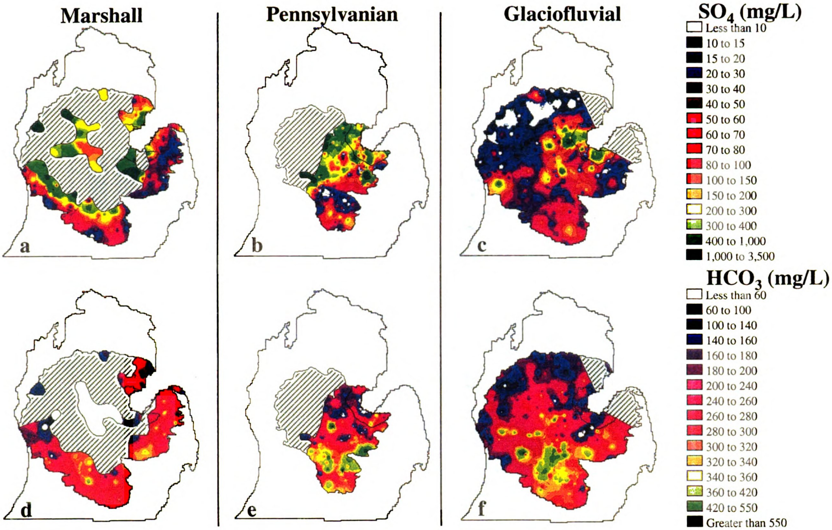


Figure 16 a-c Distribution of dissolved sulfate in the Marshall, Pennsylvanian, and Glaciofluvial aquifers
d-f Distribution of dissolved bicarbonate in the Marshall, Pennsylvanian, and Glaciofluvial aquifers

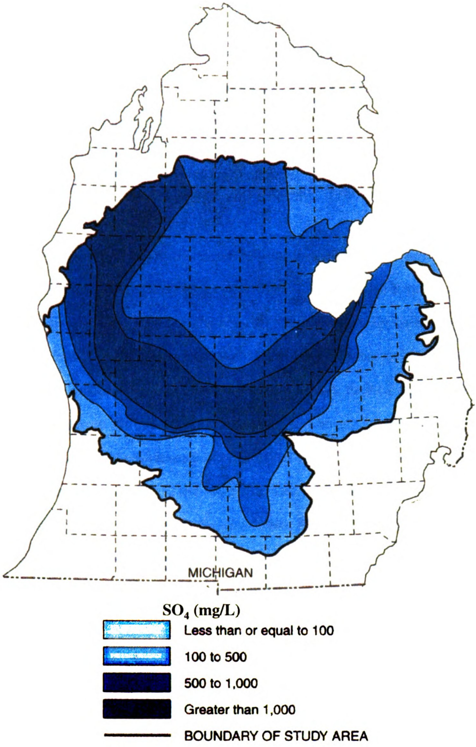


Figure17. Distribution of dissolved sulfate in the Marshall aquifer (modified from Ging et. al, 1996)

distribution maps for sulfate. The RASA used 243 samples, whereas this study used 176 samples.

The Pennsylvanian aquifer has a range less than 10 to 3,500 mg/L (Figure 16b). The highest concentrations (1,000 to 3,500 mg/L) are found in most of the western fringe of the aquifer, a zone in the western SBA, and the southeast. Relatively high concentrations (300 to 1,000 mg/L) are seen in the rest of the SBA, areas surrounding the SBA, towards the middle of the aquifer, and a few zones in the south. A belt of 15 to 20 mg/L is found to cross the south, while the remaining southern areas have intermediate dissolved sulfate concentrations of 70 to 150 mg/L.

The RASA and IDRISI dissolved sulfate maps for the Pennsylvanian aquifer follow each other very well in the western parts of the aquifer (Figure 18) (Modified from Meissner et. al, 1996). A few areas in the eastern part of the aquifer have a greater magnitude of sulfate concentrations in the IDRISI images. An area on the western SBA border and just south of the SBA have sulfate concentrations between 1,000 and 3,500 mg/L for the IDRISI image compared to lower values between 100 and 1,000 mg/L for the RASA image. Many areas in the south for the IDRISI image have concentrations between 150 and 400 mg/L, while, on the average, the RASA image has levels between 10 and 100 mg/L. These variations may be caused by the different number of sulfate data used in the construction of the sulfate maps. This study used 154 samples, and the RASA used 427 samples.

In the Glaciofluvial aquifer the range of sulfate concentrations is less than 10 to 3,500 mg/L (Figure 16c). The highest concentrations are seen in an area located on the western edge of the SBA (1,000 to 3,500 mg/L). Most of the SBA, zones to the west of the SBA, and a small zone on the western border of the aquifer have relatively high concentrations of 400 to 1,000 mg/L. Very low concentrations less than 30 mg/L are seen in north-northwest. Slightly higher levels of 40 to as high as 300 mg/L are found in the south-southwest. A low zone in sulfate levels (20 to 70 mg/L) is seen in very middle of the SBA.

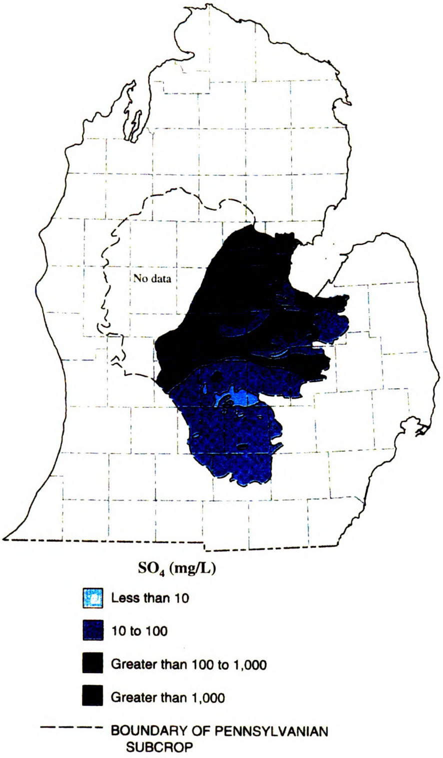


Figure 18. Dissolved sulfate concentrations in the Pennsylvanian aquifer (modified from Meissner et. al, 1996)

Like the other two aquifer units, the IDRISI and RASA map are similar to each other for the Glaciofluvial aquifer relatively well (Figure 19) (Modified from Wahrer et. al, 19960. Inconsistencies are seen in the far south and western edge of the aquifer where the IDRISI image has much higher concentration levels (200 to as high as 1,000 mg/L) compared to the RASA image, which has a range between 10 and 100 mg/L. The different number of sulfate samples used in the construction of both maps may be the reason for the inconsistencies; the RASA used 200 samples, and this study used 304 samples.

As with the chloride comparison between the RASA and this study's IDRISI images, the relative distribution patterns of sulfate concentration correlate very well in all three aquifer units. The major differences are in the Pennsylvanian and Glaciofluvial aquifers. In the Pennsylvanian distribution maps, higher concentrations (1,000 to 3,500 mg/L) are seen in the east surrounding the SBA and the midsouth in this study compared to the RASA study (100 to 1,000 mg/L) (Figure 16b and Figure 19). In the Glaciofluvial maps, incongruous areas in the western and southern fringe have relatively high values in this study (200 to 1,000 mg/L) compared to lower values of sulfate in the RASA study (10 to 1,000 mg/L) (Figure 16c and Figure 20). The variations seen with respect to all three aquifers may be due to the different amounts of data used in the construction of the diagrams. These variations can also be due to the different methods used in the construction of the distribution maps. In the RASA map construction, the hand contouring methods employed may not use outlying data that is askew form surrounding spatial data. IDRISI uses all the available data, and if outlying spatial data is amidst a very different data range distribution, IDRISI will skew the results to a medium between the two extremes.

Dissolved Bicarbonate

In the Marshall aquifer, concentrations range from less than 60 to 420 mg/L (Figure 16d). Very low concentrations are seen in the center of the basin (less than 60 mg/L). These concentrations increase to levels of 280 to 360 mg/L moving towards the south-southeastern regions of the aquifer. The northeastern and western parts of the basin have a range of 200 to 240

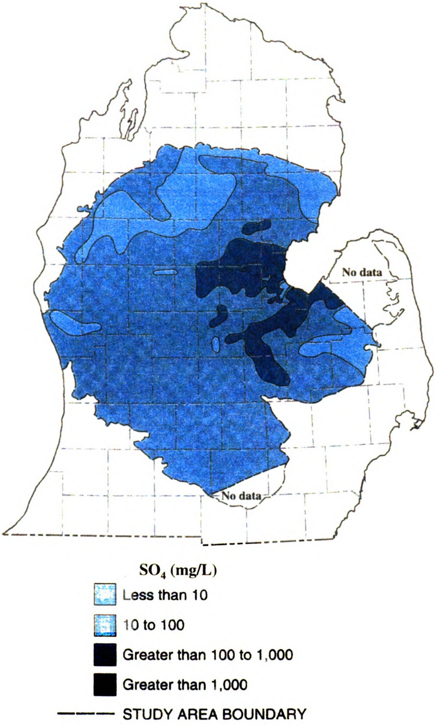


Figure 19. Distribution of dissolved sulfate in the Glaciofluvial aquifer (modified from Wahrer et. al, 1996)

mg/L. The SBA has this same relatively high concentration range with higher concentrations (240 to 260 mg/L) in the north and lower concentrations (140 to 160 mg/L) in the middle of the anomaly. The very western edge of the basin has very low concentrations (less than 60 mg/L).

In the Pennsylvanian aquifer the levels of dissolved bicarbonate have a range of less than 60 to greater than 550 mg/L (Figure 16e). The highest concentrations of 320 to greater than 550 mg/L are found in numerous regions in the southern and regions of the aquifer. Areas in the south and the southern part of the SBA have relatively high concentrations of 320 to 550 mg/L. Very low zones of less than 60 to 140 mg/L are seen in the center of the SBA and segregated zones along the western border. The remaining areas of the aquifer unit have concentrations between 200 and 280 mg/L.

In the Glaciofluvial aquifer the values of bicarbonate range from less than 60 to greater than 550 mg/L (Figure 16f). Much of the southern half of the aquifer has highs in the range of 400 to 550 mg/L with a small higher zone of greater than 550 mg/L in the southwest. The rest of the south and much of the middle have a range of 260 to 300 mg/L. These concentrations decrease to levels of less than 180 mg/L in the northernmost regions of the aquifer. The SBA has concentrations between 100 and 180 mg/L with a small high zone in the middle and northern areas of the anomaly (240 to 320 mg/L).

Dissolved Potassium

In the Marshall aquifer, values range from less than 1 to greater than 700 mg/L (Figure 20a). The maximum concentration levels (greater than 700 mg/L) are seen in the center of the aquifer and western and southern areas of the SBA. These concentrations decrease radially towards the northeast and south. The rest of the west and SBA generally has a range of 200 to 700 mg/L. The decreasing concentration levels proceed concentrically away from these higher areas down to 2 to 4 mg/L in the southern fringe and northeast.

In the Pennsylvanian aquifer the concentrations range from less than 1 to 60 mg/L (Figure 20b). Relatively high levels of 10 to 60 mg/L are found in the western SBA, southeast,

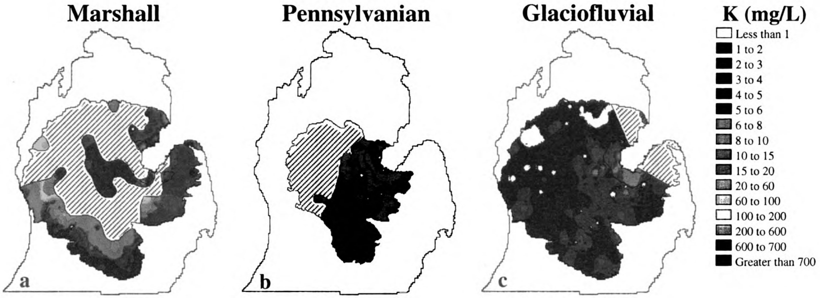


Figure 20 a -c Distribution of dissolved potassium in the Marshall, Pennsylvanian, and Glaciofluvial aquifers and western boundary of the aquifer. These concentrations decrease to concentrations of less than 4 mg/L in the south and parts of the east. Overall, concentrations in the SBA are in the range of 3 to 10 mg/L.

In the Glaciofluvial aquifer dissolved potassium concentrations are between less than 1 and 15 mg/L (Figure 20c). Concentrations are less than 4 mg/L for the entire aquifer except for the SBA and surrounding areas. In the southwestern SBA, the highest concentrations are found (10 to 15 mg/L). Relatively high concentrations (6 to 8 mg/L) are found in much of the rest of the SBA and a number of zones around the anomaly.

Dissolved Strontium

Limited data was available to produce the strontium distribution map for the Marshall aquifer. Values range from less than 80 to 80,000 mg/L (Figure 21a). The highest concentrations are found in the northwest, the western SBA, and just south and west of the SBA (10,000 to 80,000 mg/L). Relatively high zones are seen in the north, midsouth, southeast, and much of the SBA (1,000 to 10,000 mg/L). The southwestern fringe and zones in the northeast have the lowest concentrations in the aquifer (less than 80 to 150 mg/L). However, the southeastern and northeastern fringes have slightly higher values between 400 and 900 mg/L.

In the Pennsylvanian aquifer, a range of less than 80 to 80,000 mg/L is seen (Figure 21b). The highest concentrations are found on the western edge of the SBA, along the western border, and in the southeast (10,000 to 80,000 mg/L). Much of the southern and northern SBA, western fringe, and a southern zone also have relatively high concentrations of 2,000 to 10,000 mg/L. Most of the middle of the aquifer has concentrations between 1,000 and 2,000 mg/L, while the south has the lowest concentrations of less than 600 mg/L.

In the Glaciofluvial aquifer the dissolved strontium concentrations range from less than 80 to 10,000 mg/L (Figure 21c). The highest concentrations are seen in the western SBA, areas to the south and west of the SBA, and zones in the west (4,000 to 10,000 mg/L). The bulk of the SBA and a number of areas throughout the north and south have the lowest concentrations of less

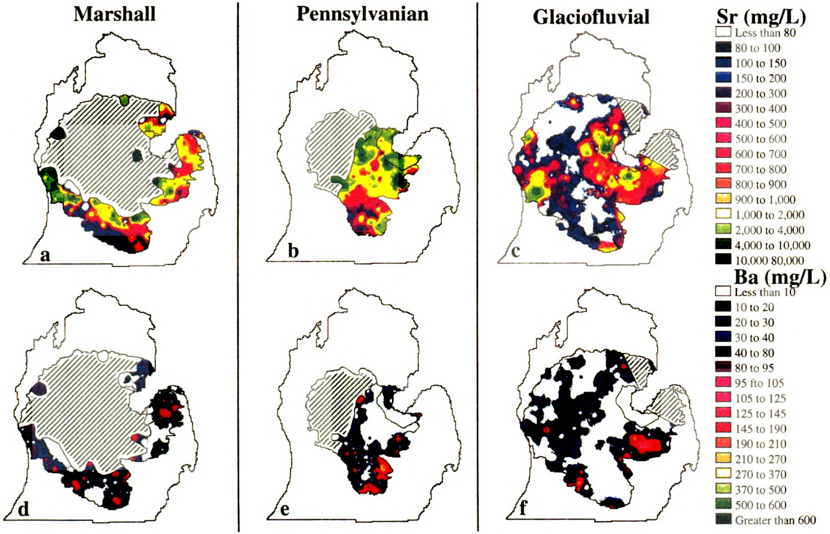


Figure 21 a-c Distribution of dissolved strontium in the Marshall, Pennsylvanian, and Glaciofluvial aquifers
d-f Distribution of dissolved barium in the Marshall, Pennsylvanian, and Glaciofluvial aquifers

than 80 mg/L. Areas west and east of the SBA and in the south have fairly high concentrations of 800 to 2,000 mg/L. The remaining parts of the aquifer have concentrations less than 300 mg/L.

Dissolved Barium

The barium distribution map for the Marshall aquifer was composed from limited data, and concentrations range from less than 10 to 270 mg/L (Figure 21d). The highest concentrations are found in the southeastern regions of the aquifer (210 to 270 mg/L). A small zone of these high concentrations is also seen in the south. A number of zones along the border of the southern half of the study have relatively high concentrations of 190 to 210 mg/L. The rest of the border zones including the SBA have values less than 80 mg/L.

The Pennsylvanian aquifer has concentrations between less than 10 and 370 mg/L (Figure 21e). A middle region covering an area from the western border to and including the SBA and surrounding areas has concentrations less than 10 mg/L. This same range is seen in the far western and midsouthern regions of the aquifer. Slightly higher concentrations (30 to 80 mg/L) are found in the western region of the aquifer. The highest concentrations in the aquifer are seen in the south-southeast (270 to 370 mg/L). Relatively high concentrations are found in a number of zones in the southern region of the aquifer and the northwest (145 to 190 mg/L).

The Glaciofluvial aquifer has values ranging from less than 10 to 270 mg/L (Figure 21f). Almost the entire aquifer unit has concentrations less than 80 mg/L including the SBA which has a range of less than 10 mg/L. Small southwestern and southeastern areas have the highest concentration levels of 210 to 270 mg/L. A small zone in the west, the south, and the northeast have fairly high values of 105 to 145 mg/L.

CUMULATIVE, INDIVIDUAL, AND COMPARATIVE ANALYSIS OF THE MARSHALL, PENNSYLVANIAN AND GLACIOFLUVIAL AQUIFERS

Cumulative Summary

In the analysis of the Marshall aquifer, chloride, sodium, calcium, magnesium, and potassium have their highest concentrations in the greater middle region of the basin. These higher concentrations of the elements include the SBA anomaly as well; as a result, a lobate pattern is seen between the center of the basin and the SBA. Chloride and sodium are at their highest concentrations in this lobate pattern. However, calcium, magnesium, and potassium demonstrate a concentrical decrease from their highest concentrations away from the middle of the aquifer towards the boundaries of the aquifer but still have very high concentrations in the SBA.

Like calcium, magnesium, and potassium, chloride and sodium also radially decrease away from their highest concentrations towards the boundaries of the aquifer. Overall, each element has its lowest concentrations in the southern fringe and northeastern section of the aquifer. This decrease in concentrations is less extreme in the northern and western regions of the basin where relative highs of the ions are seen. The minor cations (strontium and barium) have distributions that are somewhat similar to these patterns. However, due to lack of available data, only the boundary areas of the basin and SBA and surrounding areas were considered. For barium and strontium, high concentrations are found around the SBA, while low concentrations are noticed in the southern fringe and northeast region of the aquifer.

Sulfate and bicarbonate have different distribution patterns from that of the major ions in the Marshall aquifer. Sulfate does have the same areal variations as the other major ions but has a marked decrease in concentrations in the middle region of the aquifer where the other elements have their highest concentrations.

Bicarbonate distributions relay the opposite trend of the major ions in which its highs are associated with the major ions' lows, and its lows are associated with the major ions' highs. Therefore, the lowest concentrations are found in the middle of the basin and connect with the SBA. These concentrations then increase towards the boundaries of the aquifer. The observance of the bicarbonate inverse relationship trend is seen in every distribution map.

In the analysis of the Pennsylvanian aquifer, an overall decrease in the levels of concentration from the Marshall aquifer are found for each ion with the exception of bicarbonate.

All the ions except for bicarbonate and barium have their highest concentrations in the southeastern SBA, on the western fringe of the SBA, and south and west-northwest of the SBA. A relatively high area is found on the western border of the Pennsylvanian aquifer, while the southern half of the aquifer is found to have the lowest concentrations. The rest of the aquifer has intermediate concentrations. In the southern part of the aquifer higher concentrations of strontium are seen in a number of areas. Sulfate distributions are similar to the normalized patterns associated with the other major ions in this aquifer. Bicarbonate concentrations are inversely related in this aquifer unit as well with its lowest concentrations seen in and around the SBA, while having relative highs in the south. Barium has an overall low in and around the SBA with a number of high zones in the south.

In the Glaciofluvial aquifer, every ion decreases in concentration levels from the previous two aquifer units except for bicarbonate, which marks an increase in its concentrations. Excluding bicarbonate, the highest concentrations are found in and around the SBA. The southern part of the aquifer is seen to have relative highs for each of these elements. However, moving west and north towards the borders of the aquifer and away from the SBA, concentrations decrease significantly to the lowest levels of the aquifer unit. Sodium and chloride have random high areas throughout the midwestern regions of the aquifer. Sulfate, strontium, calcium, magnesium, and barium have random high concentrations throughout the western region of the aquifer as well. Bicarbonate has its highest concentrations in the southern region of the aquifer. Overall, an intermediate to high range of bicarbonate is seen throughout the basin.

Of special note in the Glaciofluvial aquifer is the "freshwater corridor" extending from the western SBA towards the south first proposed by Westjohn. Chloride and sodium have relatively high concentrations in this area. However, the rest of the ions, except for bicarbonate, which has an inverse relationship, have relatively low concentrations in the corridor.

Discussion of Ions and Comparative Analysis of Ion Pairs

Geochemical/hydrological model of the System

In light of the overall geochemical/hydrological model, two major types of water masses are involved in the system: brine and freshwater (both modern meteoric and the trapped glacial in the SBA). These end-member water masses have distinct geochemical signatures, which are developed through a number of physical-chemical mechanisms.

The brine end-member's geochemistry is determined by an evaporation sequence of seawater. This evaporation leaves the residual fluid concentrated with respect to the ions in the water. At certain stages, in the evaporation sequence, minerals composed of certain ions precipitate leaving the residual fluid depleted with respected to these ions. Depending on the extent of evolution at the Upper Pennsylvanian-Mississipian boundary in the Michigan Basin, the formation brine develops a certain geochemistry. This brine formation process is represented by the solute-solute diagrams composed for each major ion against chloride in which the ion's concentrations are seen in respect to the brine.

The freshwater end-members are generally geochemically indifferent from each other, and therefore are treated as a single water type. The geochemistry of the freshwater in the systems is meteoric in origin and mostly controlled by water-rock interactions. Of importance are the reactions occurring as the modern meteoric water moves along its hydrologic pathways from the Michigan highland areas towards the SBA and possibly the Michigan Lowlands on the western border of the aquifer. The concentrations of the ions in the freshwater end-member areshown in the solute-solute diagrams and are of course much less in magnitude then their concentrations in the brine end-member. Whereas, the evaporation sequence is the major control on the brine's geochemistry in respect to every ion, the freshwater concentrations of the ions can be affected by numerous geochemical mechanisms.

These water masses undergo degrees of interaction in the overall geochemical/hydrological model of the aquifer systems. The deep brine is advecting or diffusing up into the modern meteoric waters as they both are migrating in accordance to the hydrologic pathways of the Michigan Basin and towards the SBA and perhaps the Michigan Lowlands. Both these water masses interact with the older glacial freshwaters trapped in the sediments in the SBA. The net effect is seen in the geochemistry of the mixed solution and can support the mixing trend seen with respect to the solute-solute diagrams. Under the mixing conditions the concentrations of the ions fall along a transect between the brine and freshwater end-members. The new geochemical signatures of the mixed groundwaters are spatially represented through the distribution maps constructed for the ions in the systems. Areas of minimal brine impact are seen to keep their freshwater geochemical signature.

Chloride and Sodium

Due to the evaporation evolution of seawater in which chloride is the dominant ion, chloride salts are the last minerals to be precipitated. Therefore, chloride remains the dominant ion; this process allows the buildup of chloride in the residual brine compared to the other ions (Drever, 1988). In the system, the evaporation sequence does not progress to the point of taking much chloride out of the system from halite precipitation. Long and others (1988) determined halite to be consistently undersaturated throughout the aquifer system supporting the great amounts of chloride found. The high concentrations of chloride in brine are seen in the (Seawater evaporation transect) SET$_{Na:Cl}$ solute-solute diagram (Figure 32). These high concentrations correlate to the highs of chloride found in the middle of the Michigan Basin in the Marshall aquifer (Figure 11a).

Considering the freshwater end-member, other geochemical mechanisms are controlling chloride concentrations. Variations off the freshwater end-member of the solute-solute diagram may be associated with road deicing activity or septic tank seepage (Figure 32). The low chloride concentrations associated with the freshwaters can be seen in the distribution maps where the brine is not advecting or diffusing (Figures 6a-c). These freshwater zones are found along the aquifer borders in the Marshall aquifer, in the southern region of the Pennsylvanian aquifer, and everywhere except the SBA in the Glaciofluvial aquifer.

Areas where brine-freshwater interactions are occurring are seen in the middle of the Marshall aquifer and in the SBA in all three aquifer units where chloride concentrations are very high (Figures 6a-c). These concentrations propose that the brine is having a dominant effect on the geochemistry of the mixed solution and support the overall geochemical/hydrological model of the system and the mixing trend seen in the $SET_{Na:Cl}$ diagram (Figure 32).

Sodium is the second most abundant element in seawater before brine formation begins. Sodium is also the second most abundant ion due to the evolution of the brine in which halite is one of the last minerals to precipitate in the formation sequence. It's concentrations increase until halite precipitation begins; the evaporation sequence does not reach the point of significant halite precipitation leaving sodium very abundant in the residual solution (Drever, 1988). The high concentrations of sodium are supported by the $SET_{Na:Cl}$ diagram, brine end-member (Figure 32)and are seen spatially in the middle of the Marshall aquifer (Figure 11d).

Overall, sodium freshwater concentrations are low due to meteoric origin and seen in areas of no-brine impact along the aquifer borders in the Marshall aquifer, in the southern region of the Pennsylvanian aquifer, and everywhere except the SBA in the Glaciofluvial aquifer (Figure 11d-f). Sodium freshwater concentrations once in the groundwater system are possibly controlled by cation-exchange reactions, adsorption-desorption controls, and road deicing. These processes (Figure 32) may also affect variations off the freshwater end-member of the solute-solute diagram.

Corroborating the overall geochemical/hydrological model, sodium has its highest concentrations in the middle of the Marshall aquifer and the SBA in all three aquifers (Figure 11d-f). These are areas of high brine-freshwater interaction and support the mixing trend seen in the solute-solute diagram where concentrations fall along a linear transect between the two end-members (Figure 32).

In comparison of chloride and sodium distributions in the Marshall aquifer, distribution patterns for both ions follow each other very well with the highest concentrations for both ions found in the middle of the aquifer and the SBA (Figure 11a-f). Quantitatively, the greater natural abundance of chloride over sodium in the entire aquifer is seen. In the Pennsylvanian aquifer, the high levels of sodium found around the SBA, the southeast, and the northwest all correlate with high concentrations of chloride. In the Glaciofluvial aquifer, the spatial patterns seen for both chloride and sodium follow each other very well also. Any variations of distribution patterns seen in regards to chloride and sodium concentrations may be due to the other geochemical mechanisms affecting the respective ions. Overall, both ions follow the geochemical/hydrological model of the system.

Calcium and Magnesium

Calcium is the fifth most abundant element in respect to seawater, but through the evaporative sequence of the seawater, it is determined the third most abundant element in the formation brine. During the brine's evolution, calcite is precipitated first decreasing calcium concentrations. After a brief time lapse, concentrations increase again until dolomite is precipitated. Once again an increase in calcium concentrations occurs until gypsum is precipitated and all calcium is removed (Drever, 1988). Because the brine's evolution has not proceeded to the point where all the calcium is taken out of the system, a great amount of calcium remains. The high calcium concentrations are seen in the brine end-member in the $SET_{CA:Cl}$ diagram (Figure 33) and are found spatially in the middle of the Marshall aquifer (Figure 15a).

Freshwater calcium concentrations, which are meteoric in origin, are controlled by alternative physical-chemical mechanisms occurring within the groundwater system. Calcium concentrations are relatively low in freshwater as shown in the solute-solute diagram but scattered concentrations around the freshwater end-member are also seen (Figure 33). The relative lows of calcium concentrations are seen in no-brine impact regions in the aquifer distributions (Figure 15a-c). The mineralogical controls of calcite, dolomite, and gypsum can have an impact on calcium concentrations, which may cause the variations seen in the aquifer distributions and solute-solute diagram. Variations in calcium concentrations could also be due to adsorption/desorption or cation-exchange reactions; these latter mechanisms are especially important in areas with an abundance of clays and charged minerals, especially in the Glaciofluvial aquifer.

Upon mixing of the end-members, the brine controls the geochemistry of the mixed solutions with high calcium concentrations seen in the middle of the Marshall aquifer and in the SBA in all three aquifer units (Figure 15a-c). These distributions support the overall geochemical/hydrological model of the groundwater system and the solute-solute diagram developed for calcium (Figure 33).

Magnesium is the fourth most abundant element in seawater, but results in being the fifth most concentrated ion through the evolution of the brine. After preferential calcite formation, dolomite precipitates if conditions allow. Ideally, if the environment yields localized higher abundances of magnesium over calcium and enough bicarbonate for the reaction to occur, dolomite formation or dolomitization should result. If dolomite precipitation occurs, magnesium concentrations are depleted in the residual solution (Drever, 1988). Due to the prevailing conditions and the extent of the brine's evolution, magnesium remains relatively high in concentration in the brine and are represented in the $SET_{Mg:Cl}$ diagram (Figure 34). These high magnesium concentrations are seen in the middle of the Marshall aquifer (Figure 15d) much like the other major ions in the systems.

Freshwater magnesium concentrations are relatively low, and variations around the end-member in the $SET_{Mg:Cl}$ can be affected by other geochemical processes (Figure 34). Dolomite precipitation and dissolution reactions can be considered to affect manesium levels. Adsorption-desorption and cation-exchange reactions may also have an effect on the magnesium concentrations. These lower magnesium concentrations are seen in the no-brine impact areas in the distribution diagrams for the aquifers (Figure 15d-f).

Supporting the overall geochemical/hydrological model, relatively high concentrations of magnesium are seen in the middle of the Marshall aquifer and the SBA in all three aquifer units (Figure 15d-f). These high concentrations are due to the mixing of the brine-freshwater water masses and are geochemically characterized by the brine's geochemistry. These distributions of magnesium concentrations support the mixing transect found in the magnesium-chloride diagram (Figure 34).

In a comparison of the calcium and magnesium distribution patterns for the Marshall aquifer, both are similar to each other. A variation in a northern zone where relatively high concentrations of calcium (160 to 200 mg/L) is seen compared to relatively low values of magnesium (40 to 60 mg/L) (Figure 15 a-f). The spatial distribution map of magnesium in the Pennsylvanian aquifer is similar to that of calcium except in the southern part of the aquifer where higher concentrations of calcium (120 to 200 mg/L) are found relative to lower concentrations of magnesium (20 to 40 mg/L). In the Glaciofluvial aquifer, the spatial distribution of magnesium concentrations correlates well with that of calcium concentrations. There is a variation seen in the southern regions of the aquifer where, on the average, calcium concentrations are relatively high (90 to 160 mg/L) compared to relatively low magnesium concentrations (20 to 40 mg/L).

In the comparative analysis, all three aquifers generally have the same distribution patterns of calcium and magnesium. Variations straying from the normalized patterns set by the brine-freshwater contact areas in each distribution diagram or between each other are possibly due to the alternate chemical mechanisms affecting the concentrations of both magnesium and calcium. Overall, both ions follow the geochemical/hydrological model of the system.

Sulfate and Bicarbonate

Sulfate is the third most abundant element in seawater, and under evaporation is increasing in concentration until gypsum is formed. Because gypsum precipitation requires calcium, and much of the calcium is used up in calcite and dolomite formation, sulfate concentrations increase again after all the calcium is used up in gypsum precipitation or if no calcium is available for gypsum precipitation. Therefore, sulfate concentrations remain relatively high with respect to the brine (Drever, 1988). Overall, sulfate is the fourth most abundant ion in the brine as seen in the $SET_{SO4:Cl}$ diagram (Figure 35). These high concentrations are spatially seen in the middle region of the Marshall aquifer (Figure 16a).

In the solute-solute diagram, the brine end-member was seen to have variations in respect to sulfate concentrations (Figure 35); these results are supported by the sulfate distributions seen in the Marshall aquifer (Figure 16a). Due to sulfate reduction in areas in the middle region of Marshall aquifer where the brine is formed, sulfate concentrations are decreased significantly leaving the residual solution less concentrated with respect to sulfate.

The freshwater end-member sulfate concentrations are relatively low and meteoric in origin but are impacted by numerous geochemical processes once in the groundwater system. Variations are seen around the freshwater end-member and therefore in the freshwater zones of the aquifer units (Figure 35 and Figures 11a-c). Mineralogical controls of gypsum can play an important role in sulfate concentration variations. Variations in sulfate concentrations may also be due to the oxidation of pyrite or adsorption/desorption controls with organic matter in the Glaciofluvial aquifer.

Overall, disregarding the sulfate reduction zone in the Marshall aquifer, the distribution patterns of sulfate concentrations follow the normalized geochemical/hydrological model of the system. The mixing zones in the middle of the Marshall aquifer and the SBA in all three aquifers are relatively high with respect to sulfate (Figures 11a-c). These results support the idea of the brine controlling the water chemistry and the mixing model established by the sulfate solute-solute diagram (Figure 35).

During the brine evolution sequence, almost all of the bicarbonate is consumed in the formation of the carbonate minerals depleting bicarbonate concentrations (Drever, 1988) and resulting in the lowest concentrations among all the major ions as represented in the $SET_{HCO3:Cl}$ diagram (Figure 36). Opposite of the patterns established by the other major ions, these very low concentrations are seen in the middle of the Marshall aquifer (Figure 16d). Some scatter in data is seen around the brine end-member in the $SET_{HCO3:Cl}$ diagram. This variation is not seen spatially possibly due to large concentration range intervals; potential methanogenesis could deplete bicarbonate concentrations to a greater extent, but the overall low concentrations in these zones mask any observable effect. Sulfate reduction is also occurring potentially increasing bicarbonate concentrations, but the known middle sulfate reduction zone in the Marshall aquifer does not correlate with a high point of bicarbonate. Methanogenesis or mineralogical reactions may be occurring at an equal or faster rate than sulfate reduction thereby resulting in no alterations in concentrations.

The freshwater end-member has relatively high bicarbonate concentrations (Figure 36) and is seen in the dominant freshwater zones throughout the aquifers (Figures 11d-f). Mineralogical controls of calcite and dolomite may also have a major effect on bicarbonate concentrations in freshwater zones. These geochemical processes may be the cause of variations in the data around the freshwater end-member in the solute-solute diagram and the spatial distribution diagrams for all three aquifer units.

Like the other major ions, bicarbonate does follow the overall geochemical/hydrological model set in the system. Inversely, lows are seen in the mixing zones in the middle of the Marshall aquifer and the SBA in all three aquifer units (Figures 11d-f). These results also support the solute-solute diagram for bicarbonate (Figure 36).

In comparison between sulfate and bicarbonate in the Marshall aquifer, the relatively high areas (1,000 to 3,500 mg/L) of sulfate concentrations correspond to the relatively low areas of bicarbonate (less than 60 mg/L) concentrations (Figure 16 a-f). This general pattern is seen except in the middle of the aquifer where microbial activity is occurring possibly depleting both sulfate (sulfate reduction) to levels of 100 to 150 mg/L and bicarbonate (methanogenesis) to levels of less than 60 mg/L. In the Pennsylvanian aquifer, higher concentrations of sulfat correlate to the lower concentrations of bicarbonate and vice versa. The spatial trends seen within the Glaciofluvial aquifer also follow the inverse relationship seen between sulfate and bicarbonate. Some areas in the south and the middle of the aquifer do have highs for both bicarbonate (320 to 360 mg/L) and sulfate (100 to 200 mg/L). Overall, both elements' distributions are similar to the pattern suggested by the other major ions and therefore the geochemical/hydrological model of the system. If sulfate or bicarbonate concentrations are different from the expected patterns derived from the geochemical/hydrological model or each other, mineralogical controls, desorption of sulfate from soils or oxidation of pyrite could be occurring.

Potassium

Potassium is the least abundant of the major ions in the brine due to its lower concentrations in the pre-evaporated seawater. Potassium salts do not precipitate until the very late stages of evaporation. Therefore, potassium concentrations are relatively high but are still low compared to the other major ions (Drever, 1988). The SET_{K-Cl} diagram (Figure 37) shows these high concentrations as well as the middle of the spatial map of Marshall aquifer (Figure 20a).

Overall, potassium concentrations in freshwaters are low (Figure 37) and are seen in no-brine impact areas in the aquifer distribution maps for potassium (Figures 15a-c). Variations and scattered data around the freshwater end-member may be due to cation-exchange or adsorption/desorption controls with regards to clays or mineral weathering, such as plagioclases.

Potassium distributions are similar to the patterns suggested by the overall geochemical/hydrological model of the system. The middle of the Marshall aquifer and the SBA in all three aquifer units have high potassium concentrations (Figures 15a-c). These observations correlate to the hypothesized mixing of the water masses and the results found in the potassium solute-solute diagram (Figure 37). Variations off the normalized spatial patterns established in light of the geochemical/hydrological model may be due to the alternate geochemical mechanisms controlling potassium.

Strontium

Due to lack of data for strontium in the Marshall aquifer, a solute-solute diagram was not constructed. However, strontium is known to be present in the brine due to its concentrations in the original seawater; it is not precipitated out as readily as the major ions during evaporation and therefore remains in the residual solution (Drever, 1988). The high concentrations found in the middle of the Marshall aquifer for the major ions are not seen in respect to strontium due to lack of data (Figure 17a). Adsorption/desorption and mineral weathering reactions in the groundwater system most likely control freshwater concentrations of strontium. Overall, the strontium concentrations are low in freshwater dominated zones (Figures 12a-c).

Generally, strontium distributions do follow the patterns set by the geochemical/hydrological model of the groundwater system. High concentrations are found in and around the SBA in all three aquifer units (Figure 17a-c). These results support the brine-freshwater interaction zones present in the systems. Variations off this trend may be due to water-rock interactions affecting strontium.

Barium

Lack of data did not make it viable to construct a solute-solute diagram for barium. Barium is not a known component of seawater and therefore would not be greatly impacted during the evolution of the brine. In the Marshall aquifer, barium concentrations do not allow any interpretations to be made in respect to the geochemical/hydrological model (Figure 21d). The lower concentrations found in every aquifer, even if they correspond to freshwater zones, are most likely due to the overall low abundances of barium (Figure 21d-f). The variations in the barium concentrations may be due to adsorption/desorption reactions involving the indigenous minerals of the aquifer system. Therefore, the barium distributions do not generally correspond to the overall geochemical/hydrological model of the system.

DISTRIBUTIONS AND ANALYSIS OF THE SATURATION STATES OF INDIGENOUS MINERALS IN GROUNDWATERS IN THE MARSHALL, PENNSYLVANIAN, AND GLACIOFLUVIAL AQUIFERS

The saturation states of calcite, dolomite, gypsum, and quartz are investigated in light of the overall geochemical/hydrological model of the groundwater system to see if any spatial pattern can be derived from the constructed distribution diagrams for the aquifer units. A comparative analysis between the minerals and their ionic components in the groundwater is also addressed in order to assess the possible mineralogical impacts on the aqueous geochemistry of the aquifer systems. The relative concentrations of these ions in the groundwaters are discussed in noted areas of differing saturation states and relative to their concentrations in surrounding spatial areas.

Calcite Saturation States

In every aquifer unit calcite is in equilibrium with respect to most of the groundwater in the system with saturation index levels between -0.424 to 0.424. In the Marshall aquifer this trend is seen, but an overall range of -1.970 to 1.343 is seen (Figure 22a). Very undersaturated areas

(-1.970 to -0.424) are located just north of the SBA, in the southwest region and a small southern zone of the aquifer. The two southwestern zones and the zone just north of the SBA correspond to low calcium concentrations of less than 20 mg/L (Figure 15a). A low of bicarbonate (less than 60 mg/L) is seen in the northernmost southwestern undersaturation area, while in the southernmost southwestern zone concentrations are no different relative to surrounding areas (Figure 16d). The northeastern undersaturation zone has bicarbonate concentrations that are no different relative to surrounding areas, but is analogous to a low of calcium (less than 20 mg/L). The small-undersaturated zone in the south also has relatively low calcium concentrations between 70 to 90 mg/L. Bicarbonate concentrations in this southern zone are no different relative to surrounding areas.

An area of highly supersaturated waters (0.620 to 1.343) is located in the southeastern

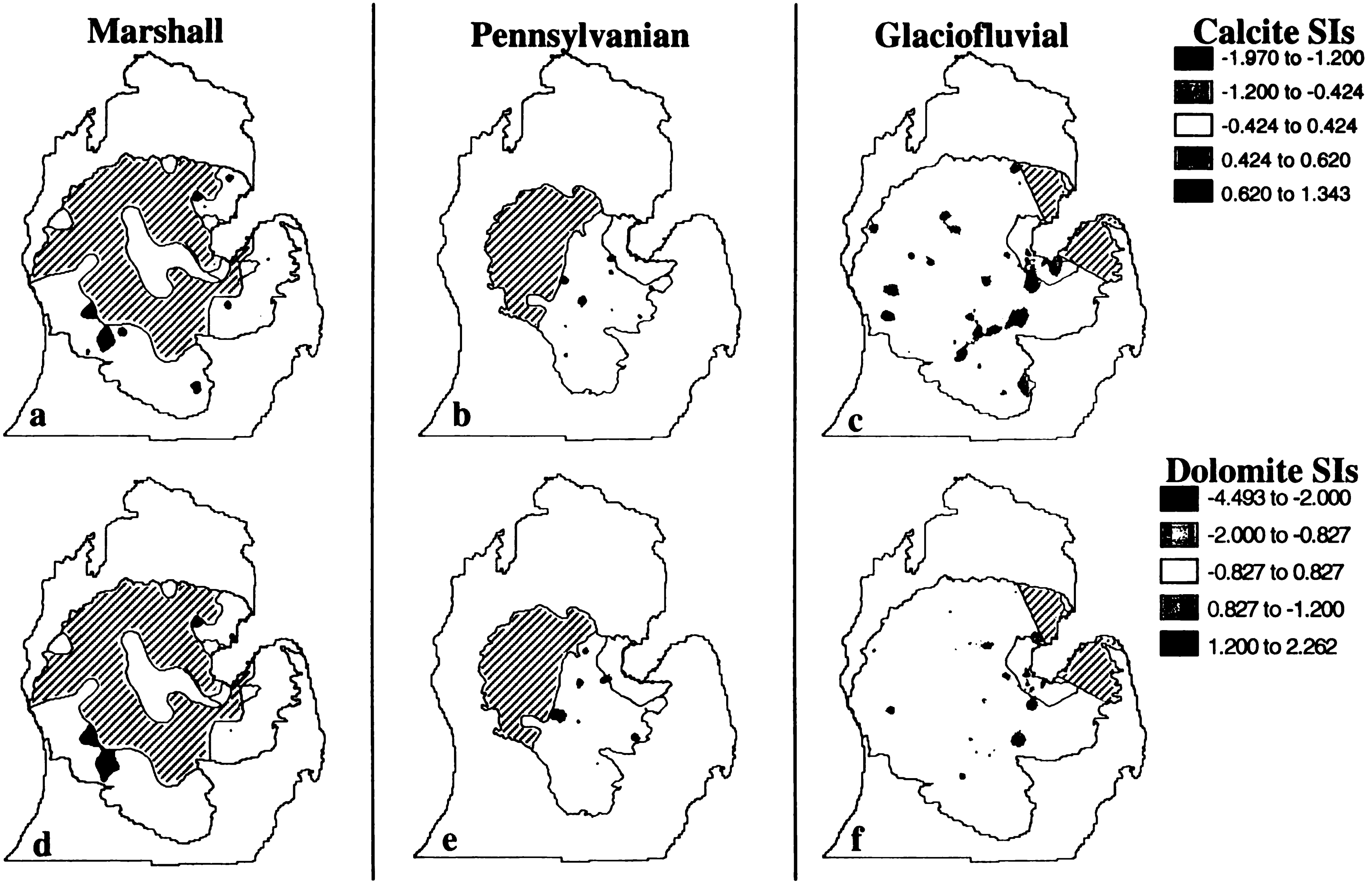


Figure 22 a-c Distribution of calcite saturation indices in the Marshall, Pennsylvanian, and Glaciofluvial aquifers
d-f Distribution of dolomite saturation indices in the Marshall, Pennsylvanian, and Glaciofluvial aquifers

region of the aquifer. This supersaturated zone has calcium and bicarbonate concentrations that are no different relative to surrounding areas. Numerous zones in the east and southwest are slightly supersaturated (0.424 to 0.620). The easternmost southwestern zone is associated with a high of calcium (300 to 600 mg/L), while in the other areas, calcium concentrations are no different relative to surrounding areas. Highs of bicarbonate are found in the easternmost southwestern zone (320 to 340 mg/L), the point just east of the SBA (340 to 360 mg/L), and just north of the SBA (240 to 260 mg/L). In the other slightly supersaturated zones, bicarbonate concentrations are no different relative to surrounding areas. The rest of the aquifer including the SBA is in equilibrium with respect to calcite (-0.424 to 0.424).

In the Pennsylvanian aquifer, calcite SIs are between -1.200 and 1.343 (Figure 22b). Calcite is mostly in equilibrium (-0.424 to 0.424) throughout the aquifer (Figure 15b and 11e). There are two zones of undersaturation (-1.200 to -0.424) on the southeastern boundary of the aquifer and in the western SBA. The undersaturation zone in the southeast corresponds to low values of calcium (less than 20 mg/L). Bicarbonate highs (greater than 550 mg/L) are found in this area. The larger undersaturation zone in the western SBA corresponds to relatively high bicarbonate concentrations (280 to 300 mg/L) and low calcium concentrations (less than 20 mg/L).

Two zones of highly supersaturated (0.620 to 1.343) waters in the middle of the aquifer and just south of the SBA have calcium and bicarbonate concentrations that are no different relative to surrounding areas. Numerous zones of slightly supersaturated waters (0.424 to 0.620) are seen in the east and middle-midsouthern region of the aquifer. All these zones correlate to lows of calcium with a range of 50 to 90 mg/L. The four slightly supersaturated zones in the middle-midsouth correspond to bicarbonate highs that range between 320 to greater than 550 mg/L. The SBA slightly supersaturated zone correlates to a low of bicarbonate (60 to 100 mg/L), while in the zone just west of the SBA bicarbonate concentrations are no different relative to surrounding areas.

The Glaciofluvial aquifer has a calcite SI range of -1.970 to 1.343 (Figure 22c). Most of the aquifer is saturated with respect to calcite (-0.424 to 0.424). Highly undersaturated zones (-1.970 to-0.424) are found throughout the SBA. Calcium highs (115 to 200 mg/L) are associated with the northernmost and southernmost zones, while a calcium low (less than 20 mg/L) is seen in the middle zone (Figure 15c). The bicarbonate concentrations are low (100 to 180 mg/L) in these highly undersaturated areas (Figure 16f). Slightly undersaturated zones (-1.200 to -0.424) are found in the western SBA, just west and north of the SBA, and in the southern region of the aquifer. All the slightly undersaturated zones have a low of calcium (less than 50 mg/L). A low of bicarbonate (100 to 140 mg/L) is associated with the southern zone and zone just west of the SBA. The other two slightly undersaturated zones on the western SBA border and in the north have bicarbonate concentrations that are no different relative to surrounding areas.

Numerous zones of highly supersaturated waters (0.620 to 1.343) are found along a belt covering an area from the western SBA towards the southwest and in the midwestern region of the aquifer. Very high calcium values (160 to 600 mg/L) are found in the SBA areas and an area just west of the SBA. The two westernmost zones correlate to relatively high concentrations of calcium (70 to 115 mg/L). The SBA highly supersaturated zone is correlated to very low bicarbonate concentrations (less than 60 mg/L). The area just west of the SBA has relatively low values of bicarbonate (160 to 180 mg/L). All the other areas are correlated to very high bicarbonate levels (400 to 420 mg/L).

Slightly supersaturated waters (0.424 to 0.620) are found in a number of zones in the aquifer. The far western-southwestern zone is associated with high calcium concentrations (200 to 300 mg/L), while the northeastern zone is associated with very low calcium concentrations (less than 20 mg/L). The other slightly supersaturated areas have calcium levels no different relative to surrounding areas. All the slightly supersaturated areas have high bicarbonate values ranging from 260 to 340 mg/L.

In light of the overall geochemical/hydrological model of the system, calcite is in equilibrium with respect to the groundwaters. These saturated waters are seen in respect to brine dominated waters, freshwater zones, and brine-freshwater interaction areas and support the frequency histograms made for calcite SIs in the MI-RASA (1996). In end-member dominated waters, the saturation state of calcite depends mostly on factors such as pH, pCO_2, and temperature.

In consideration of brine-freshwater mixing zones suggested through the geochemical/hydrological model and ion distribution maps for the aquifer systems, PHRQPITZ was used to simulate the mixing of fresh groundwater and brine in a closed system. None of the minerals studied were kept in equilibrium in this mixing model. The geochemistries of the end-member waters were taken from the Marshall aquifer database as a representative of the groundwaters in the system (Table 1). In the model, brine was added to the freshwater in the proportions: 0.1, 0.25, 0.50, 0.75, and 0.95. The major results determined from this model were the saturation states of calcite, dolomite, and gypsum (Table 2). In the end-member mixing model, calcite saturation indices were determined to be slightly positive but in the error range used in this study for calcite equilibrium (-0.424 to 0.424) (Table 2). Therefore, in the relevant mixing zones saturated waters should and did result.

In light of the equilibrium state of calcite in respect to most of the groundwaters, conditions pose that dissolution and precipitation of calcite is occurring at the same rate. Therefore, neither calcium nor bicarbonate result in being added or taken from the groundwater system. These results suggest that fast reaction rates of calcite are occurring in response to the brine-freshwater interaction or any other mechanisms that would cause the groundwaters to fall into disequilibrium. The system is equilibrating itself fast enough and therefore not resulting in any "trend-like" spatial pattern from the brine-freshwater mixing zones in light of the geochemical/hydrological model.

In the few areas of undersaturation ($SI=\log_{10}IAP/K_{sp}<- 0.5\log_{10}K_{sp}$) throughout the aquifers, calcite has the potential to dissolve adding calcium and bicarbonate to the groundwater.

Table 1. Chemistry of brine and freshwater end member solutions used in the PHRQPITZ closed system simulations.

Parameter	Brine (mg/L)	Freshwater (mg/L)
Calcium	10,905.61	70.69
Magnesium	2,587.98	17.008
Sodium	60,033.24	3.1887
Potassium	434.42	1.2005
Chloride	115,246.32	0.8004
Sulfate	572.8	28.01
Total alkalinity	58.15	229.89
pH	6.0373	7.3496
Temperature	28.8 degrees Celsius	13 degrees Celsius

Table 2. Calcite, dolomite, and gypsum saturation index results from the PHRQPITZ simulations.

Brine to Freshwater Mixing Proportions	Calcite SI	Dolomite SI	Gypsum SI
0.10 to 0.90	0.2415	0.5052	-0.2615
0.25 to 0.75	0.3178	0.6135	-0.4197
0.50 to 0.50	0.3624	0.62	-0.7015
0.75 to 0.25	0.335	0.4709	-1.0482
0.95 to 0.05	0.1686	0.0496	-1.6046

The dissolution of calcite will occur until these elements reach certain concentration levels and conditions are met (pH and temperature especially) making the groundwater saturated (in equilibrium) with respect to calcite; this drive towards saturation is the natural tendency of the system. Quantitatively, relative lows of both bicarbonate and calcium are the ideal levels of concentration as defined by the above equation for saturation indices.

The contact time with calcite and availability of calcite are some other prevailing parameters involved in the dissolution kinetics. Langmuir (1979) found that weeks or even months of residence time can be necessary for dissolution to proceed to equilibrium with respect to calcite (and dolomite) disregarding that laboratory experiments suggested a shorter time span of hours to days. And due to the kinetics of the system, if dolomite and/or gypsum are present and the groundwaters are undersaturated with respect to dolomite/gypsum, gypsum then dolomite will dissolve preferentially over calcite. In most cases in the Marshall aquifer, lows of calcium and highs of bicarbonate are associated with areas of undersaturation. This trend of low concentrations of calcium and high concentrations of bicarbonate in undersaturated zones is also seen in the Pennsylvanian and Glaciofluvial aquifers. Variations from this trend may be caused by the numerous geochemical mechanisms occurring within the groundwater system with respect to these ions.

In areas of supersaturation ($SI=\log_{10}IAP/K_{sp} > 0.5\log_{10}K_{sp}$), calcite is forming through the reaction of calcium and bicarbonate depleting both ions with respect to the groundwater. Unlike dissolution kinetics, calcite does not need to be present for precipitation to occur (however activation sites aid in the reaction), but time still poses a constraint on the reaction. The constant dissolution of gypsum adding calcium to the system may also be a controlling factor in lieu of the common ion effect (Freeze and Cherry, 1979). Supersaturated waters precipitate calcite until the groundwater becomes saturated with respect to calcite. Enough calcium and bicarbonate must be available for precipitation to occur, which leads to the proposition that relatively high amounts of both elements would be found in the groundwater in supersaturated areas as defined by the above equation. And due to the different K_{sp} values of the indigenous minerals in the system, calcite would precipitate preferentially over dolomite and gypsum. However, in the Marshall aquifer, highs of calcium and lows of bicarbonate are found in association with the supersaturated zones. Variations from this trend may be caused by the numerous geochemical mechanisms occurring within the groundwater system with respect to these ions.

Dolomite Saturation States

Dolomite SIs of the groundwaters in the Marshall aquifer have values from -4.493 to 2.262 (Figure 22d). The groundwaters are normally in equilibrium (-0.827 to 0.827). A small slightly supersaturated zone (0.827 to 1.200) is seen in the middle of the basin and corresponds to highs of magnesium (greater than 11,000 mg/L) and calcium (greater than 40,000 mg/L) and lows of bicarbonate (less than 60 mg/L) (Figure 15a, Figure 15d, and Figure 16d). Another slightly supersaturated point is seen just south of the SBA and has calcium or bicarbonate concentrations no different relative to surrounding areas. However, this zone is identified by a low of magnesium (10 to 20 mg/L).

Zones of highly undersaturated waters (-4.493 to -0.827) are located in the southwest and just north of the SBA. All three zones are correlated to calcium lows (less than 20 mg/L) and magnesium lows (less than 10 mg/L). The two southwestern zones have bicarbonate highs of 240 to 280 mg/L, but the northeastern zone has bicarbonate concentrations no different relative to surrounding areas. A rather large zone of slightly undersaturated waters (-2.000 to -0.827) is seen in the northwestern part of the aquifer. Calcium has high levels of 600 to 4,000 mg/L in this zone. Magnesium is also relatively high (400 to 1,000 mg/L), while bicarbonate is identified by low concentrations in this area (100 to 140 mg/L).

The range of dolomite saturation indices in the Pennsylvanian aquifer is between -4.493 and 1.200 (Figure 22e). Much like the Marshall distribution of dolomite saturation indices, the Pennsylvanian groundwaters are largely in equilibrium (-0.827 to 0.827). Numerous slightly undersaturated zones (-0.827 to -2.000) are seen on the western border of the SBA, south, west, and northwest of the SBA, and in the southern region of the aquifer. The slightly undersaturated zone on the western border of the SBA corresponds to low values of magnesium (less than 10 mg/L) and calcium (less than 20 mg/L) and high concentrations of bicarbonate (300 to 320 mg/L) (Figure 15b, Figure 15e, and Figure 16e). The undersaturated zones to the west, northwest, and south of the SBA are associated with lows of calcium (less than 70 mg/L) and magnesium (less than 20 mg/L). Bicarbonate has low concentrations in the zone west of the SBA (less than 60 mg/L) and the area northwest of the SBA (160 to 180 mg/L) and a high in the zone to the south of the SBA (greater than 550 mg/L). A low of calcium (less than 20 mg/L), a low of magnesium (less than 10 mg/L), and a high of bicarbonate (400 to 420 mg/L) identify the small slightly undersaturated zone in the south. A largely undersaturated zone (-0.827 to -4.493) found in the center of the aquifer corresponds to a low of bicarbonate (100 to 140 mg/L), a low of magnesium (less than 10 mg/L), and a low of calcium (less than 20 mg/L).

A small slightly supersaturated zone (0.827 to 1.200) is located just southeast of the very undersaturated area in the middle of the aquifer. This zone is associated with a relative high of magnesium (40 to 50 mg/L) but has calcium and bicarbonate concentrations no different relative to surrounding areas.

The Glaciofluvial aquifer has a dolomite saturation index distribution of -4.493 to 2.262 Most of the groundwaters are saturated (-0.827 to 0.827) with respect to dolomite (Figure 22f). Two zones of very undersaturated waters (-4.493 to -0.827) are found in the center of the SBA, while a third is found just off the western border of the SBA. The zone just west of the SBA has high magnesium (less than 10 mg/L) and calcium (less than 20 mg/L) concentrations, but has bicarbonate concentrations no different relative to surrounding areas (Figure 15c, Figure 15f, and Figure 16f). The southern SBA's very undersaturated zone corresponds to a low of calcium (less than 20 mg/L), magnesium (10 to 20 mg/L), and bicarbonate (100 to 140 mg/L). In the third zone in the SBA, concentrations of all three ions are no different from surrounding areas.

Two large zones of slightly undersaturated waters (-2.000 to -0.827) are seen just northwest of the SBA and on the northern SBA border. The slightly undersaturated zone just northwest of the SBA corresponds to highs of magnesium (60 to 80 mg/L), calcium (135 to 180 mg/L), and bicarbonate (320 to 340 mg/L). A low of calcium (20 to 40 mg/L), magnesium (less than 10 mg/L), and bicarbonate (100 to 140 mg/L) are analogous to the northern SBA slightly undersaturated zone.

Three highly supersaturated areas are seen in the Glaciofluvial aquifer, one in the center of the SBA, one in the southeastern region of the aquifer, and one due west of the SBA. The highly supersaturated zone west of the SBA correlates to lows of calcium (20 to 40 mg/L), magnesium (10 to 20 mg/L), and bicarbonate (180 to 200 mg/L). The southeastern zone has magnesium and calcium concentrations no different relative to surrounding areas but is associated with a high of bicarbonate (340 to 360 mg/L). The highly supersaturated zone in the SBA corresponds to a high of bicarbonate (340 to 360 mg/L), calcium (300 to 600 mg/L), and magnesium (50 to 60 mg/L).

Numerous zones of slightly supersaturated waters (0.827 to 1.200) are found in the southwestern SBA and just off the southwestern border of the SBA and in the middle-south, west, and northwest regions of the aquifer. All the zones in the middle-south of the basin with slightly supersaturated waters are associated with highs of calcium (90 to 115 mg/L), bicarbonate (400 to 550 mg/L), and magnesium (50 to 60 mg/L). The western zone is analogous to highs of calcium (70 to 90 mg/L), magnesium (30 to 40 mg/L), and bicarbonate (400 to 420 mg/L). Relative highs of magnesium (10 to 20 mg/L), bicarbonate (260 to 280 mg/L), and calcium (50 to 70 mg/L) are seen in correlation with the northwestern slightly supersaturated zone. The southwestern SBA zone corresponds to a low of calcium (20 to 40 mg/L) and magnesium (10 to 20 mg/L) and a high of bicarbonate (260 to 280 mg/L). The slightly supersaturated zone just off the southwestern SBA border has concentrations of calcium, magnesium, and bicarbonate no different relative to surrounding areas.

Dolomite is mostly in equilibrium with respect to the groundwaters in all three aquifer units which supports the results found in the MI-RASA study with respect to the frequency histograms for dolomite SIs. Brine, freshwaters, and mixed solutions seen between the two end-members are saturated with respect to dolomite. As seen with calcite, the end-member mixing model determined dolomite SIs to be in equilibrium with regards to the saturation interval (-0.827 to 0.827) (Table 2). Therefore, no real pattern is derived from the brine advecting or diffusing into the freshwater of the systems in light of the overall geochemical/hydrological model. Due to the fast reaction rate of dolomite, the mineral attains equilibrium regardless of any physical-chemical mechanisms occurring within the system that would disrupt the equilibrium state of dolomite.

Overall, the three aquifers have highs of calcium and magnesium and lows of bicarbonate associated with areas of supersaturation. Some of these zones of dolomite supersaturation correspond to supersaturated zones of calcite also. This case being, calcite would preferentially precipitate over dolomite due to faster reaction rates. In zones of dolomite undersaturation, lows of calcium and magnesium are found relative to highs of bicarbonate. If calcite and dolomite undersaturation zones overlap, dolomite would dissolve first. Variations from these trends of relative ions concentrations with respect to undersaturated and supersaturated zones may be caused by the numerous geochemical mechanisms occurring within the groundwater system with respect to these ions.

Gypsum Saturation States

Gypsum SIs of the groundwaters range between -4.000 to 0.229 in the Marshall aquifer (Figure 23a). Largely undersaturated (-4.000 to -1.500) waters are seen in the northern SBA, just north of the SBA and along the entire southern boundary from east to west including the southern SBA. Every one of these very undersaturated zones are analogous to a lows of calcium (less than 90 mg/L) and sulfate concentrations (less than 60 mg/L) (Figure 15a and Figure 16a). However, the zone just north of the SBA is associated to a high of sulfate (200 to 300 mg/L) while having calcium concentrations no different relative to surrounding areas. A large northwestern-middle zone and two zones in the southern half of the aquifer are in equilibrium with respect to gypsum (-0.229 to 0.229). These saturated areas are analogous to highs of both calcium (greater than 40,000 mg/L) and sulfate (200 to 3,500 mg/L) except for the center of the aquifer where a low of sulfate (100 to 150 mg/L) is seen. The rest of the basin is seen to be in the slightly undersaturated state (-1.500 to -0.229) have calcium and sulfate concentrations no different relative to surrounding areas. However, these slightly undersaturated areas do have higher concentrations than the very undersaturated zones.

The Pennsylvanian aquifer has gypsum SI levels of -6.980 to 0.229 (Figure 23b). A number of areas throughout the south, western fringe, SBA, and areas surrounding the SBA are in the slightly undersaturated state (-1.500 to -0.229). All these slightly undersaturated areas are identified by highs of calcium (135 to 40,000 mg/L) and sulfate (100 to 3,500 mg/L) (Figure 15b and Figure 16c). In more undersaturated waters (-4.000 to -1.500) lows of calcium (less than 90 mg/L) and bicarbonate (less than 100 mg/L) are seen. Two greatly undersaturated zones (-6.980 to 0.229) are seen in the southern region of the aquifer and just west of the SBA. The zone west of the SBA is analogous to a high of calcium (300 to 600 mg/L) but has sulfate concentrations no different from surrounding areas. Lows for both calcium (less than 20 mg/L) and sulfate (less than 10 mg/L) are seen in the southern greatly undersaturated zone. Three saturated zones (-0.229 to

-0.229) are seen in the western region of the aquifer, while a small saturated zone is found on the western SBA border. These saturated zones are correlated to highs of both calcium (300 to 4,000 mg/L) and sulfate (1,000 to 3,500 mg/L).

The Gypsum SI distribution for the Glaciofluvial aquifer has a range of -4.000 to 1.225 (Figure 23c). Most of the aquifer has groundwaters that are fairly undersaturated with respect to gypsum (-4.000 to -1.500). This entire aquifer has concentrations of calcium and sulfate no different relative to surrounding areas (Figure 15c and Figure 16c). Zones of slightly undersaturated waters (-1.500 to -0.229) are found along the western border, SBA, and areas west

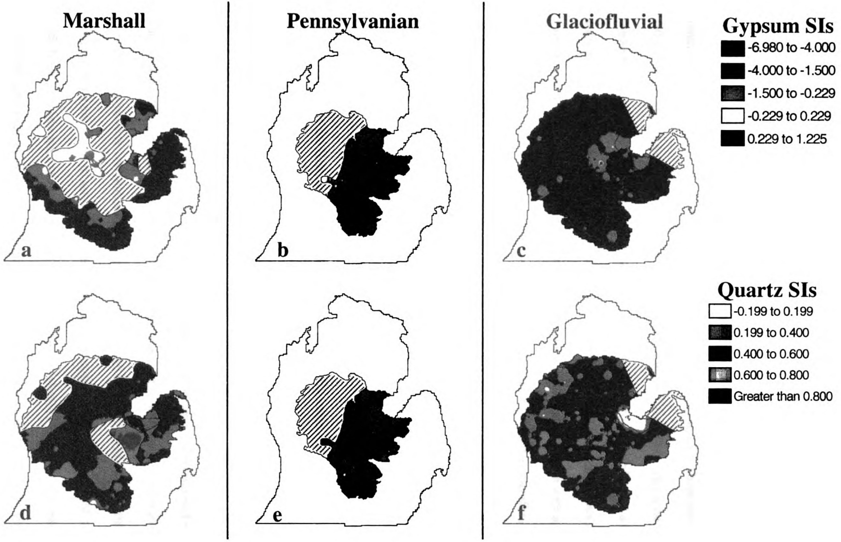


Figure 23 a-c Distribution of gypsum saturation indices in the Marshall, Pennsylvanian, and Glaciofluvial aquifers
d-f Distribution of quartz saturation indices in the Marshall, Pennsylvanian, and Glaciofluvial aquifers

and south of the SBA. All these zones except for the two most northwestern areas of slightly undersaturated waters are associated with fairly high levels of calcium (135 to 300 mg/L) and sulfate (150 to 3,500 mg/L). The southernmost of these other two slightly undersaturated zones has calcium concentrations no different relative to surrounding areas but is analogous to relative low of bicarbonate (60 to 100 mg/L). The northernmost northwestern zone is associated with a relative high of calcium (40 to 50 mg/L) and bicarbonate (15 to 20 mg/L). Three saturated zones (-0.229 to 0.229) are seen in this aquifer; all three are just west of the SBA. The zone just off the western border of the SBA is associated to a high of calcium (300 to 600 mg/L) and a high of sulfate (1,000 to 3,500 mg/L). The two zones farther west of the SBA are analogous to a low of calcium (20 to 40 mg/L) and sulfate (30 to 40 mg/L). One supersaturated zone with a range of 0.229 to 1.225 is found adjacent to the two saturated zones west of the SBA, therefore having the same correlation.

In all three aquifer units gypsum is generally undersaturated to varying degrees. These results support the gypsum SIs values determined by the mixing model (Table 2). A large zone of saturated waters are found in the midwest along with a number of zones in the Marshall aquifer, while only a few point are seen in the shallower aquifer units. Of the four minerals considered, gypsum would be the first mineral to dissolve due to its low K_{sp} value. And unlike calcite and dolomite, the saturation states of gypsum depends mostly on the influence (mixing) of the brine on the freshwaters in respect to the overall geochemical/hydrological model.

The general trend seen with respect to the saturation states of gypsum is in accordance with lower concentrations of calcium and sulfate associated with very undersaturated waters. A pattern is determined in which the closer the groundwaters get to saturation relative to SI values, the higher the relative concentrations of calcium and sulfate seen. The highest concentrations of both elements are found in saturated waters in the aquifer system. Areas of minimal brine contact with fresh groundwaters as the dominant water source are analogous to more undersaturated areas, whereas areas of greater brine impact are identified by less undersaturated to saturated areas. Dissolution of gypsum should actively be occurring especially in the southern Jurassic gypsum deposits in the Marshall and Pennsylvanian aquifers and entire glacial drift deposits in the Glaciofluvial aquifer.

Quartz Saturation States

Quartz is mostly in the supersaturated state within the three aquifers. Quartz SIs in the Marshall aquifer range from -0.199 to greater than 0.800 (Figure 23d). Highly supersaturated states (greater than 0.800) are seen in the southeastern region of the aquifer. Numerous zones in the southwest and surrounding the greatly supersaturated zones are very supersaturated with respect to quartz (0.600 to 0.800). Areas in the south, west, SBA, and just south of the SBA are just above saturation in the supersaturated state (0.199 to 0.400). A small zone in the south is in equilibrium with respect to quartz (-0.199 to 0.199). The remaining areas of the aquifer are in the slightly fairly supersaturated state with a range of 0.400 to 0.600.

In the Pennsylvanian aquifer with a range of quartz SI levels of -0.199 to 0.800, the very supersaturated levels (0.600 to 0.800) are seen in zones in the middle, southeast, and south (Figure 23e). The SBA, areas surrounding the SBA, and areas in the south are slightly supersaturated with a range of 0.199 to 0.400. Numerous zones along the southern and western borders of the aquifer are in equilibrium with respect to quartz (-0.199 to 0.199). The rest of the aquifer is fairly supersaturated with respect to quartz (0.400 to 0.600).

In the Glaciofluvial aquifer, the saturation indices range for quartz is -0.199 to 0.800 (Figure 23f). Areas in the middle-midwest and southeast are very supersaturated (0.600 to 0.800). Zones along the entire border of the aquifer are slightly supersaturated (0.199 to 0.400). The SBA and a few areas in the west have saturated levels with respect to quartz (-0.199 to 0.199). The rest of the aquifer has fairly supersaturated groundwaters with respect to quartz (0.400 to 0.600).

As expected all three aquifers are mostly supersaturated with respect to quartz with intermittent zones of saturation. The largest of these saturation zones is located in the SBA in the

Glaciofluvial aquifer where the brine is known to have a great impact. Like gypsum, quartz saturation states are in effect controlled by the brine's interaction with the fresh groundwater and therefore alter with respect to the geochemical/hydrological model of the system, but a strong relationship can not be suggested. This trend is only seen in the Pennsylvanian and Glaciofluvial aquifers. Upon examination of the Pennsylvanian aquifer, areas in and around the SBA anomaly have slightly saturated conditions (-0.199 to 0.400). In the Glaciofluvial aquifer, the SBA is saturated with respect to quartz (-0.199 to 0.199). These observations somewhat follow the trend that higher TDS concentrations reduce the stability and therefore SIs of quartz. Overall, the high stability and K_{sp} value of quartz considered, the present conditions drive for the precipitation of quartz.

COMPARISON BETWEEN AQUIFER AND SLICE ANALYSES

Overall, in a comparison between the slice distribution maps and the aquifer unit distribution maps, the same "generalized" spatial patterns are seen in regards to the dissolved ion concentrations in the groundwater; this interpretation is in accordance with the overall geochemical/hydrological model of the aquifer systems. However, a variation is seen in the northwestern part of the 200 feet and less slice in which low concentrations of the studied ions are found, while no indication of these low concentrations are found in the Marshall aquifer distribution maps. Another difference found in the 201 to 300 feet slice is in the west-northwest region of the aquifer. This region has high concentrations, whereas no aquifer unit has these high concentrations in the area. Two distinct zones of the highly concentrated waters, one in the east/SBA and one in the middle of the aquifer, is found in the intermediate slices; relatively concentrated waters are also seen in the western region of the aquifer in these slices. The distribution maps of the Marshall and Pennsylvanian aquifers do not have these high levels found in the two separate zones or the western region of the aquifers. A more consistent relationship is observed between the shallower slices and the Pennsylvanian and Glaciofluvial aquifers in which the highest concentrations are found in and around the SBA.

The reason for the discrepancies found between the aquifer and slice distributions lies within the IDRISI production of the maps. If higher concentrations of any element were located in the same vicinity and above or below that of lower concentrations in the aquifer distributions, the higher concentrations would mask the lower concentrations. Variations produced by the IDRISI maps may be seen regarding the availability of spatial data in an area as well. If there are numerous points with the same concentration range clustered in an area and a point out of that range is in this cluster, the anomalous valued point will be masked.

Overall, the slice distributions aided in relaying the minor variances and bypassing the lack of congruity between the aquifer units. They were able to provide a more detailed look at the deviations found in the normalized patterns associated with the elements in light of the geochemical/hydrological model and between the studied ion pairs. Considering this, the slice distributions allowed a better idea of the localized migration patterns of the brine and the other active geochemical controls occurring in the aquifer system. However, the overall examination of the slice analyses supported the results and conclusions in the aquifer analyses.

CONCLUSION

In the Michigan Basin Aquifer System brine has evolved in the middle of the Marshall aquifer and is actively advecting or dispersing upwards and towards the Saginaw Bay Area due to regional hydrological controls. Modern fresh waters of meteoric origin are recharging and flow along the hydrological pathways from the Michigan highland areas towards the SBA. The SBA has freshwaters that are trapped in the region's sediments that are derived from cooler glacial periods. These three groundwater masses each have a certain geochemical character but interact with each other thereby defining a new geochemical signature in the mixed solution in relevant contact zones. The concept of these three water masses' geochemistries and their activity within the Michigan Basin establishes an overall geochemical/hydrological model to the aquifer systems studied.

Areas of brine formation are heavily concentrated, whereas the freshwaters' geochemistries have low concentrations of ions. In the areas of the water mass interactions, the brine has a dominant control on the resulting chemistry of the mixed groundwaters. The brine's impact is seen distinctively through the distribution diagrams composed for the major and minor ions of the groundwater system for the aquifer units.

These diagrams demonstrate the active geochemical evolution of the groundwater in the Michigan Basin Aquifer System and were investigated in light of the overall geochemical/hydrological model. The diagrams support the hypothesis that relative high concentrations are produced in brine-freshwater interaction zones, especially the SBA, except for bicarbonate where an inverse relationship is seen. Generalized patterns are established for the aquifers in which most of the ions follow relative to the brine contact areas. (Barium and strontium can not totally be normalized to these patterns due to incomplete and unsound data.) These diagrams spatially support the results determined by the solute-solute plots developed for the study.

Considering areas of minimal or no-brine impact where older groundwaters and occurring meteoric recharge are the dominant water source, other chemical mechanisms may have possible controls the ions' concentrations and therefore distributions in the aquifers. The most probable physical-chemical processes are biological activity (sulfate reduction and methanogenesis), mineralogical controls, cation-exchange reactions, adsorption-desorption reactions, and anthropogenic inputs. Generally, the normalized patterns in freshwater zones have lower concentration distributions in comparison to brine contact zones set by the geochemical/hydrological model. Overall, variations from the normalized spatial patterns may be associated to the various physical-chemical mechanisms in areas of major or minimal brine interaction. A special case is seen in the lower depths of the system where biological activity is pronounced in highly concentrated groundwaters.

Of special note in the Glaciofluvial aquifer is the "freshwater corridor" extending from the western SBA and south. Chloride and sodium have relatively high concentrations in this area. These high concentrations lead to the proposition of brine impact on the groundwater. However, the rest of the ions, except for bicarbonate which has an inverse relationship, have relative low concentrations in the corridor alluding to fresh water being flushed through highly permeable sediments. This sedimentology is different from the rest of the SBA, which has finer sediments thereby causing slow flushing and a build-up of ion concentrations through the brine-freshwater interaction.

To gain further insight into the mineralogical controls on the system and the possible effect of the brine-freshwater interaction on the saturation states of the indigenous minerals in the system, distribution diagrams for the minerals' saturation indices were composed and investigated in light of the overall geochemical/hydrological model. Calcite and dolomite are generally noticed to be in the saturated state relaying that their reactivities are fast enough as not to be controlled by the brine-freshwater interaction or any other chemical mechanisms that could disturb the minerals' equilibrium with respect to the groundwater. Therefore, these maps do not follow any observable pattern set by the brine-freshwater mixing areas and contradicts the hypothesis that the interaction zones would affect and produce a trend in respect to signature saturation states with respect to both minerals. Gypsum generally is seen closer to saturation in brine contact areas and more undersaturated in fresher water areas therefore corresponding to the geochemical/hydrological model and supporting the hypothesis. Quartz has the opposite effect where fresher waters are more supersaturated, and brine-contact, high TDS waters are closer to saturation thereby abiding to the geochemical/hydrological model and hypothesis. However, this is only found in the SBA in the Pennsylvanian and Glaciofluvial aquifers.

Depth interval maps were constructed in order to define a more continuous trend of the water chemistry found in the aquifer system. Upon analysis, they conclusively support the trends and results found in the aquifer units for both ion concentrations and mineral saturation states and the overall geochemical/hydrological model. Both the aquifer and slice analyses give an insight into the areal variations in the aqueous chemistry at a regional and localized level. Regionally, the Michigan Basin's freshwater supply zones are determined and utilization for municipal, agricultural, and industrial factions can be mandated.

APPENDIX A

GEOCHEMICAL ANALYSIS OF ESTABLISHED DEPTH INTERVALS

DISTRIBUTION OF DISSOLVED ION CONCENTRATIONS IN GROUNDWATER FROM ESTABLISHED DEPTH INTERVALS

Having examined the spatial distributions of the various ion concentrations and mineral saturation indices indigenous in the groundwater and aquifer systems of the three major aquifer units, the analyses of these same variables are necessary at more discreet and detailed levels to provide support for the aquifer analysis and the geochemical model established for this study. This analysis mode is done at different, uniform depth intervals throughout the aquifer system. All slice intervals are based on the height of the well sample above sea level and are designated as less than 200 feet (includes negative concentrations which are found below sea level), 201 feet to 300 feet, 301 feet to 400 feet, 401 feet to 450 feet, 451 feet to 500 feet, 501 feet to 600 feet, 601 feet to 800 feet, and greater than 801 feet.

Dissolved Chloride

In the deepest 200 feet and less depth, dissolved chloride concentrations range from less than 1 to concentrations greater than 180,000 mg/L (Figure 24a). The highest concentrations (greater than 180,000 mg/L) are seen in the middle-midwestern regions of the study area. These concentrations decrease away from the midwest towards the northwest to levels below 1 mg/L. This decrease in concentrations is not as drastic towards the areas in the western SBA and just west SBA having levels of 600 to 20,000 mg/L. Most of the middle of the study area has concentrations between 200 to 1,500 mg/L. The lowest concentrations are found in the northwest and a small zone just southwest of the SBA (0 to 20 mg/L). The far west has relatively high concentrations of 3,000 to 20,000 mg/L as well as the south (1,500 to 3,000 mg/L).

The 201 to 300 feet slice has chloride concentrations between less than 1 and 20,000 mg/L (Figure 24b). The highest concentrations of 4,000 to 20,000 mg/L are found in the northwest and southeast. Fairly high concentrations area also seen in a small southern zone and a zone just off the western border of the SBA (1,500 to 3,000 mg/L). The SBA, the surrounding SBA, and areas in the western region of the study area have a range between 200 and 1,500 mg/L. The middle of the study area and just west of the SBA have relatively low concentrations of less than 20 mg/L. The west also has relatively low concentrations of 50 to 100 mg/L.

The next depth interval, 301 to 400 feet, has chloride levels between 2 and 20,000 mg/L (Figure 24c). The southeastern and central parts of the SBA has relatively high concentrations ranging between 1,500 to 3,000 mg/L. This high concentration level is also seen in a small zone in the midsouthern region of the study area. The highest concentrations are found just south of the SBA (3,000 to 20,000 mg/L). The remaining regions of the study area have levels between 200 to 1,500 mg/L. The lowest concentrations are found in the northern part of the SBA (50 to 100 mg/L), just west of the SBA, and in the south-middle and midwest (2 to 30 mg/L).

The 401 to 450 feet slice has dissolved chloride concentrations between 2 and 3,000 mg/L (Figure 24d). Some small areas in the southeastern part of the SBA have the highest concentrations (600 to 3,000 mg/L). Two small zones in the western part of the study area and a rather large zone west of the SBA also have these high concentrations. The northern SBA has slightly lower concentrations of 200 to 600 mg/L. The surrounding SBA and western regions of the study area have a range of 50 to 600 mg/L. The south and middle have the lowest concentrations between 2 and 30 mg/L. This range is also seen in a small zone in the far northwest, west, and numerous zones around the SBA.

The 451 to 500 feet interval has a concentration range of 2 to 3,000 mg/L (Figure 24e). The highest concentration zones are in the southeastern region of the SBA, just south of the SBA, and a small western area (600 to 3,000 mg/L). The remaining SBA, the surrounding SBA, the west, and the east have concentrations between 50 to 600 mg/L. The middle including the surrounding SBA, east, and a few western areas surrounding the high concentration zone have the lowest concentrations of 2 to 50 mg/L.

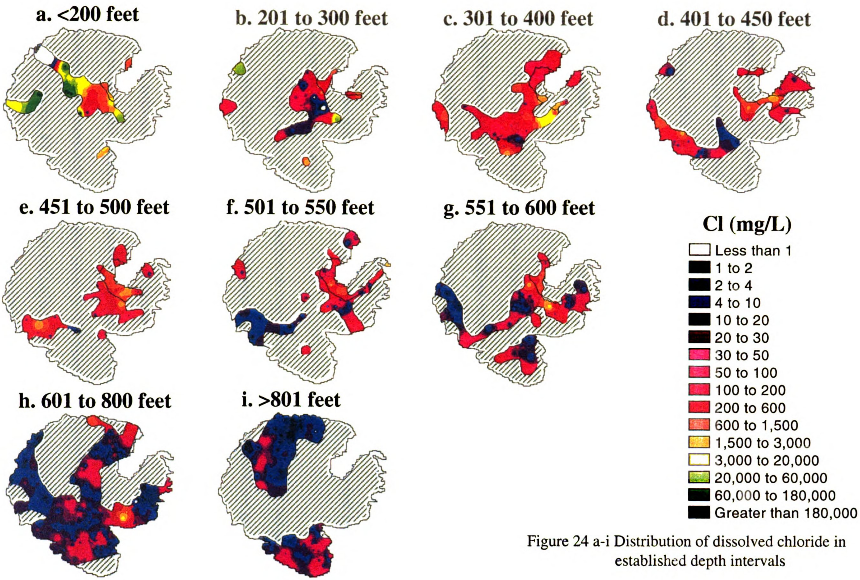


Figure 24 a-i Distribution of dissolved chloride in established depth intervals

The 501 to 550 feet slice has concentrations ranging from less than 1 to 3,000 mg/L (Figure 24f). The highest concentrations are found in the middle of the SBA with a very small zone ranging between 1,500 and 3,000 mg/L. Another area of the same range is found on the eastern border of the study area. The overall concentrations in the SBA are between 200 and 1,500 mg/L except for the northeastern section of the SBA. The northeastern SBA has a range of less than 1 to 100 mg/L. This concentration range is also found in regions in the west, southeast, middle, and a small northeastern region of the study area. The concentration limits of 100 to 600 mg/L are seen in a number of zones around the SBA, a small southern zone, and a northwestern zone. A western-southwestern region of the study area has the lowest concentrations of 1 to 20 mg/L.

The 551 to 600 feet interval has dissolved chloride concentrations between 1 and 20,000 mg/L (Figure 24g). Concentrations are highest between 3,000 and 60,000 mg/L in zones just south of the SBA. Another high concentration zone of 1,500 to 3,000 mg/L is found just west of the SBA. Most of the areas north and south of the SBA including a zone in the southwest have concentration levels of 200 to 1,500 mg/L. The middle, western, and southern regions of the study area have zones with concentrations between 4 to 20 mg/L, while the far east and the west have levels between 1 and 10 mg/L.

The 601 to 800 feet slice distribution map for chloride has levels between less than 1 and 20,000 mg/L (Figure 24h). Relatively high levels are seen in the western SBA and its surrounding areas (50 to 600 mg/L) with the highest concentrations found in an area just south of the SBA (3,000 to 20,000 mg/L). The western region of the study area and zones in the midsouth, southeast, and northeast of the study area have a range between 4 and 20 mg/L. Areas in the middle, south, and northeast have relatively high concentrations of 50 to 1,500 mg/L. The remaining areas surrounding the higher zones have low concentrations between 20 and 100 mg/L.

The upper 801 feet and greater interval has a chloride concentration range between 1 and 200 mg/L (Figure 24i). The southern region of the slice has fairly high concentrations of 50 to

200 mg/L in the south. Relatively high concentration zones (30 to 100 mg/L) are also seen in the south and northwest. The rest of the study area along with the SBA have a concentration range of less than 1 to 20 mg/L.

Dissolved Sodium

The 200 feet and less depth interval sodium distribution has a range of less than 5 to 72, 500 mg/L (Figure 25a). The midwestern region of the study area has high concentrations of 20,000 to 72,500 mg/L. These concentrations decrease towards the boundaries of the study area. However, a high of the same magnitude is found in the southeast, while regions in the middle of the study area and northwest have a low range of less than 5 to 60 mg/L. Concentrations of 2,000 to 20,000 mg/L are seen in the southwestern part of the SBA. The remaining areas of the SBA have a slightly lower, but still relatively high range of 600 to 2,000 mg/L. The rest of west, surrounding SBA, and a small southern zone has the concentration range of 1,000 to 20,000 mg/L, except for a zone just north of the SBA that has concentrations of 400 to 600 mg/L.

The 201 to 300 feet slice map has a sodium range of less than 5 to 72,500 mg/L (Figure 25b). A high (20,000 to 72,500 mg/L) is found in the southeast, while another high concentration zone is found in the far west and surrounding the southeastern high (4,000 to 20,000 mg/L). The western SBA border region has a zone with fairly high concentrations of 1,000 to 2,000 mg/L. The eastern and western SBA, areas just to the south of the SBA, and zones in the southern and central regions of the study area have relatively high concentrations of 400 to 1,000 mg/L. The center of the study area and numerous areas to the west of the SBA have a low of 5 to 100 mg/L, while the mideast along with two zones in the west have a concentrations of 150 to 600 mg/L.

The 301 to 400 feet interval sodium distribution has a concentration range between less than 5 and 20,000 mg/L (Figure 25c). The western and southern SBA have relatively high concentrations between 1,000 and 2,000 mg/L. This same range is seen in a small southern zone. A slightly higher range of 2,000 to 20,000 mg/L is found in areas south and southeast of the SBA. Other high concentration zones are seen west of the SBA, far west, and in the middle of the study area (400 to 1,000 mg/L). The northern and eastern SBA and areas east and just north of the SBA have concentrations of 80 to 200 mg/L. Low concentrations between less than 5 and 60 mg/L are found in the middle-midwest of the study area and just west of the SBA. The rest of the study area has a range of 150 to 400 mg/L.

The 401 to 450 feet slice has a sodium concentration range of less than 5 to 2,000 mg/L (Figure 25d). The highest concentration levels are found in the SBA, the surrounding SBA, and a zone in the far west (400 to 2,000 mg/L). Surrounding the high concentration zones in the study area are concentration levels of 150 to 400 mg/L. This concentration range is also seen in a small southern zone. The rest of the study area has intermediate concentrations of 80 to 150 mg/L with very low concentrations found in the midsouth, numerous zones around the SBA, and the western border (less than 60 mg/L).

The distribution map of sodium for the 451 to 500 feet interval has a range of less than 5 to 2,000 mg/L (Figure 25e). The highest concentrations are found in the SBA and surrounding areas and a small zone in the far western region of the study area (600 to 2,000 mg/L). The rest of the east and west have slightly lower levels of 150 to 250 mg/L. The lowest concentrations are found in the middle and a few zones in the far east including the eastern SBA and western border region (less than 60 mg/L).

The 501 to 550 feet slice has a dissolved sodium range of less than 5 to 2,000 mg/L (Figure 25f). The highest concentrations are in the middle of the SBA (600 to 2,000 mg/L). This range is also seen in a far eastern region along the border of the study area. The remaining SBA, some small zones in the west, and areas to the north and south of the SBA have relatively high concentrations as well (100 to 400 mg/L). The lowest concentrations are found in a southwestern region extending towards the center of the study area, southeast, northeast, and west (less than 60 mg/L). The remaining areas of the study area have concentrations of 60 to 100 mg/L.

The range of dissolved sodium for the 551 to 600 feet slice is less than 5 to 2,000 mg/L (Figure 25g). The highest concentrations are found in regions to the west and south of the SBA

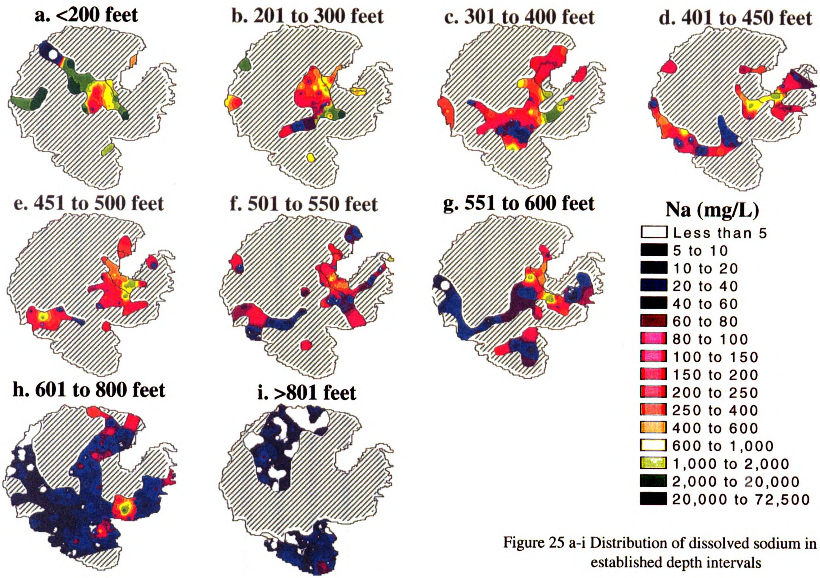


Figure 25 a-i Distribution of dissolved sodium in established depth intervals

(600 to 2,000 mg/L). Most of the SBA has relatively high concentrations of 250 to 600 mg/L. A large region in the southeast and a smaller zone in the south have concentrations between 150 and 400 mg/L. Most of the west, far east including the northern SBA, and far south have the lowest concentrations found at this depth (less than 60 mg/L). Large areas in the south have an intermediate concentration range of 60 to 150 mg/L.

The 601 to 800 feet interval has concentrations between less than 5 to 2,000 mg/L (Figure 25h). The surrounding areas of the SBA to the west and north have levels of 20 to 80 mg/L. The highest concentrations are found in the southeast and a small zone in the south (400 to 2,000 mg/L) and far north (150 to 400 mg/L). The lowest concentrations are found in the west with levels of less than 10 mg/L.

The upper 801 feet and greater interval has a sodium concentration range less than 80 mg/L (Figure 25i). Most of the study area has a range of 0 to 40 mg/L. A small high concentration zone (60 to 80 mg/L) is found in the very southern tip of the study area.

Dissolved Calcium

The 200 feet and less slice range has concentrations from 20 to greater than 40,000 mg/L (Figure 26a). The midwestern region of the study area has the highest concentrations of 20,000 to greater than 40,000 mg/L, and these concentrations decrease moving away from the midwest towards the boundaries. Zones of lower concentrations (20 to 90 mg/L) are found in the northwestern regions of the study area and just west of the SBA anomaly. Zones in the western SBA, southeast, and west have concentrations ranging from 600 to 4,000 mg/L. The northern SBA and areas west-northwest of the SBA have slightly lower but still relatively high concentrations of 200 to 600 mg/L. This latter concentration level is also seen in a small southern zone.

The 201 to 300 feet slice has a range of dissolved calcium concentrations of less than 20 to 4,000 mg/L (Figure 26b). The highest concentrations are found in zones in northwestern and southeastern regions of the study area (600 to 4,000 mg/L). Relatively high concentrations are also seen in the deep south and southwest (300 to 600 mg/L). The middle and western regions of the study area, discounting the other high concentration zones, have concentrations between 150 to 160 mg/L with a small zone on the western border of the study area having concentrations between 70 to 90 mg/L. A number of small zones just west of the SBA have high concentrations of 160 to 300 mg/L. The SBA along with an area extending southwest from its western border have lower concentrations, much like that of the far west, of less than 90 mg/L. These lower concentrations are also found in the eastern SBA.

The 301 to 400 feet slice interval has concentrations ranging between less than 20 and 4,000 mg/L with the highest concentrations (600 to 4,000 mg/L) found in the southeast (Figure 26c). Relatively high concentrations are also seen in the midwestern region of the study area and west of the SBA along with a zone in the southeast (300 to 600 mg/L). The eastern and western borders, midwestern and eastern SBA, and an area extending from the western border of the SBA towards the southwest have a range of less than 105 mg/L. The northern and southern SBA and a number of zones in the midsouth-southwest and northeast have relatively high concentrations of 160 to 300 mg/L.

The 401 to 451 feet slice interval has a dissolved calcium range between less than 20 and 600 mg/L (Figure 26d). The highest concentrations are in the northwest and a small western zone (300 to 600 mg/L). The remaining eastern region of the study area including the SBA has concentrations less than 90 mg/L. A small area of intermediate dissolved calcium concentrations of 160 to 200 mg/L is found just southwest of the SBA also.

The 451 to 500 feet slice has calcium levels of less than 20 to 4,000 mg/L (Figure 26e). The highest concentrations of 600 to 4,000 mg/L are found in a small midwestern zone. A small zone in the southwestern SBA has fairly high calcium concentrations of 200 to 600 mg/L along with a slightly less concentrated area just southwest of the SBA (200 to 300 mg/L). A relatively high range of 135 to 200 mg/L is found in a western area, the eastern and northern SBA, and just south, west, and north of the SBA. The middle of the study area, small zones in the far west and

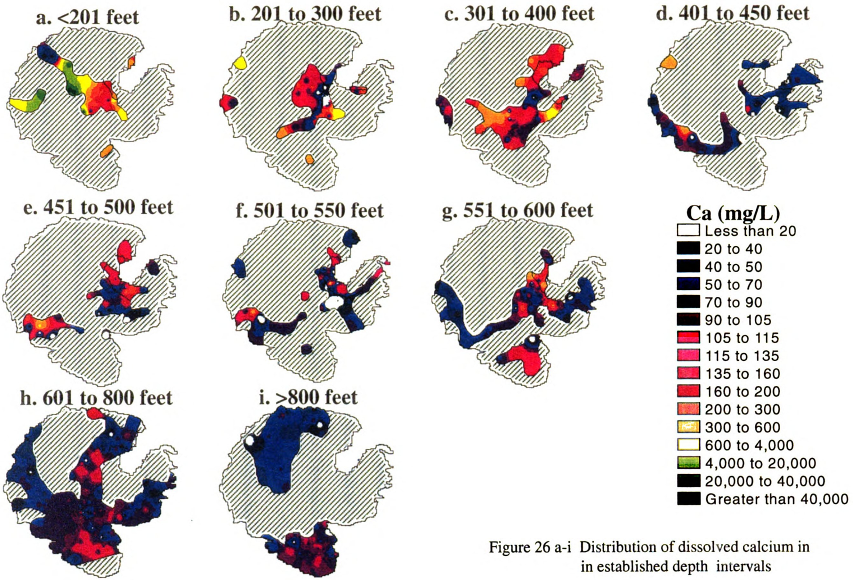


Figure 26 a-i Distribution of dissolved calcium in in established depth intervals east, and south-southeast have lower concentrations of less than 70 mg/L. The remaining areas in the south and west, most of the northeast, and the remaining SBA have fairly high concentrations of 70 to 135 mg/L.

The 501 to 550 feet slice interval has calcium concentrations between less than 20 and 600 mg/L (Figure 26f). A high concentration zone of 300 to 600 mg/L is seen in the center of the SBA and a zone in the west. The northern, southeastern, and far western SBA have relatively high concentrations of 115 to 300 mg/L. These same concentrations are seen to the north of SBA, far east, middle, and surrounding the noted high concentration zones of the study area. The remaining areas of the east and the most of the west including the northwest have low concentration levels less than 90 mg/L.

The 551 to 600 feet depth interval has calcium concentrations between less than 20 and 600 mg/L (Figure 26g). The highest concentrations (300 to 600 mg/L) are found in the central SBA, western SBA border region, and just south of the SBA. Relatively high concentrations of 135 to 300 mg/L are also found around these high concentration zones (including the remaining SBA), just west of the SBA, and in a southern zone. The remainder of the south and numerous zones in the middle of the study area have relatively high concentrations of 105 to 135 mg/L. The rest of the study area including the entire west-midwest and northern SBA have concentrations below 90 mg/L.

The 601 and 800 feet slice has dissolved calcium concentrations ranging from less than 20 to 300 mg/L (Figure 26h). A region covering an area from the northern to southern border of the study area have numerous zones of the high concentrations (115 to 300 mg/L). The northwestern SBA has concentrations of 70 to 115 mg/L. The remainder of the study area in the east and west including the rest of the SBA has a range of less than 90 mg/L.

The shallowest 801 feet and greater slice has the lowest concentrations between 0 and 160 mg/L (Figure 26i). The highest concentration areas are in the southern tip with concentrations ranging between 90 and 135 mg/L including one small zone of 135 to 160 mg/L.

A lone zone in the midnorth also has the relatively high range of 90 to 135 mg/L. The northern and remaining southern region of the study area have lower concentrations below 90 mg/L.

Dissolved Magnesium

The 200 feet and less slice interval of dissolved magnesium concentrations range between less than 10 and greater than 11,000 mg/L (Figure 27a). The highest concentrations (greater than 11,000) are found in the center of the study area, and these concentrations decrease away from the center to concentrations of 4,000 to 11,000 mg/L around the central high concentration zone. Fairly high concentrations of 200 to 1,000 mg/L are found in the southeast, areas in the mideast, and a western zone. Most of the SBA has a relative high of 60 to 200 mg/L. A small southern zone has relatively high concentrations of 120 to 200 mg/L. The lowest concentrations of magnesium (less than 50 mg/L) are found just north and west of the SBA and in a northwestern zone of the study area.

The 201 to 300 feet interval has concentrations ranging from less than 10 to 1,000 mg/L (Figure 27b). The highest concentrations between 400 to 1,000 mg/L are found in the southeast and northwest. A northeast to southwest region (covering the middle of the study area and including the middle and eastern sections of the SBA) has lower concentrations of less than 40 mg/L. This range is also seen in the far western region of the study area. The central SBA and regions just west of the SBA have the lowest concentrations of less than 10 mg/L. Highs of magnesium (40 to 60 mg/L) are found in small zones just west of the SBA and the south.

The 301 to 400 feet slice map has a dissolved magnesium range of less than 10 to 400 mg/L (Figure 27c). The highest concentrations (200 to 400 mg/L) at this interval are found in the southeast. Slightly lower but relatively high concentrations are found in the middle, far west, and a small zone in the south (60 to 100 mg/L). These relatively high concentrations (60 to 100 mg/L) are also found in the northern part of the SBA and areas northwest-west and south of the SBA. The rest of the study area including the remaining SBA has concentrations less than 40 mg/L.

The 401 to 450 feet slice ranges in concentration between less than 10 and 100 mg/L (Figure 27d). The highest concentrations are seen in a small zone in the west with a range of 80 to 100 mg/L. Most of the west and middle has higher concentrations relative to the rest of the study area with concentrations between 20 and 50 mg/L. The northern and southern SBA have concentrations between 10 and 30 mg/L much like the rest of the eastern study area except for the southeast which has the lowest concentrations of less than 10 mg/L.

The 451 to 500 feet interval has dissolved magnesium concentrations of less than 10 to 120 mg/L (Figure 27e). The SBA has slightly higher concentrations relative to the rest of the study area (except for the far west) with concentrations of 80 to 100 mg/L found in the southwestern section of the anomaly. A relatively high concentration zone of 60 to 80 mg/L is found just south of the SBA also. An even higher concentration range of 80 to 120 mg/L is found in a small zone in the west. Zones in the south-southeastern region of the study area have extremely low concentrations of less than 10 mg/L. The rest of the study area (the middle and east), including the remaining SBA, have concentrations between less than 40 mg/L.

The 501 to 550 feet slice has concentrations between less than 10 and 80 mg/L (Figure 27f). The highs (50 to 80 mg/L) are found in a small southwestern section of the SBA including zones southwest of the SBA and on the eastern border of the study area. Another high concentration zone of the same range is found in the west. Most of the remaining study area has concentrations between 20 and 50 mg/L; this range includes the remaining SBA. The lowest concentrations (less than 10 mg/L) are found just southwest of the SBA and in the southwestern region of the study area.

The 551 to 600 feet slice has a range between less than 10 and 200 mg/L (Figure 27g). A small section on the northwestern border region of the SBA has concentrations between 120 to 200 mg/L, while a small zone just south of the SBA has slightly lower concentrations between 80 and 100 mg/L. The remaining SBA and the middle of the study area has lower concentrations between 30 and 50 mg/L. These fairly high levels are also found in zones in the south. Regions

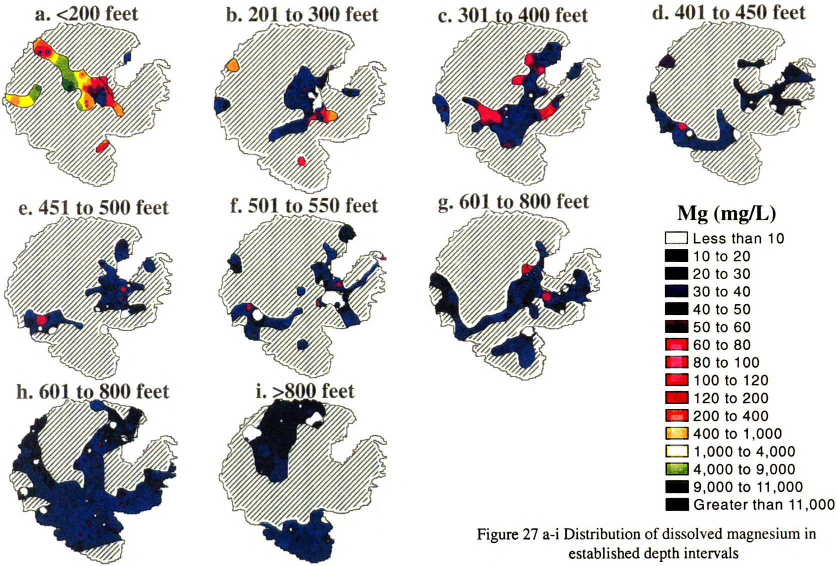


Figure 27 a-i Distribution of dissolved magnesium in established depth intervals in the west have levels between 10 to 30 mg/L. The south-southeastern border has an even lower range of less than 20 mg/L.

The 601 to 800 feet slice has a range between less than 10 and 80 mg/L (Figure 27h). Two south-southeastern zones and a small zone northwest of the SBA have slightly higher concentrations than the rest of the study area with a range between 50 and 80 mg/L. The SBA along with the rest of the study area has concentrations of less than 40 mg/L. Amidst the average concentration distribution, slightly higher concentrations of 40 to 50 mg/L are found in regions throughout the south and in two small zones west of the SBA.

The 801 feet and greater interval has concentrations of less than 10 to 40 mg/L (Figure 27i). The southern region has relatively high concentrations of 30 to 40 mg/L. Most of the south has a range of 20 to 30 mg/L, while only a few zones in the north are at these concentrations. The rest of the study area has a dissolved magnesium concentrations of less than 30 mg/L.

Dissolved Sulfate

The first depth interval (200 feet and less) for sulfate concentrations has a range of less than 10 to 3,500 mg/L. The highest levels are found in the southeast, midnorth, and the western border of the study area (1,000 to 3,500 mg/L). This high range of 1,000 to 3,500 mg/L is also found in the southwestern SBA. These concentrations decrease towards the middle/northwest from a range of 400 to 1000 mg/L down to concentrations as low as 80 to 100 mg/L in the middle. The lowest concentrations are found in the northwest (less than 70 mg/L).

The 201 to 300 feet interval has a range of less than 10 to greater than 3,500 mg/L (Figure 28b). The highest dissolved sulfate concentrations (1,000 to 3,500 mg/L) are found in the northwest and southeast. Zones found in the southwest and middle also have these high concentrations. Relatively high concentrations are found throughout the rest of the study area including the northwestern SBA, west, and south (200 to 1,000 mg/L). A slightly lower concentration zone covers an area from the western border of the SBA towards the midsouthern region of the study area (70 to 150 mg/L). This large zone has even less concentrated, intermittent areas with levels less than 70 mg/L. The rest of the SBA has fairly high concentrations (100 to 300 mg/L).

The 301 to 400 feet slice has levels of dissolved sulfate between less than 10 and 3,500 mg/L (Figure 28c). The highest concentrations (1,000 to 3,500 mg/L) are seen in the midwest and the southeast along with a few areas just west-northwest of the SBA. These sulfate concentrations decrease to the west to levels less than 100 mg/L. A relatively high concentration zone is also found in the south and the northern and southern SBA (300 to 1,000 mg/L). The lowest concentrations of less than 40 mg/L are found in the far eastern and western SBA. This same low range is also found in small zones in the south and west of the SBA. A region that covers an area from the western SBA to the south has a concentration range of 60 to 200 mg/L. This range is also found east of the SBA, while the remaining midwest and surrounding SBA have concentrations between 200 and 1,000 mg/L.

The 401 to 450 feet distribution diagram for dissolved sulfate has a range of less than 10 to 3,500 mg/L (Figure 28d). The highest concentrations (1,000 to 3,500 mg/L) are found in the northwestern region of the study area. A fairly high concentration zone (400 to 1,000 mg/L) is found in the south, and these concentrations decrease towards the western border and just northwest of it to levels of less than 50 mg/L. Another high of 400 to 1,000 mg/L is also found in the low concentration distribution in the southwest and just southwest of the SBA. The SBA has relatively high concentrations of 100 to 200 mg/L. The east-southeast including a small zone in the southwestern SBA and a small zone southwest of the SBA have a low sulfate concentrations of less than 50 mg/L.

The 451 to 500 feet slice has sulfate concentrations between less than 10 and 3,500 mg/L (Figure 28e). The SBA and surrounding areas have relatively high concentrations of 400 to 1,000 mg/L in the northern and southern sections of the anomaly. The highest concentrations (1,000 to 3,500 mg/L) are found in small zones just northwest of the SBA and in the western region of the study area. A low concentration zone (less than 20 mg/L) is seen in the middle of the SBA.

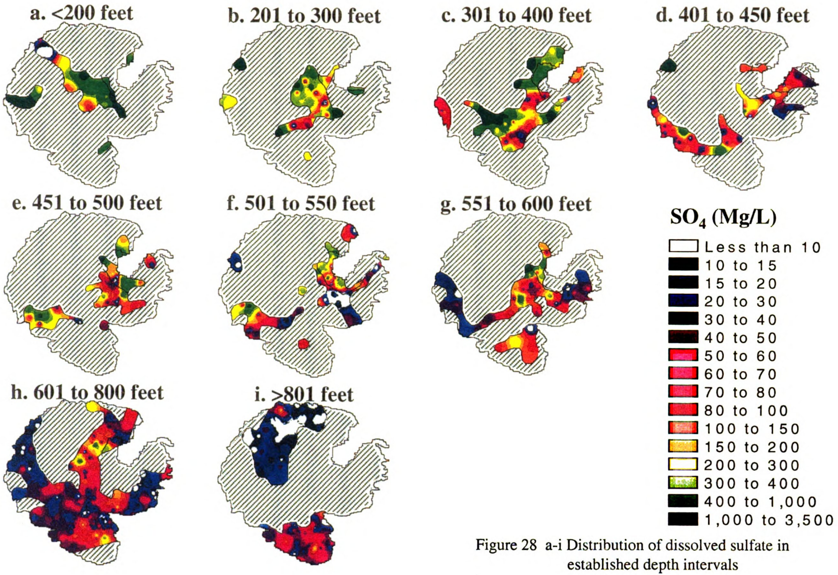


Figure 28 a-i Distribution of dissolved sulfate in established depth intervals

Areas on the northern border of the SBA and just south and southwest of the SBA have relative highs of 300 to 1,000 mg/L also. Concentrations in the middle and west are between 80 to 300 mg/L. The midwest and two zones in the southeast along with a small zone in the east have low concentrations of less than 50 mg/L.

A concentration range of less than 10 to 3,500 mg/L is found in the 501 to 551 distribution diagram for sulfate (Figure 28f). Higher concentrations are found in and around the SBA (200 to 1,000 mg/L). A very high sulfate range of 1,000 to 3,500 mg/L is found in a western zone. A range of 200 to 1,000 mg/L is also seen in the very middle of the study area. The northwest has concentrations that are between 0 and 20 mg/L. The east (above and below the Saginaw Bay) and midwest have sulfate concentrations less than 100 mg/L with a very low concentration zone of less than 10 mg/L in the southwestern SBA and just south of the SBA.

The 551 to 600 feet slice has the same range of less than 10 to 3,500 mg/L (Figure 28g). The highest concentrations are found on the northwestern border region of the SBA (1,000 to 3,500 mg/L). Small zones just south of the SBA and the middle of the study area have a relatively high range of 400 to 1,000 mg/L. The SBA is relatively high in respect to sulfate concentrations (200 to 1,000 mg/L). The west and east are at concentrations less than 40 mg/L, while the south and middle are at slightly higher concentrations of 80 to 300 mg/L. This latter high range is also seen just north of the SBA. A low of less than 10 mg/L is seen on the southern border of the study area.

The 601 to 800 feet interval has a sulfate range of less than 10 to 1,000 mg/L (Figure 28h). Two high concentration zones (400 to 1,000 mg/L) are found just west of the SBA. The surrounding areas also have relatively high concentrations of 100 to 400 mg/L. The south also has these same concentrations. The west and the east generally have concentrations less than 50 mg/L. In this distribution area, intermittent highs of 70 to 150 mg/L are seen.

The 801 feet and greater sulfate distribution has a range of less than 10 and 300 mg/L (Figure 28i). Small zones in the north and south have a range of 150 to 300 mg/L. The remaining southern region of the study area has a range of 30 to 100 mg/L. The rest of the northern region of the study area has concentrations less than 40 mg/L.

Dissolved Bicarbonate

The first slice map (200 feet and less) for bicarbonate has a range of less than 60 to greater than 550 mg/L (Figure 29a). The lowest concentrations (less than 60 mg/L) are found in the midwestern region of the study area. These concentrations increase to relatively high levels of 160 to 240 on the western and eastern borders of the study area including the western SBA. A high is seen in the middle-eastern region of the study area (400 to greater than 550 mg/L). A very low concentration zone (less than 60 mg/L) is seen to the west of this high concentration area. A low of 100 to 140 mg/L is also found in the southeast.

The next 201 to 300 feet bicarbonate map has a range of less than 60 to 360 (Figure 29b). Low concentrations less than 160 mg/L are found in the southeast, western border of the SBA, areas just west of the SBA, and the northwest. The lowest concentrations in the study area (less than 60 mg/L) are also found just west of the SBA. The highest concentrations of 320 to 360 mg/L are found in the south and southeast (just west of the low concentration zone). Another rather large high concentration zone (320 to 340) is found in the middle of the study area. The rest of the study area is between 200 and 280 mg/L.

The 301 to 400 feet depth interval has dissolved bicarbonate concentrations of 100 to 420 mg/L (Figure 29c). The highest zones of bicarbonate concentrations (320 to 420 mg/L) are found in the southern part of the study area. Relative highs of 260 to 300 mg/L are found in the eastern and northern SBA and surrounding the SBA. The areas surrounding these high concentration zones also have fairly high concentrations of 180 to 260 mg/L. These high concentrations are also found near the western boundary of the study area. The lowest concentrations (100 to 180 mg/L) are found in the midwest, northeast, midnorthern SBA, and just west of the SBA.

The 401 to 450 feet slice has bicarbonate levels between less than 60 to 420 mg/L (Figure 29d). The highest concentrations (320 to 420 mg/L) are found in the south, the west, the southeastern part of the SBA, and a zone just south of the SBA. The rest of the SBA and surrounding areas also have relatively high bicarbonate levels of 280 to 320 mg/L. The concentrations in the south decrease towards the west to lower concentrations (160 to 180 mg/L) in the study area; a zone just west of the SBA also has this same low range. The lowest concentrations are seen in the far east, far northwest, and southwest of the SBA (less than 140 mg/L).

The 451 to 500 feet slice has dissolved bicarbonate concentrations between less than 60 and 420 mg/L (Figure 29e). Two south-southeastern zones have the highest concentrations (320 to 420 mg/L). The southwestern SBA and an eastern zone have fairly high concentrations of 320 to 340 mg/L. Highs (300 to 340 mg/L) are also seen to the east of the SBA and in the midwest. The concentrations between the SBA and the south decrease to levels less than 240 mg/L and to the west to the same low range. Very low concentrations of less than 60 mg/L are found in the middle of the study area and west. The remaining SBA, northwest, and eastern areas surrounding the Saginaw Bay have concentrations of 100 to 240 mg/L.

The 501 to 551 feet bicarbonate distribution map has a range of less than 60 to 550 mg/L (Figure 29f). The highest concentrations are found in the midsouthern region of the study area (420 to 550 mg/L). Fairly high levels (300 to 420 mg/L) are found in the middle of the SBA, south and east of the SBA, and far midwest. Concentrations decrease to less than 160 mg/L west of the SBA high concentration zones. This range is seen in much of the SBA also. Most of the west, east, middle SBA, and a zone just north of the SBA and including the northern SBA have relatively high concentrations of 200 to 300 mg/L. A high of 300 to 320 mg/L is also found in the midsouth surrounding the highest concentrations in the study area.

The 551 to 600 feet bicarbonate concentration range is between 100 to 420 mg/L (Figure 29g). Most of the southern region of the study area and a western zone have high bicarbonate levels between 320 and 420 mg/L. The SBA has the lowest concentrations of 100 to 180 mg/L in its central section. However, highs (320 to 360 mg/L) are seen in the southwestern SBA and

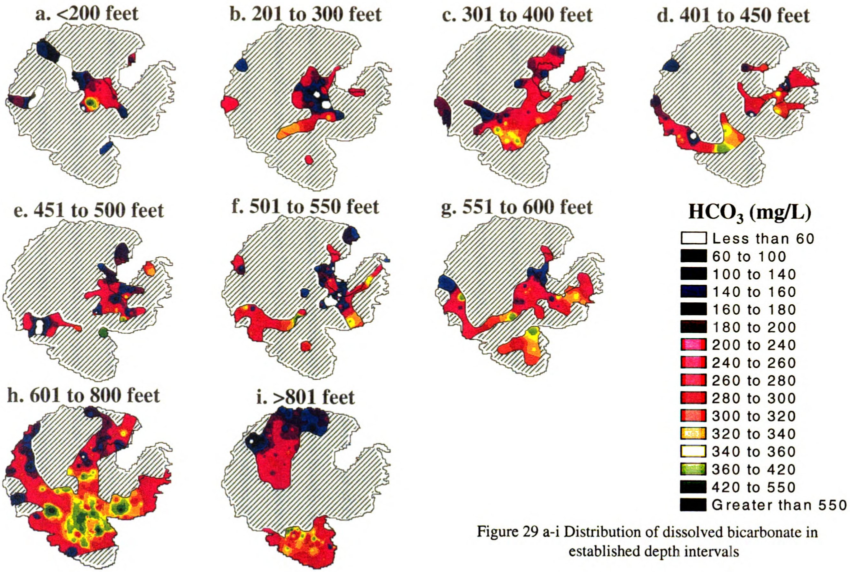


Figure 29 a-i Distribution of dissolved bicarbonate in established depth intervals areas just south of the SBA. Lower levels (100 to 180 mg/L) are also found in the northwestern region of the study area and a number of areas surrounding the SBA. The rest of the east and west have concentrations of 200 to 320 mg/L.

The 601 to 800 feet slice has a bicarbonate range of less than 60 to greater than 550 mg/L (Figure 29h). Numerous high concentration zones (420 to greater than 550 mg/L) are found in the south, but most of the south, middle areas, and a small northeastern zone have a slightly lower concentration range of 300 to 420 mg/L. The rest of the border regions of the study area including the northern SBA are between 140 and 260 mg/L, and these concentrations decrease to levels of less than 140 mg/L in some areas in the west and north.

The 801 feet and greater bicarbonate distribution has a range of less than 60 to 550 mg/L (Figure 29i). The southern half of the study area has a few high concentration zones of 420 to 550 mg/L but averages between 300 to 420 mg/L. A small zone of the same range is found in the northern region of the study area. Much of the northern half of the study area is between 160 and 280 mg/L including a few zones of less than 140 mg/L found on the northern border.

Dissolved Potassium

The 200 feet and less dissolved potassium distribution map has a range of 1 to greater than 700 mg/L (Figure 30a). The highest concentrations of potassium are found in the middle-midwest of the study area (greater than 700 mg/L). These concentrations decrease to the lowest concentrations of 1 to 6 mg/L in the northwestern and northeastern border regions of the study area and just west of the SBA. Most of the west and midwest has a potassium range of 200 to 700 mg/L. A high concentration zone is seen just south of the SBA with levels between 100 and 200 mg/L. Most of the SBA has relatively high concentrations between 15 and 20 mg/L. A zone on the far western border of the study area has these concentrations (15 to 60 mg/L) as well.

The 201 to 300 feet depth interval, potassium range is less than 1 to 200 mg/L (Figure 30b). At this depth the highest concentrations (100 to 200 mg/L) are found in the northwestern region of the study area, while the lowest concentrations (less than 4 mg/L) are found in the middle. Regions in the south and southeast have relatively high concentrations (15 to 20 mg/L) compared to the rest of the study area including most of the SBA, which has concentrations of 5 to 8 mg/L. The western SBA, an area just west of the SBA, and the southwest have relatively high concentrations of 8 to 15 mg/L. A high of 20 to 60 mg/L is seen in the south also.

The 301 to 400 feet slice has potassium concentrations between less than 1 and 60 mg/L (Figure 30c). The midwest has low concentrations (less than 4 mg/L). This range is also seen in the northern and southeastern SBA, far east, and the middle-midsoutheast. The higher concentration zones of the interval (8 to 20 mg/L) are found in the western SBA, just south-southwest and northwest of the SBA, and in the southern and western regions of the study area. The highest concentrations of 20 to 60 mg/L are found just south of the SBA. The rest of the SBA along with the remaining study area have a relatively low concentration range of 5 to 8 mg/L.

The 401 to 450 feet potassium distribution has levels between less than 1 and 15 mg/L (Figure 30d). At this depth the highest concentrations in the study area are found in the southern SBA and areas just southwest of the SBA (8 to 15 mg/L). A small zone in the west also has these high concentrations. The eastern SBA, most of the areas surrounding the SBA, a small zone in the midsouth, and an area in the midwest have the next highest concentrations of 6 to 8 mg/L. The northern SBA has slightly lower concentrations of 5 to 6 mg/L. The majority of the study area has range of less than 5 mg/L.

The 451 to 500 feet depth interval has potassium concentrations between less than 1 and 15 mg/L (Figure 30e). The highest concentrations are found in the southern and northern SBA and just south of the SBA with a range of 8 to 15 mg/L. The rest of the SBA, areas surrounding the SBA, a far eastern zone, a middle zone, and west have relatively high potassium levels of 4 to 8 mg/L also. The remainder of study area has the lowest dissolved potassium concentrations of less than 4 mg/L.

The 501 to 551 feet slice has potassium levels between less than 1 and 15 mg/L (Figure

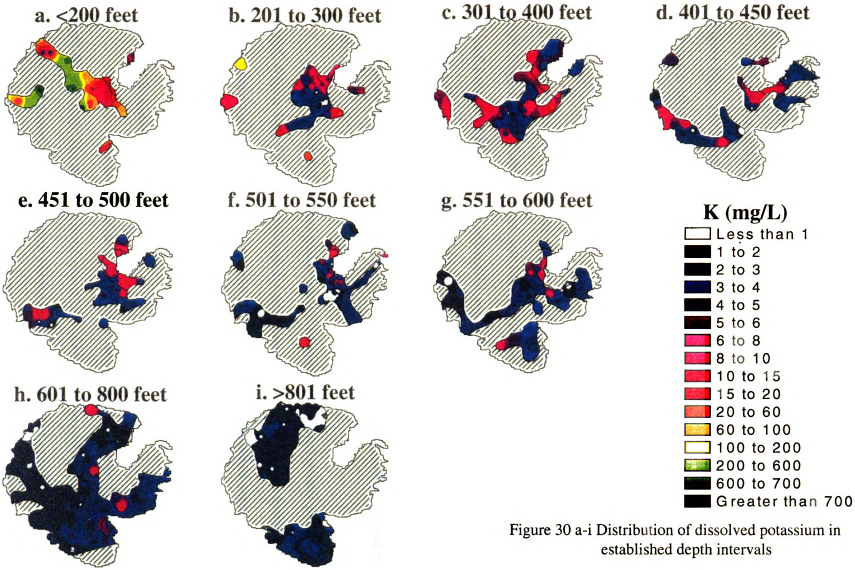


Figure 30 a-i Distribution of dissolved potassium in established depth intervals

30f). The highest concentrations are found in a large zone in the south (6 to 15 mg/L). This same range is also seen in numerous zones in the SBA along with areas just north of the SBA and on the eastern border of the study area. The rest of the study area has low levels of less than 3 mg/L.

The 551 to 600 feet potassium concentration range is between less than 1 and 10 mg/L (Figure 30g). The highest potassium concentrations (6 to 10 mg/L) are found in the SBA, just west and south of the SBA, and in a zone in the southwest. Areas in the northern and southern SBA, to the north and east of the SBA, and from the SBA towards the south have potassium levels between 3 to 4 mg/L. Much of the remaining study area has lower concentrations of less than 3 mg/L.

The 601 to 800 feet potassium distribution has concentrations between less than 1 and 15 mg/L (Figure 30h). The highest concentrations in the study area with respect to potassium (6 to 15 mg/L) are found south and west of the SBA and in the northern and southern regions of the study area. The northern and southern SBA and the surrounding SBA which are included in a region covering an area from the northern to southern border have higher concentrations (2 to 6 mg/L) compared to the rest of the study area (less than 2 mg/L), especially in the northeast and west.

The shallowest 801 feet and greater interval has potassium levels between less than 1 and 6 mg/L (Figure 30i). Two very small high concentration zones (4 to 6 mg/L) are found in the southern region of the study area. These zones are surrounded by intermediate concentrations between (2 to 4 mg/L). These concentrations are also found in two zones in the north. The rest of the study area has concentrations less than 2 mg/L.

Dissolved Strontium

Strontium levels for the 200 feet and less slice range between less than 80 and 80,000 mg/L (Figure 31a). The strontium distributions have the highest concentrations (10,000 to 80,000 mg/L) in the far west, southeast, a small middle and southern zone, and a small region on the western border of the SBA. A low of 700 to 800 mg/L is also found in the very middle of the study area, while a low of less than 80 mg/L is found in the northwest. The rest of the SBA has a relatively high concentration range of 2,000 to 10,000 mg/L, while the middle-midsouthern region of the study area has concentrations of a slightly lower magnitude (1,000 to 2,000 mg/L). The area just north of the SBA has relatively high concentrations of this same range.

The 201 to 300 feet slice has concentrations between less than 80 and 80,000 mg/L (Figure 31b). The highest concentrations are found in the southeast, northwest, and a small zone in the south (10,000 to 80,000 mg/L). The northern SBA has relatively high concentrations of 1,000 to 2,000 mg/L, while the eastern SBA and areas just west of the SBA have an even higher range of 4,000 to 10,000 mg/L. This latter high range of 4,000 to 10,000 mg/L is also found in a southwestern zone. However, the middle of the SBA and areas just to the west have relatively low concentrations of less than 300 mg/L. The midsouthern region of the study area has a range between 600 to 800 mg/L, while the remaining regions, especially the west, have relatively high concentrations of 1,000 to 2,000 mg/L.

The 301 to 400 feet strontium distribution has a range of less than 80 to 80,000 mg/L (Figure 31c). The highest concentrations (10,000 to 80,000 mg/L) are found in the southeast. Relatively high strontium concentrations (4,000 to 10,000 mg/L) are found in the west, midwest, and southeast including the southern SBA. This concentration range is also found in the northern SBA and areas just west of the SBA. Most of the remaining SBA, the majority of the surrounding SBA, middle, and west have fairly high concentrations of 1,000 to 4,000 mg/L. Lows of less than 300 mg/L are found in the midsouth, northeast, southeastern SBA, and an area just southwest of the SBA. Surrounding these low concentration zones and a midwestern zone are concentrations of 600 to 1,000 mg/L.

The 401 to 450 feet strontium concentration range is between less than 80 and 80,000 mg/L (Figure 31d). The highest concentrations are found in two zones in the west-northwest (10,000 to 80,000 mg/L). The northern and southern SBA along with much of the east and western border zones of the study area have concentrations between 1,000 and 4,000 mg/L. A

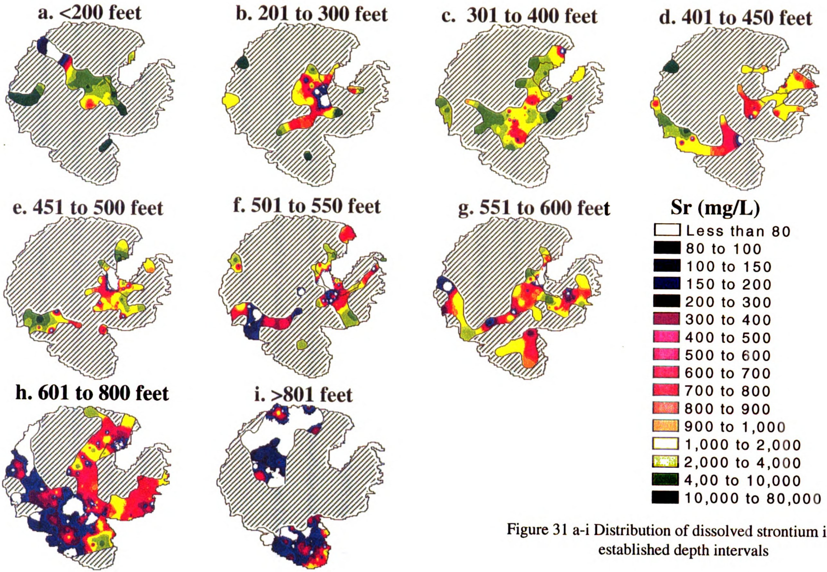


Figure 31 a-i Distribution of dissolved strontium in established depth intervals single zone along the western border of the study area does have slightly higher concentrations of 4,000 to 10,000 mg/L. The southern region of the study area and southwest of the SBA have concentrations of less than 500 mg/L. The concentrations surrounding these lows leading up to the relatively high concentration areas in the SBA and west have levels between 500 and 800 mg/L.

The 451 to 500 feet slice has dissolved strontium concentrations of less than 80 to 80,000 mg/L (Figure 31e). The western SBA and areas west of the SBA have very low concentrations of less than 80 mg/L. Two zones in the midwest also have this low concentration range. A small zone in the northeastern SBA and in the western region of the study area have concentrations between 10,000 and 80,000 mg/L. The west, the southeastern and central SBA, and just south and north of the SBA have relatively high concentrations also of 2,000 to 10,000 mg/L. The rest of the study area is between 800 and 2,000 mg/L with numerous zones in the middle of the study area and just west of the SBA having lower levels of 600 to 800 mg/L.

The 501 to 550 feet strontium distribution has a range of less than 80 to 10,000 mg/L (Figure 31f). The western SBA, areas just west of the SBA, and far west have the lowest concentrations of less than 80 mg/L. The highest concentrations (2,000 to 10,000 mg/L) are found in numerous zones in the northwest, south, and east including the northern and southern SBA. Zones in the south, northwest, and the much of the east are between 900 and 2,000 mg/L. The midwest has concentration zones between 400 and 600 mg/L.

The 551 to 600 feet slice has a strontium concentration range of less than 80 to 10,000 mg/L (Figure 31g). The highest concentrations of the study area (2,000 to 10,000 mg/L) are found in the northwestern and southern border region of the SBA, north of the SBA, southeast, and southwest. Most of the central and eastern SBA have concentrations of less than 80 mg/L. The northern SBA has levels of 500 to 2,000 mg/L. This concentration range is also seen in the south, west, southwest, and northeast. Lower concentration zones (less than 500 mg/L) are found in the middle, midsouth, northwest, and numerous zones in the east.

The 601 to 800 feet strontium distribution has concentrations between less than 80 and 10,000 mg/L (Figure 31h). The highest concentrations (4,000 to 10,000 mg/L) are found in a zone in the south. Areas in the northern and southern SBA, surrounding SBA, and on the northern and southern border have the next highest range of 1,000 to 4,000 mg/L. Numerous zones in the west and west of the SBA also have relatively high concentrations of 800 to 2,000 mg/L. The rest of the study area has concentrations less than 500 mg/L with the northern SBA and western border region of the study area having the lowest concentrations of less than 80 mg/L.

The 801 feet and greater depth interval has a dissolved strontium range of less than 80 to 4,000 mg/L (Figure 31i). The highest concentrations (1,000 to 4,000 mg/L) are found along the southern-southwestern border region and small zones in the north. Relative highs of 300 to 700 mg/L are found in the midsouth and two northern zones. The rest of the north and south have concentrations of less than 300 mg/L. Most of the north and two large regions along the northern border of the southern region of the study area have the lowest concentrations of less than 80 mg/L.

Dissolved Barium

The 200 feet and less slice has barium concentrations between less than 10 and 210 mg/L (Figure 32a). The highest concentrations are in the southeast (190 to 210 mg/L). These high concentrations are seen just west-northwest of the SBA and south, and a low of 30 to 80 mg/L is found in the middle-midwest. A small relatively high concentration zone (95 to 105 mg/L) is found due west and north of the SBA also. Most of the SBA and a region covering an area from the SBA towards the southwestern border have relatively low concentrations of less than 20 mg/L. In this region is a lower zone of less than 10 mg/L, which includes the western SBA. Concentrations of 20 to 30 mg/L are found in the northwest.

The 201 to 300 feet slice has barium levels of less than 10 to 600 mg/L (Figure 32b). The highest concentrations are found in a western zone (500 to 600 mg/L). Concentrations in the center are at much lower levels of less than 10 mg/L. This low range is also found in the central and southern SBA. High concentration zones (190 to 210 mg/L) are seen in the southeastern and northwestern region of the study area. These concentrations decrease towards the SBA to levels less than 30 mg/L. The eastern SBA has concentrations of barium between 95 to 105 mg/L.

The 301 to 400 feet barium distribution has a concentration range between less than 10 and 190 mg/L (Figure 32c). Much of the midwest and east including the borders of the SBA and surrounding areas have barium concentrations less than 10 mg/L. The rest of the areas along the southern border of the SBA are less than 80 mg/L. A high concentration zone (145 to 190 mg/L) is found in the south, while other relatively high concentration zones are found just south of the SBA and in the middle of the study area (80 to 105 mg/L). A small zone of the latter range is also found on the western border of the study area. The northern SBA has a barium concentration range of 40 to 80 mg/L. A high (80 to 105 mg/L) is found in the southeastern SBA.

The 401 to 450 feet slice has barium levels between less than 10 and 145 mg/L (Figure 32d). Most of the SBA and areas surrounding the SBA have barium concentrations less than 10 mg/L. This low concentration range is also seen in the northwest. The highest concentrations (95 to 145 mg/L) are found in zones in the east, midsouth, and west. A high concentration zone of 80 to 95 mg/L is found just south of the SBA. Most of the south, east, and west have barium ranges between 10 and 80 mg/L.

The 451 to 500 feet barium distribution has a concentration range between less than 10 and 190 mg/L (Figure 32e). The low barium concentrations (less than 10 mg/L) are found in the middle, midwest, and east (including the SBA). The west has concentrations between 10 and 40 mg/L, while areas along with the border in the south-southeastern region of the study area have slightly higher concentrations between 30 and 80 mg/L. The highest concentrations (145 to 190 mg/L) are found just south of the SBA, while fairly high concentrations (105 to 145) are found in numerous zones in the east-southeast.

The 501 to 551 feet slice has dissolved barium levels between less than 10 and 190 mg/L

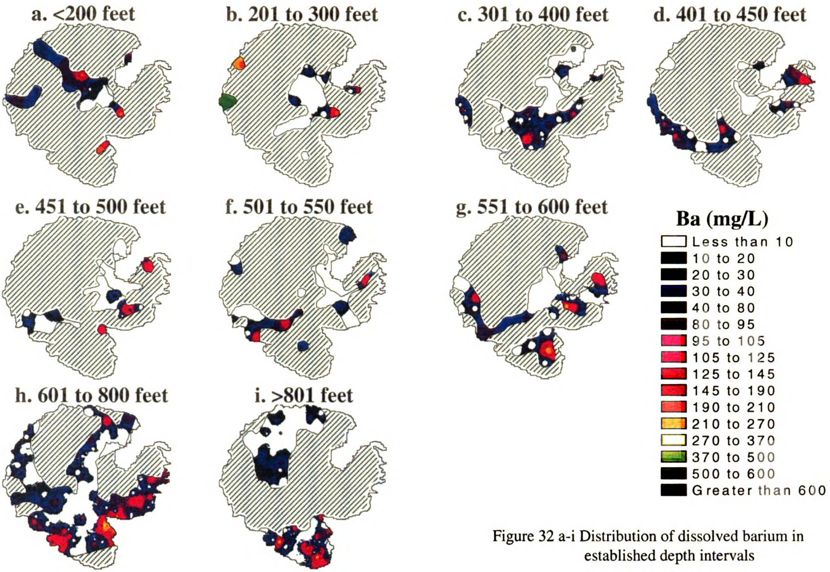


Figure 32 a-i Distribution of dissolved barium in established depth intervals

(Figure 32f). The highest concentrations (105 to 190 mg/L) are found in the east and a few zones in the southwest. Most of the south and east have relatively high barium levels between 30 and 80 mg/L. The northwest, middle, and the SBA have an range of less than 30 mg/L.

The 551 to 600 feet barium distribution concentration range is between less than 10 and 270 mg/L (Figure 32g). High concentration zones of 210 to 270 mg/L are found in the south and just south of the SBA. Other relatively high concentrations (80 to 145 mg/L) are found in the east around the borders of the SBA, the northern SBA, the west, and surrounding the highest concentration zones of 210 to 270 mg/L. Most of the SBA, areas surrounding the SBA, and middle and northwestern parts of the study area have low concentrations of less than 10 mg/L. Many areas along the northeastern, western, southern, and eastern borders of the study area have barium concentrations between 30 to 80 mg/L. The remaining regions of the study area have concentrations of less than 30 mg/L.

The 601 to 800 mg/L slice has a barium concentration range of less than 10 to 370 mg/L (Figure 32h). High concentration zones of 210 to 370 mg/L are found in areas in the south. Other areas on the southern border and a small zone in the northeast have relatively high concentrations also of 105 to 190 mg/L. A zone covering and area from the western border of the SBA and the southwest along with an area in the northwest have the lowest concentrations of less than 10 mg/L. Much of the north, west, and areas south of the SBA have a barium range of 30 to 80 mg/L. The remainder of the northwestern region of the study area has concentrations less than 30 mg/L.

The 801 and greater barium distribution range is between less than 10 and 270 mg/L (Figure 32i). The highest concentration zones (190 to 270 mg/L) are found in two areas in the southern region of the study area. The rest of the south has relative highs of 30 to 190 mg/L except for a low concentration region (less than 10 mg/L) covering an area from the northern to southern border and the eastern border of the southern region. The northern region and a small zone in the southern region have a range of less than 30 mg/L. A lone high of 30 to 80 mg/L is found on the southeastern border of the northern region.

CUMULATIVE, INDIVIDUAL, AND COMPARATIVE ANALYSIS OF ESTABLISHED DEPTH INTERVALS

Cumulative Summary

In the 200 feet and less depth interval distribution maps, the highest concentrations for every ion except for barium, sulfate, and bicarbonate are found in the middle-midwest. These concentrations decrease towards the northwest to the lowest concentrations in the study area. Concentrations also decrease towards the SBA and fall to a low in the mideast but rise to relatively high concentrations in the southern SBA and southeast. Relative highs are also found in the south and west but are far less in magnitude than in the middle-midwest. A single zone just off the northern border of the SBA has intermediate concentrations.

Sulfate follows this same basic patterning trend in the 200 feet and less slice but has slightly lower concentrations in the mideastern region of the study area. Bicarbonate has an inverse relationship with respect to lower concentrations in the middle-midwest. Its concentrations increase somewhat towards the SBA/southeast and is at a maximum in the mideast where the other major ions are low, except for sulfate. Barium also follows the normalized pattern set by the other major ions but has an extreme low covering an area from the western border of the SBA towards the west-southwest.

In the 201 to 300 feet depth interval diagrams, the highest concentrations for every element excluding bicarbonate are found in the northwest and southeast. Barium also has its highest concentrations in the far west where the other elements have a relative low. Relative highs for every element are found in the south and southwest. These concentrations decrease towards the SBA to the lowest concentrations in the study area just off the western border of the

SBA. Concentrations then increase slightly moving into the northern SBA. Relatively low to intermediate concentrations are seen in the eastern SBA except for barium where a relative high is seen. Relatively high concentrations for most ions are found due west of the SBA also. Barium also differs from the other ion concentration distributions in respect to its extreme lows found throughout the middle and east including the SBA. Bicarbonate again complies with the opposite trend in this depth interval. Discrepancies in the bicarbonate distribution are seen in the south-southwest where highs are found and in the west and mideast where lows are found.

In the 301 to 400 feet distribution maps for every element except barium and bicarbonate, the highest concentrations are seen in the southeast and southwestern SBA. Relative highs are also found in the middle, west, south, and just west of the SBA. Concentrations decrease in the midsouth and just west of the SBA. Levels generally increase in the midwestern SBA except for sulfate, magnesium, and calcium where low to intermediate concentrations are found. The rest of the study area including the northern SBA have intermediate concentrations with a number of lows. These same areas have relatively high concentrations with respect to sulfate and strontium. Another variation is seen in the northern SBA where lows of sodium and chloride concentrations are seen, while calcium and magnesium have high concentrations. Again bicarbonate complies with the inverse patterning in this depth interval. Barium has the same general trends as the other elements though an extreme low is found in the SBA and surrounding areas along with a large midwestern zone.

In the 401 to 450 feet slice, the highest concentrations are found in a discreet western zone and in the southeastern SBA discounting bicarbonate. However, calcium concentrations are relatively low throughout the SBA. Relative highs of the ions are also found in a northwestern zone except for sodium, chloride, and barium for which relative lows are seen. The southwestern boundary of the study area has intermediate concentrations with a number of lows along the border. These concentrations increase to a high in the midsouth but decrease again moving towards the SBA and the middle of the study area. Intermediate to high concentrations are found in the northern SBA and areas surrounding the SBA. However, potassium, sodium, sulfate, and strontium have relatively high concentrations, while barium has extremely low concentrations. Bicarbonate follows the general inverse trend except in the midsouth where a high is seen.

In the 451 to 500 feet slice, the highest concentrations of every ion excluding bicarbonate and barium are found in the southern SBA, just south of the SBA, and in a lone western zone. A few lows surround the high concentration zone in the west including a very low concentration zone in the middle of the study area. The rest of the western region of the study area has intermediate concentrations. The mideast has intermediate concentrations as well moving towards the SBA where slightly higher concentrations are found in the northern section of the anomaly. The middle zones have relatively low concentrations. However, in these middle zones, sulfate has very high concentrations and very low concentrations in the central SBA, which strays from the normalized patterns. Considering the entire suite of elements excluding bicarbonate and barium, lows are found just east of the SBA and far south-southeast also.

Bicarbonate complies with the inverse relationship seen throughout the other slice maps. However, a low is found in the middle of the study area much like the other ions. Barium differs from the normal trends observed in the south-southeast and east of the SBA where highs are found. Barium also has an extreme low in the SBA and relative lows in the far west.

Excluding bicarbonate and barium, the 501 to 550 feet slice distributions have highs in and around the SBA. However, strontium has an extreme low in this region. A zone of very low concentrations is found in areas south-southeast of the SBA. Relatively high concentrations are found just to the west and south of this low concentration zone. High levels of dissolved ions are also found just north of the SBA and in the south. Relatively low concentrations are found in much of the west along with a small zone in the middle of the study area. Despite this patterning trend, numerous highs of sulfate, calcium, and magnesium are found in these areas. Strontium also has a lone high concentration zone in the west. Another high of strontium is found in the northwest where the other elements display lows. Bicarbonate again patterns itself opposite that of the other ions. Barium has extremely low concentrations in and around the SBA except for a zone in the east in which a high is found. Two other highs are also found in an intermediate barium concentration zone in the west.

In the 551 to 600 feet distribution maps, the highest concentrations are found on the southern SBA border region and west of the SBA except for barium and bicarbonate. Relative highs are found throughout the rest of the SBA and surrounding SBA. Strontium has very low concentrations in the middle of the SBA. Another relative high of strontium is found in the southwest, while a general low is seen east of this zone. Lows of the ions are also found in the midwest and west-northwestern border region, while the remainder of the study area in the middle-midwest and far east have intermediate concentrations. Magnesium and potassium have relative highs in a midwestern zone.

Bicarbonate conforms to the inverse trend seen throughout the aquifer system. Barium has its highest concentration just south of the SBA much like the other elements but also has highs in the south, west, and east. The SBA and the rest of the surrounding areas are very low in barium concentrations, and intermediate concentrations are found throughout the rest of the study area.

In the 601 to 800 feet distribution maps, the highest concentrations are found south of the SBA except for calcium and barium. A bicarbonate high and calcium low is found in this area. Discounting barium and bicarbonate, a general high concentration region covers an area from the northern to southern border; sulfate and strontium have high concentration zones in this region. Intermediate concentrations are found in the northern SBA and southeast, while another relatively high concentration zone is seen in the east. The majority of the west has very low concentrations. Barium conforms to these normalized trends as well but has its highest concentrations on the south-southeastern border of the study area, and another high is found in the southeast. Barium also has a major low concentration zone in the middle of the study area. Bicarbonate no longer follows the opposite trend that well. However, the normal inverse relationship is still relevant in the west and north-northwest of the SBA.

The shallowest 801 feet and greater distribution maps have the highest concentrations in the southern region of the study area excluding bicarbonate. The rest of the south and much of the north have relatively intermediate concentrations. Overall, the north has lower concentrations. High concentration zones are seen in the north especially on the very northern border of the study area where very high concentrations of strontium are found. Bicarbonate follows the opposite trend very well in the south, and also has its highest concentrations in this region. Relatively low to intermediate concentrations of bicarbonate are found in the northern region with highs found in the center and lows on the northern border.

Discussion of Ions and Comparative Analysis of Ion Pairs

Chloride and Sodium

In the 200 feet and less depth interval, the sodium and chloride distributions correlate well with each other at this level, especially considering the high concentration concentrations found in the midwest and the southeast (Figure 24a and Figure 25a). In the 201 to 300 feet slice, the distribution patterns for sodium at this depth interval are similar to the distributions of chloride except in the center of the study area (Figure 24b and Figure 25b). Both ions have relatively low concentrations in the middle of the study area. However, the areal extent of the lower concentrations of chloride (less than 20 mg/L) is much greater than the areal extent of the lower concentrations of sodium (5 to 100 mg/L).

The spatial patterns of sodium concentrations in the 301 to 400 feet depth interval do correspond well to the chloride distributions, especially considering the southeastern high concentration zone and the southern SBA, which also has high concentrations (Figure 24c and Figure 25c). In these areas chloride has a range of 12,000 to 60,000 mg/L, while sodium has a range of 1,000 to 20,000 mg/L. In the 401 to 450 feet slice, the distributions of both ions are similar to each other (Figure 24d and Figure 25d). The high sodium concentrations (400 to 2,000 mg/L) in the SBA, surrounding SBA, and in the west correlate to the high chloride concentration regions (600 to 3,000 mg/L). The general spatial extent of these high concentration zones is much greater for sodium than that of chloride.

The sodium and chloride spatial patterns for the 451 to 500 feet interval do correlate well with each other (Figure 24e and Figure 25e). The high concentration areas for chloride (600 to 3,000 mg/L) in the SBA, surrounding SBA, and in the west have a greater areal extent than do the high concentration areas of sodium (600 to 2,000 mg/L). In the 501 to 550 slice, the distributions of sodium and chloride are similar to each other (Figure 24f and Figure 25f). Some eastern zones have relatively high chloride concentrations (200 to 600 mg/L) compared to relatively low concentrations of sodium (less than 50 mg/L). However, a high of sodium (200 to 250 mg/L) is associated to a low of chloride (1 to 2 mg/L) in the midsouthwest.

For the 551 to 600 feet slice, the distribution patterns of sodium and chloride follow each other very well (Figure 24g and Figure 25g). Comparing the spatial patterns of sodium and chloride for the 601 to 800 feet depth interval, the relative highs and lows of the ions of the study area correspond very well with each other (Figure 24h and Figure 25h). The spatial distribution patterns of sodium and chloride are similar to each other for the 801 feet and greater depth interval (Figure 24i and Figure 25i). The spatial extent of higher concentrations in the north and south cover more area for chloride (30 to 100 mg/L) than for sodium (60 to 80 mg/L).

Calcium and Magnesium

The distribution patterns in the 200 feet and less slice for magnesium do correlate with those of calcium very well at this depth interval except in areas north of the SBA (Figure 26a and Figure 27a). Relatively low magnesium (20 to 40 mg/L) concentrations are found in this region. A consistently and fairly high concentration range of calcium (300 to 600 mg/L) is found in the same area along with the rest of the SBA and study area. The same trends of distribution in the 201 to 300 feet slice are seen relative to calcium concentrations except in the southwest where relatively high concentrations of calcium (300 to 600 mg/L) are seen compared to low concentrations of magnesium (less than 40 mg/L) (Figure 26b and Figure 27b). Comparatively, in the 301 to 400 feet distribution, higher concentrations are seen in the western-southwestern region of the study area for calcium (160 to 300 mg/L) (Figure 26c). Magnesium has a low range of less than 40 mg/L in this area (Figure 27c).

Like magnesium in the 401 to 450 feet depth interval, the calcium distribution has low concentrations in the northwest and a small zone just west of the SBA (Figure 26d and Figure 27d). In this northwestern area calcium has concentrations of 300 to 600 mg/L, while magnesium has concentrations of 40 to 50 mg/L. A small high concentration zone of calcium (160 to 200 mg/L) just west of the SBA corresponds to the general low of magnesium (20 to 30 mg/L). Overall, the general spatial pattern of both calcium and magnesium are similar to each other.

As expected, the calcium distributions for the 451 to 500 feet depth interval have the same trends (Figure 26e and Figure 27e). The spatial configurations for both magnesium and calcium are similar one another in the 501 to 550 feet slice as well (Figure 26f and Figure 27f). In the 551 to 600 feet slice the same calcium distribution pattern is seen relative to magnesium but to a greater areal extent (Figure 26g and Figure 27g). More of the southern and middle regions of the study area are fairly concentrated with respect to calcium (115 to 300 mg/L) than magnesium (30 to 50 mg/L).

The calcium and magnesium distributions for the 601 to 800 feet interval are very similar to each other (Figure 26h and Figure 27h). However, much higher calcium concentrations (90 to 300 mg/L) than magnesium are seen in a middle region covering the length of the study area from the north to south, and especially in the south. In these regions magnesium has levels of 30 to 80 mg/L. The same spatial patterns are seen with respect to calcium and magnesium concentrations in the 801 feet and greater slice (Figure 26i and Figure 27i). However, in the corresponding high concentration zone in the south, calcium (135 to 160 mg/L) is much more concentrated than magnesium (30 to 40 mg/L).

Sulfate and Bicarbonate

In comparison to sulfate in the 200 feet and less slice, bicarbonate's spatial patterns have relative lows (less than 140 mg/L) in areas where sulfate has relative highs (1,000 to 3,500 mg/L) except for the middle and northwestern regions of the study area (Figure 28a and Figure 29a). Fairly low concentrations of sulfate (less than 70 mg/L) are found in these areas and correlate to lows of bicarbonate (less than 140 mg/L). However, a mideastern sulfate low (100 to 150 mg/L) corresponds to a bicarbonate high (greater than 550 mg/L).

The inverse spatial patterns of bicarbonate are similar to sulfate in the 201 to 300 feet slice except for the relative high of bicarbonate found in the midsouthwest (320 to 340 mg/L) (Figure 28b and Figure 29b). In this region, both ions have high dissolved concentrations; sulfate has concentrations of 1,000 to 3,500 mg/L. As expected, the inverse relationship between sulfate and bicarbonate is seen in the 301 to 400 feet slice (Figure 28c and Figure 29c). In the 401 to 450 feet distribution, the highs of sulfate (400 to 3,500 mg/L) in the northwest, west, and southwest of the SBA do correspond to the lows of bicarbonate (less than 140 mg/L) (Figure 28d and Figure 29d). An exception is seen in the south where both ions have high concentrations. In this region bicarbonate has a range of 320 to 420 mg/L, and sulfate has a high of 400 to 1,000 mg/L.

In the 451 to 500 feet slice, discounting the relative bicarbonate highs in the south-southeast and southwestern SBA (240 to 420 mg/L), sulfate distribution patterns do correlate with bicarbonate distribution patterns (Figure 28e and Figure 29e). Sulfate also has high concentrations in these areas with concentrations between 100 to 1,000 mg/L. The spatial patterns of bicarbonate are similar to those of sulfate in the 501 to 550 feet slice (Figure 28f and Figure 29f). However, highs of bicarbonate (90 to 420 mg/L) correlate with relative highs of sulfate in the SBA (400 to 1,000 mg/L), north of the SBA (400 to 1,000 mg/L), southeast (40 to 50 mg/L), and south (80 to 100 mg/L). Lows of both bicarbonate (less than 60 mg/L) and sulfate (less than 10 mg/L) are found just south of the SBA. The distribution patterns for bicarbonate correlate very well with the distribution patterns of sulfate in the 551 to 600 feet maps (Figure

28g and Figure 29g).

In the 601 to 800 feet interval, the distribution patterns for sulfate follow the same general patterns as bicarbonate except in a small northwestern zone where they are both have relative highs (Figure 28h and Figure 29h). Here, bicarbonate has a range of 280 to 300 mg/L, while sulfate has a range of 60 to 70 mg/L. The spatial configurations for sulfate are similar to those of bicarbonate concentrations in the greater than 801 feet slice also (Figure 28i and Figure 29i). However, in the south, both ions have high concentrations where bicarbonate has a range of 320 to 550 mg/L, and sulfate has a high range of 60 to 300 mg/L.

Potassium, Strontium, and Barium

The potassium distribution maps constructed for the slices are similar to the major ion spatial slice maps (Figure 30a-i). Within the slice distributions, the general pattern of strontium concentrations follow that of the major ions (Figures 31a-i). In the slice distributions, the pattern of barium does not completely follow that of the major ions, such as sodium and chloride (Figure 32a-i).

DISTRIBUTION AND ANALYSIS OF THE SATURATION STATES OF INDIGENOUS MINERALS IN GROUNDWATERS IN ESTABLISHED DEPTH INTERVALS

Calcite Saturation States

Most of the slices are in equilibrium (-0.424 to 0.424) with respect to calcite. The first slice interval, 200 feet and less, has a range of SIs of -0.424 to 0.624 (Figure 33a). The study area is entirely in equilibrium (-0.424 to 0.424) except for a small zone just southwest of the SBA. This slightly supersaturated zone (0.424 to 0.620) to the southwest of the SBA is associated with a low of calcium (70 to 90 mg/L) and a high of bicarbonate (240 to 260 mg/L) (Figure 26a and Figure 29a).

In the 201 to 300 feet interval, calcite SIs have a range of -1.200 to 0.620 with respect to the groundwater in the study area (Figure 33b). Most of the study area is in equilibrium (-0.424 to 0.424) with respect to calcite. Two zones of slightly supersaturated waters (0.424 to

0.620) are seen in the southwest, center of the study area, and the western SBA. The larger southwestern undersaturated zone corresponds to both calcium (300 to 360 mg/L) and bicarbonate (320 to 360 mg/L) highs (Figure 26b and Figure 29b). The small middle undersaturated zone corresponds to a calcium high (135 to 160 mg/L) but has bicarbonate concentrations no different from surrounding areas. The slightly undersaturated zone (-1.200 to -0.424) in the western SBA is analogous to a low of calcium (less than 60 mg/L) and a high of bicarbonate (280 to 300 mg/L).

In the 301 to 400 feet interval, the calcite SIs range from -0.424 to 1.343 (Figure 33c). The majority of the study area is in equilibrium (saturated) with respect to calcite. A very small zone in the middle of the study area is very supersaturated (0.424 to 1.343) with respect to calcite. This small zone is associated with a high of calcium (160 to 200 mg/L) but has bicarbonate concentrations no different relative to surrounding areas (Figure 26c and Figure 29c). The small slightly supersaturated zone (0.424 to 0.620) just east of the very supersaturated zone is identified by a high of bicarbonate (320 to 340 mg/L) but has calcium concentrations no different relative to surrounding areas.

The next 401 to 450 feet level has a range of -0.424 to 0.620 where the entire study area is in the saturated state with respect to calcite (-0.424 to 0.424) except for a slightly supersaturated zone (0.424 to 0.620) in the middle of the study area (Figure 33d). This slightly supersaturated zone has calcium concentrations no different relative to surrounding areas but is correlated to a high of bicarbonate (400 to 420 mg/L) (Figure 26d and Figure 29d).

The 451 to 500 feet slice has a range of calcite SIs between -1.970 and 1.343 (Figure 33e). The southwestern border of the SBA is highly supersaturated with respect to calcite (0.424 to 1.343). Here, bicarbonate has low concentrations (60 to 100 mg/L), but calcium concentrations are no different relative to surrounding areas (Figure 26e and Figure 29e). Slightly supersaturated zones (0.424 to 0.620) are found in the SBA, just south of the SBA, and in the west and south. In both the SBA zones, calcium has low concentrations (20 to 40 mg/L), while bicarbonate has

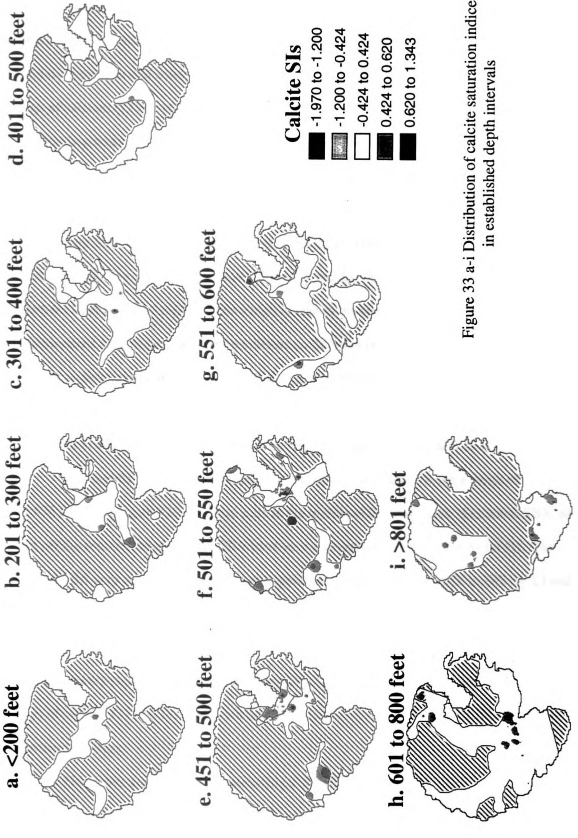


Figure 33 a-i Distribution of calcite saturation indices in established depth intervals relatively high concentrations (240 to 260 mg/L). The western zone does indicate a relative high of bicarbonate (200 to 240 mg/L) while a low (100 to 140 mg/L) is seen with the zone just south of the SBA. Calcium concentrations are no different relative to surrounding areas in these slightly supersaturated zones. The far southern slightly supersaturated zone is analogous to a high of calcium (135 to 160 mg/L) but has bicarbonate concentrations no different relative to surrounding areas.

Very undersaturated waters (-1.970 to -0.424) are found in the much of the SBA and a large southwestern zone. Lows of bicarbonate are seen relative to all the undersaturated zones in the southern SBA (100 to 140 mg/L) and northern SBA (160 to 180 mg/L), while a high is associated with the southwestern zone (260 to 180 mg/L). A low is seen for calcium in the northern SBA (20 to 40 mg/L), while a high is seen in the southern SBA (200 to 300 mg/L). The southwestern zone has calcium concentrations no different relative to surrounding areas. A small slightly undersaturated zone (-1.200 to -0.424) just south of the SBA corresponds to a low of calcium (less than 20 mg/L) and a high of bicarbonate (400 to 420 mg/L). The remainder of the study area at this depth is in equilibrium with respect to calcite (-0.424 to 0.424).

The middle 501 to 550 feet distribution diagram for calcite SIs has a range of -1.970 to 1.343 (Figure 33f). A large zone in the middle of the study area, the central SBA, and just off the southern border of the SBA have very supersaturated SIs (0.424 to 1.343). The central SBA very supersaturated zone corresponds to a high of calcium (300 to 600 mg/L) and bicarbonate (400 to 420 mg/L) (Figure 26f and Figure 29f). A low of calcium (less than 20 mg/L) and a relative high of bicarbonate (260 to 280 mg/L) correspond to the southern SBA zone. The larger very supersaturated zone in the middle of the study area is associated with a relative high of calcium (115 to 135 mg/L) but concentrations of bicarbonate are no different relative to surrounding areas.

Numerous areas in the east, including a small central SBA zone, and west have groundwaters that are slightly supersaturated with respect to calcite (0.424 to 0.620). The far northwestern zone is identified by a high of bicarbonate (240 to 260 mg/L) but has calcium concentrations no different relative to surrounding areas. The northeastern and SBA zones are identified by a low of calcium (less than 40 mg/L) and bicarbonate (less than 160 mg/L). The remaining slightly supersaturated zones have calcium concentrations no different relative to surrounding areas. The middle and southwestern slightly supersaturated zones correlate to a high of bicarbonate (400 to 420 mg/L). A very undersaturated zone (-1.970 to -0.424) is found in the west and corresponds to a low of calcium (less than 20 mg/L), while bicarbonate concentration levels are no different relative to surrounding areas. Two zones, one in the center of the SBA and one in the western SBA, are slightly undersaturated (-1.200 to -0.424) but have bicarbonate levels no different relative to surrounding areas. The westernmost SBA zone corresponds to a low of calcium concentrations (less than 20 mg/L), but the other SBA zone has calcium levels no different relative to surrounding areas. The rest of the study area is saturated with respect to calcite (-0.424 to 0.424).

In the 551 to 600 feet slice calcite saturation indices range from -1.200 to 1.343 (Figure 33g). A zone of slightly undersaturated SIs (-1.200 to -0.424) is found just west of the SBA. This undersaturated zone is associated with a low of calcium (less than 20 mg/L) but has bicarbonate concentrations no different relative to surrounding areas (Figure 26g and Figure 29g). Two zones of highly supersaturated waters (0.424 to 1.343) are found, one just north of the SBA and the other in the western region of the study area. The western zone correlates to a high of bicarbonate (400 420 mg/L) but has calcium concentrations no different relative to surrounding areas. The zone just north of the SBA correlates to a relative low of calcium (70 to 90 mg/L) but has bicarbonate concentrations no different relative to surrounding areas. Most of the study area is saturated with respect to calcite (-0.424 to 0.424).

The 601 to 800 feet interval has a calcite SI range of -1.970 to 1.343 (Figure 33h). Most of the study area is in equilibrium with respect to calcite (-0.424 to 0.424) except for small zones in the northeast and midsoutheast where an undersaturated state is found (-0.424 to 1.343). Most of the southern zones correspond to relatively high levels of bicarbonate (340 to 550 mg/L), while the far northeastern, large southeastern, and far western zones have bicarbonate concentrations no different relative to surrounding areas (Figure 29h). The small slightly supersaturated zone just west of the northeastern zone is correlated to a relative low of bicarbonate (160 to 180 mg/L). The two northernmost southern supersaturated zones correspond to a relative high of calcium (105 to 135 mg/L) (Figure 26h). The other supersaturated zones have calcium concentrations no different relative to surrounding areas. A very undersaturated zone (-1.970 to -1.200) just north of the SBA is associated with a low of calcium (less than 20 mg/L) but has bicarbonate concentrations no different relative to surrounding areas.

The shallowest depth interval distribution (801 feet and greater) has a range of -1.200 to 1.343 (Figure 33i). Most of the study is in the saturated state with respect to calcite (-0.424 to 0.424), but there two small areas, one in the south and one in the north, that are very supersaturated with respect to calcite (0.424 to 1.343). The southern very supersaturated region is analogous to a high of calcium (105 to 115 mg/L) and bicarbonate (420 to 550 mg/L) (Figure 26i and Figure 29i). The northern supersaturated zone is identified by a high of bicarbonate (320 to 340 mg/L) but has calcium concentrations no different relative to surrounding areas. Other zones of slight supersaturation (0.424 to 0.620) are found throughout the midnorthern and southern study area. The southernmost zone in the south corresponds to a high of calcium (115 to 160 mg/L) but has bicarbonate concentrations no different relative to surrounding areas. The other southern zone is identified by a bicarbonate high (400 to 420 mg/L), while having calcium concentrations no different relative to surrounding areas. The midsouthern northern zone corresponds to a low of bicarbonate (160 to 180 mg/L) while having calcium concentrations no different relative to surrounding areas. The other slightly supersaturated areas have calcium and bicarbonate concentrations no different relative to surrounding areas.

Two zones of undersaturated SIs (-1.970 to -0.424) are found on the northern and southeastern borders but have concentrations of bicarbonate no different relative to surrounding areas. The northern zone is indicated by a relative high of calcium (50 to 70 mg/L), and the southern zone is also identified by a high of calcium (90 to 105 mg/L).

Dolomite Saturation States

The lowest 200 feet and less interval has a dolomite saturation range of -2.000 to 0.827 (Figure 34a). A zone of slightly undersaturated waters (-2.00 to -0.827) is found just west and northeast of the SBA. The undersaturated area just west of the SBA corresponds to a relative low of magnesium (40 to 50 mg/L) and bicarbonate (180 to 200 mg/L) but has calcium concentrations no different relative to surrounding areas (Figure 26a, Figure 27a, and Figure 29a). The zone northeast of the SBA is correlated to a relative low of bicarbonate (160 to 180 mg/L) and a high of calcium (300 to 600 mg/L), but has magnesium concentrations no different relative to surrounding areas. The rest of the study area is in the saturated state with respect to dolomite (-0.827 to 0.827).

The 201 to 300 feet slice has a dolomite SI range of -2.000 to 0.827, but almost the entire study area is in equilibrium with respect to dolomite (-0.827 to 0.827) (Figure 34b). A slightly undersaturated zone of dolomite (-2.000 to -0.827) is found on the western border of the SBA and just northwest of the SBA. Lows of calcium (less than 40 mg/L) and magnesium (less than 10 mg/L) and highs of bicarbonate (260 to 280 mg/L) are seen in the western SBA region (Figure 26b, Figure 27b, and Figure 29b). The slightly undersaturated zone northwest of the SBA is analogous to a low of bicarbonate (160 to 180 mg/L) and a relative high of calcium (135 to 160 mg/L) but has concentrations of magnesium no different relative to surrounding areas.

The 301 to 400 feet distribution of dolomite has a range of -4.493 to 1.200 (Figure 34c). Again most of the study area is in the saturated state (-0.827 t0 0.827). A zone of highly undersaturated waters is found in the very middle of the study area (-4.493 to -0.827). This undersaturated zone coincides with lows of magnesium (less than 10 mg/L), calcium (less than 20 mg/L), and bicarbonate (100 to 140 mg/L) (Figure 26c, Figure 27c, and Figure 29c). Just southeast of this undersaturated zone is a slightly supersaturated zone (0.424 to 1.200). This

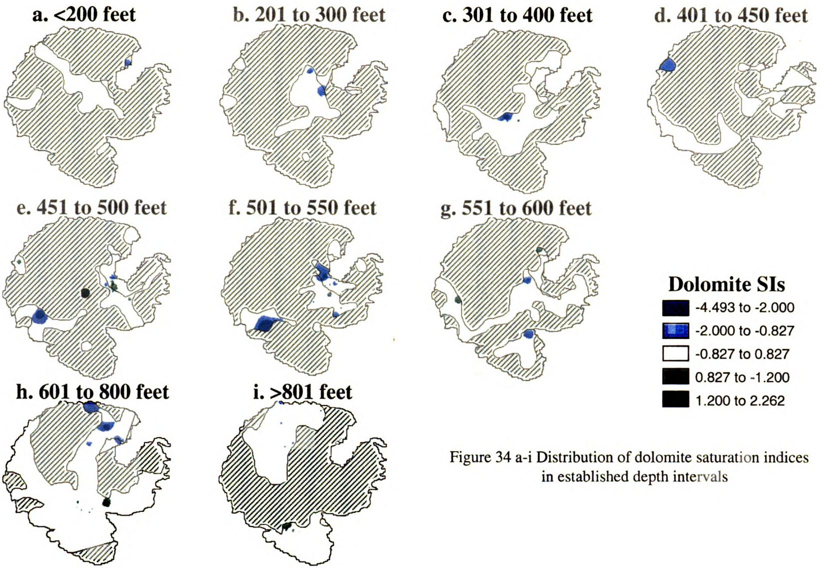


Figure 34 a-i Distribution of dolomite saturation indices in established depth intervals supersaturated zone corresponds to relative highs of calcium (160 to 200 mg/L) and magnesium (40 to 50 mg/L) but has bicarbonate distributions no different relative to surrounding areas.

The 401 to 450 feet slice has levels between -0.827 and 2.262 (Figure 34d). The far northwestern region of the study area is slightly undersaturated (-2.000 to -0.827). This region corresponds to a low of bicarbonate (100 to 140 mg/L) and relative highs of both calcium (300 to 600 mg/L) and magnesium (40 to 50 mg/L) (Figure 26d, Figure 27d, and Figure 29d0. The rest of the study area be in equilibrium with respect to dolomite (-0.827 to 0.827).

The 451 to 500 feet depth interval has a very large dolomite SI range of -4.493 to 1.200 (Figure 34e). A large zone of very undersaturated waters (-4.493 to -0.827) is found in the southwestern study area and the midnorthern part of the SBA. The southwestern zone corresponds to very low concentrations of calcium (less than 20 mg/L) and magnesium (less than 10 mg/L) and a high of bicarbonate (260 to 280 mg/L) (Figure 26e, Figure 27e, and Figure 29e). The SBA undersaturated zone is indicated by a low of magnesium (20 to 30 mg/L) and calcium (70 to 90 mg/L) and a relative high of bicarbonate (180 to 200 mg/L).

Three zones of slightly undersaturated waters (-2.000 to -0.827) are found in the central region of the SBA, the middle, and southeastern region of the study area. The southeastern slightly undersaturated zone corresponds to a high of bicarbonate (400 to 420 mg/L) and a low of both magnesium (less than 10 mg/L) and calcium (less than 20 mg/L). The SBA slightly undersaturated zone is identified by lows of calcium (less than 20 mg/L), magnesium (20 to 30 mg/L), and bicarbonate (100 to 140 mg/L). The small middle zone correlates to a high of calcium (135 to 160 mg/L) and a low of bicarbonate (100 to 140 mg/L) but has magnesium concentrations no different relative to surrounding areas.

Small slightly supersaturated (0.827 to 1.200) zones are found in western SBA, on the western border of the SBA, and just south of the SBA. The western SBA zones correspond to lows of calcium (20 to 40 mg/L) and magnesium (10 to 30 mg/L) and a high of bicarbonate (240 to 260 mg/L). The zone on the western border of the SBA is indicated by a low of bicarbonate

(60 to 100 mg/L) but has magnesium and calcium concentrations no different relative to surrounding areas. The zone just south of the SBA is analogous to a low of calcium (20 to 40 mg/L) and magnesium (less than 10 mg/L) but has bicarbonate levels no different relative to surrounding areas. The remaining regions of the study area are saturated with respect to dolomite (-0.827 to 0.827).

The 501 to 550 feet distribution for dolomite SIs has a range of -4.493 to 2.262 (Figure 34f). A rather large area in the southwest and a zone in the center of the SBA has highly undersaturated waters (-4.493 to -0.827). The southwestern undersaturated area coincides with a low of calcium (less than 20 mg/L) and magnesium (less than 10 mg/L) and a high of bicarbonate(260 to 280 mg/L) (Figure 26f, Figure 27f, and Figure 29f). The SBA very undersaturated zone has calcium and magnesium concentrations no different relative to surrounding areas but correlates to a relative high of bicarbonate (180 to 200 mg/L). A slightly undersaturated zone (-2.000 to -0.827) is seen on the western border of the SBA and is affiliated with lows of calcium (less than 20 mg/L) and magnesium (less than 10 mg/L) but has no effect on bicarbonate chemistry.

Large zones in the middle of the study area and on the western edge of the SBA are very supersaturated (1.200 to 2.262). The western SBA supersaturated zone corresponds to a relative high of bicarbonate (320 to 340 mg/L) and calcium (300 to 600 mg/L) but has magnesium concentrations no different relative to surrounding areas. The large middle very supersaturated zone has bicarbonate or magnesium concentrations no different relative to surrounding areas but is correlated to a relative high of calcium (115 to 135 mg/L). Slightly supersaturated zones (0.827 to 1.200) are found just south of the SBA and in the northwestern part of the study area also. The zone just south of the SBA has a relative high of calcium (40 to 50 mg/L) and bicarbonate (260 to 280 mg/L) but has magnesium levels no different relative to surrounding areas. The northwestern zone corresponds to a high of bicarbonate (260 to 280 mg/L) but has magnesium and calcium concentrations no different relative to surrounding areas. The rest of the study area is in equilibrium with respect to dolomite (-0.827 to 0.827).

The 551 to 600 feet dolomite SI distribution diagram has a range of -4.493 to 1.200 where the majority of the study area is in the saturated state (-0.827 to 0.827) (Figure 34g). A small zone just west of the SBA is in the very undersaturated state (-4.493 to -0.827). This very undersaturated area is associated with a low of calcium (less than 20 mg/L) and magnesium (less than 10 mg/L), while having a relative high of bicarbonate (200 to 240 mg/L) (Figure 26g, Figure 27g, and Figure 29g). A small slightly undersaturated zone (-2.000 to -0.827) is found in the southern region of the study area and corresponds to lows of magnesium (less than 10 mg/L) and calcium (less than 20 mg/L) and a high of bicarbonate (400 to 420 mg/L). Areas in the northeast and west are slightly supersaturated (0.827 to 1.200). The western zone is correlated to a relative high of bicarbonate (400 to 420 mg/L), calcium (50 to 70 mg/L), and magnesium (20 to 30 mg/L). The northeastern slightly supersaturated zone is associated with a relative low of calcium (70 to 90 mg/L) and magnesium (20 to 30 mg/L) but has bicarbonate concentrations no different relative to surrounding areas.

The 601 to 800 feet slice has a range is between -4.493 and 2.262 (Figure 34h). Most of the study area is in the saturated state with respect to dolomite (-0.827 to 0.827). A large zone just north of the SBA is highly undersaturated (-4.493 to -0.827), while slightly undersaturated zones (-1.200 to -0.827) are on the northern border of the SBA and just west-northwest of the SBA. The very undersaturated zone has bicarbonate concentrations no different relative to surrounding areas but is associated with lows of both magnesium (less than 10 mg/L) and calcium (less than 20 mg/L) (Figure 26h, Figure 27h, and Figure 29h). The slightly undersaturated zone just west-northwest of the SBA corresponds to lows of magnesium (less than 10 mg/L), calcium (less than 20 mg/L), and bicarbonate (0 to 60 mg/L). The slightly undersaturated zone in the northern SBA corresponds to a low of calcium (20 to 40 mg/L), magnesium (less than 20 mg/L), and bicarbonate (100 to 140 mg/L).

Areas in the midsouth and the southeast are highly supersaturated (0.827 to 2.262). The midsouthern supersaturated areas correspond to highs of bicarbonate (300 to 420 mg/L) and lows of magnesium (less than 30 mg/L). The westernmost of these supersaturated zones corresponds to a low of calcium (less than 20 mg/L), while the other zones correspond to relative highs of calcium (90 to 105 mg/L). The southeastern supersaturated zone has magnesium concentrations no different relative to surrounding areas but is identified by a relative high of calcium (105 to 115 mg/L) and bicarbonate (400 to 420 mg/L).

The 801 feet and greater dolomite SI distribution has a range of -0.827 to 1.200 (Figure 34i). A large zone in the south, a small zone just south of the larger area in the south, and a small zone in the midnorth is in the slightly supersaturated state (0.827 to 1.200). The large southern supersaturated zone corresponds to relatively high calcium (90 to 115 mg/L), magnesium (30 to 40 mg/L), and bicarbonate (340 to 420 mg/L) levels (Figure 26i, Figure 27i, and Figure 29i). The small southern zone corresponds to a low of magnesium (less than 10 mg/L) and calcium (less than 20 mg/L) and a high of bicarbonate (400 to 420 mg/L). The small northern zone is identified by a high of bicarbonate (260 to 280 mg/L) but has calcium and magnesium concentrations no different relative to surrounding areas.

Numerous zones in the northern region are slightly undersaturated with respect to dolomite (-2000 to -0.827). Only the southernmost of these zones has a relative low of calcium (40 to 50 mg/L), but the rest of the zones have calcium levels no different relative to surrounding areas. Magnesium levels no different relative to surrounding areas are seen in the slightly undersaturated zones. A low of bicarbonate (140 to 160 mg/L) is associated with both the midnorthern and northernmost zones. The mideastern zone is correlated with a bicarbonate high (320 to 340 mg/L). A bicarbonate high is also seen in the northeastern zone (180 to 200 mg/L). The rest of the study area is in the saturated state with respect to dolomite (-0.827 to 0.827).

Gypsum Saturation States

The 200 feet and less slice has a gypsum SI range of -6.980 to 0.229 (Figure 35a). The center of the study area is highly undersaturated (-6.980 to -1.500), while a northwestern zone is slightly undersaturated (-4.000 to -1.500). The middle highly undersaturated zone is indicated by a low of calcium (less than 200 mg/L) but has sulfate concentration no different relative to surrounding areas (Figure 26a and Figure 28a). The northwestern slightly undersaturated zone corresponds to a low of calcium (20 to 50 mg/L) and sulfate (less than 15 mg/L).

A large southeastern area, the entire western border, and a few zones in the midnorthern region of the study area are saturated with respect to gypsum (-0.229 to 0.229). All these saturated areas except for a small zone, with respect to sulfate, in the midsouthern region of the study area correspond to highs of both calcium (600 to 4,000 mg/L in the eastern zones and 20,000 to greater than 40,000 mg/L in the western zones) and sulfate (1,000 to 3,500 mg/L in the eastern zones and 200 to 300 mg/L in the western zones). The small midsouthern zone corresponds to a relative low of sulfate (100 to 150 mg/L). The rest of the study area is in the slightly undersaturated state (-1.500 to -0.229) but has calcium and sulfate levels no different relative to surrounding areas.

The 201 to 300 feet distribution diagram for gypsum SIs has a range of -4.000 to 0.229 (Figure 35b). Zones of saturation (-0.229 to 0.229) are found in the northwest, southwest, and southeast. All three zones correspond to highs of calcium (300 to 4,000 mg/L) and sulfate (1,000 to 4,000 mg/L) (Figure 26b and Figure 28b). Areas in the west, midsouth, SBA, and surrounding SBA are fairly supersaturated with respect to gypsum (-4.000 to -1.5000). These fairly supersaturated waters correspond to lows of both calcium (less than 40 mg/L) and sulfate (less than 100 mg/L). An exception is seen in the west with respect to sulfate where only slightly lower concentrations are seen (200 to 300 mg/L). The rest of the study area is known to be in the slightly undersaturated state with respect to gypsum (-1.500 to -0.229). These slightly

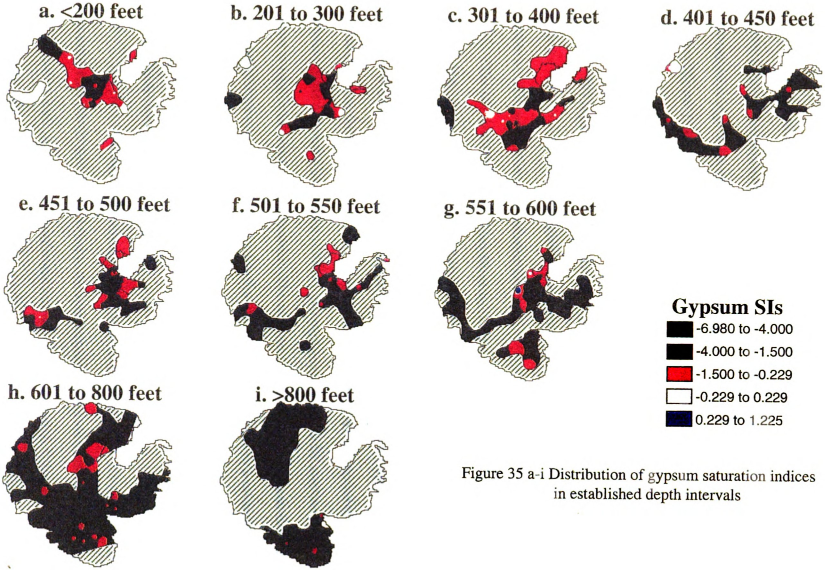


Figure 35 a-i Distribution of gypsum saturation indices in established depth intervals supersaturated zones have calcium and sulfate concentrations no different relative to surrounding areas.

The 301 to 400 feet interval has a range of -4.000 to 0.229 with saturated zones (-0.229 to 0.229) in the midwestern and southeastern regions of the study area (Figure 35c). These areas correspond to high levels of calcium (300 to 4,000 mg/L) and sulfate (1,000 to 4,000 mg/L) (Figure 26c and Figure 28c). Large zones in the midsouth, far west, SBA, and just east and west of the SBA are fairly undersaturated with respect to gypsum (-4.00 to -1.500). These undersaturated areas are associated with low levels of calcium (less than 200 mg/L) and sulfate (less than 100 mg/L). The rest of the study area is in the undersaturated state also, but to a lesser degree (-0.229 to -1.500). These slightly supersaturated areas have concentrations of calcium or sulfate no different relative to surrounding areas.

The 401 to 450 feet interval has the same range as the previous two slices (-4.00 to 0.229) (Figure 35d). An area of saturation (-0.229 to 0.229) is found in the northwest and is identified by high concentration zones of calcium (300 to 600 mg/L) and sulfate (1,000 to 3,500 mg/L) (Figure 26d and Figure 28d). Slightly undersaturated zones (-1.500 to -0.229) are found along the northern border, far west, south, and just west of the SBA. These areas correspond to highs of calcium (90 to 600 mg/L) and sulfate (100 to 1,000 mg/L) except for the far southern and eastern zones in regards to calcium concentrations. The southern zone has calcium concentrations no different relative to surrounding areas, while the eastern zone is identified by a calcium low (less than 20 mg/L). The rest of the study area is in a fairly supersaturated state (-4.000 to -1.500). Relative lows of both calcium (less than 90 mg/L) and sulfate (less than 100 mg/L) are identified in these fairly supersaturated groundwaters.

The 451 to 500 feet slice has a range of -4.00 to 0.229 (Figure 35e). The same small saturated zone (-0.229 to 0.229) is found in the western region of the study area as seen in the previous slice map. Again this supersaturated zone corresponds to a high of both calcium (600 to 4,000 mg/L) and sulfate (1,000 to 4,000 mg/L) (Figure 26e and Figure 28e). Slightly undersaturated zones (-1.500 to -0.229) are found in the northern and southern SBA, just off the eastern border of the SBA, middle, and far west. These areas are associated with highs of both calcium (115 to 300 mg/L) and sulfate (200 to 1,000 mg/L). Relative lows of calcium (less than 115 mg/L) and sulfate (less than 200 mg/L) are identified in the rest of the study area which have fairly supersaturated waters (-4.000 to -1.500).

The 501 to 550 feet distribution has a range of -4.00 to -0.229 (Figure 35f). Slightly undersaturated zones (-1.500 to -0.229) are found in the northeast, northern and southern SBA, just west and east of the SBA, and far west and east. Overall, these slightly undersaturated zones correspond to highs in calcium (90 to 600 mg/L) and sulfate (100 to 3,500 mg/L) (Figure 26f and Figure 27f). The remainder of the study area is fairly undersaturated (-4.000 to -1.500) with respect to gypsum. Relative lows of both calcium (less than 90 mg/L) and sulfate (less than 100 mg/L) are associated with these areas.

The 551 to 600 feet depth interval has a gypsum SI range of -6.980 to 1.225 (Figure 35g). A zone of supersaturated waters (0.229 to 1.225) is found just west of the SBA. This supersaturated zone is associated with a low of calcium (less than 10 mg/L) and a relative high of sulfate (150 to 200 mg/L) (Figure 26g and Figure 28g). A small saturated zone (-0.229 to 0.229) is found on the western border of the SBA and is analogous to relative highs of both calcium (300 to 600 mg/L) and sulfate (1,000 to 3,500 mg/L). The northern SBA, areas just west of the SBA, and two southern regions are slightly undersaturated (-1.500 to -0.229). These areas are identified by highs of calcium (115 to 600 mg/L) and sulfate (150 to 1,000 mg/L). However, a very low calcium concentration zone (20 to 40 mg/L) and a relatively low sulfate concentration zone (70 to 80 mg/L) are found in the western SBA zone. Relatively low concentrations of calcium (less than 115 mg/L) and sulfate (less than 150 mg/L) are associated with the remaining study area that is fairly undersaturated with respect to gypsum (-4.000 to -1.500). A southern very supersaturated zone (-6.980 to -4.000) is seen and associated with very low levels of both calcium (less than 20 mg/L) and sulfate (less than 10 mg/L).

The 601 to 800 feet gypsum SI distribution has values ranging from -4.00 to -0.229 (Figure 35h). Numerous areas of slightly undersaturated (-1.500 to -0.229) waters are found in the north, midsouth, west, and east. These zones are associated with high concentrations of both calcium (115 to 300 mg/L) and sulfate (100 to 1,000 mg/L) except for the two westernmost zones (Figure 26h and Figure 28h). The northwestern zone correlates to a low of sulfate (less than 10 mg/L) and only a relative high of calcium (70 to 90 mg/L). The midwestern zone correlates to a relative high of sulfate (70 to 80 mg/L) and a low of calcium (40 to 50 mg/L). Again, the majority of the study area has a fairly undersaturated range of -4.000 to -1.500 and overall can be associated to relative lows of calcium (less than 115 mg/L) and sulfate (less than 100 mg/L).

The uppermost 801 feet and greater slice has a gypsum SI range of -4.000 to -0.229 (Figure 35i). A few small zones in the south are in the slightly supersaturated state with respect to gypsum (-1.500 to -0.229). These zones correlate to highs of both calcium (50 to 80 mg/L) and sulfate (100 to 300 mg/L) (Figure 26i and Figure 28i). The rest of the study area is in the fairly supersaturated state (-4.000 to -1.500) and corresponds to lows of calcium (less than 50 mg/L) and sulfate (less than 100 mg/L).

Quartz Saturation States

The initial 200 feet and less quartz saturation index distribution has a range of 0.199 to greater than 0.800 (Figure 36a). Much of the southeast and some small zones in the midnorth are highly supersaturated with respect to quartz (greater than 0.800). Areas in the south, west, SBA, and areas surrounding the SBA have slightly supersaturated levels of 0.199 to 0.400. The remaining study area is also fairly supersaturated with SIs between 0.400 to 0.800.

The 201 to 300 feet slice has a range of 0.199 to 0.800 (Figure 36b). At this depth most of the center of the study area and a small zone in the western SBA are in the fairly supersaturated state with respect to quartz (0.400 to 0.600). Numerous zones throughout the center of the study area and the southeast are very supersaturated (0.600 to 0.800). The remainder of the study area including the anomalous SBA is in a slightly supersaturated state (0.199 to 0.400).

The 301 to 400 feet depth interval has quartz SIs between 0.199 to 0.800 (Figure 36c). Two zones in the midsouth are in the very supersaturated state with respect to quartz (0.600 to 0.800). The northern and southern SBA, areas just south and west of the SBA, numerous zones in the middle and west are slightly supersaturated (0.199 to 0.400). Much of the study area is in the fairly supersaturated state (0.400 to 0.600).

The 401 to 450 feet quartz saturation index distribution has values that range between 0.199 and 0.800 (Figure 36d). Three zones in the midwest and one in the far northwest are very supersaturated with respect to quartz (0.600 to 0.800). The SBA, surrounding SBA, most of the southeast, and two areas in the west are slightly supersaturated with respect to quartz (0.199 to 0.400). The rest of the study area is in the fairly supersaturated state (0.400 to 0.600).

The 451 to 500 feet quartz SI value range is between -0.199 and 0.800 (Figure 36e). Most of the west, the middle of the study area, and areas east including the eastern part of the SBA are fairly supersaturated (0.400 to 0.600). Areas in the southeast and on the border of the SBA are in the slightly supersaturated state (0.199 to 0.400). A few zones in the west are in the very supersaturated state (0.600 to 0.800). Most of the SBA and a zone just south of the SBA are in the saturated state with respect to quartz (-0.199 to 0.199).

The 501 to 550 feet depth interval has a range of -0.199 to 0.800 (Figure 36f). The middle region of the SBA is in the saturated state (-0.199 to 0.199). Areas on the SBA border and in the south and southeast are in the slightly supersaturated state (0.199 to 0.400). Areas in the western region of the study area are very supersaturated (0.600 to 0.800). The remainder of the study area is in the fairly supersaturated state (0.400 to 0.600).

The 551 to 600 feet slice has quartz saturation index values between -0.199 to 0.800 (Figure 36g). The middle SBA again is saturated with respect to quartz (-0.199 to 0.199). Numerous areas in the south, southeast, and surrounding the saturated area are slightly

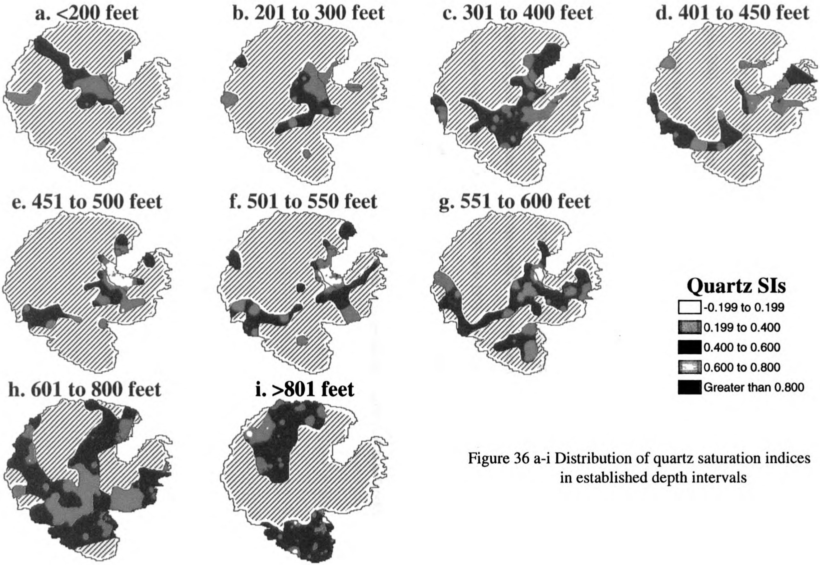


Figure 36 a-i Distribution of quartz saturation indices in established depth intervals supersaturated with respect to quartz (0.199 to 0.400). Areas on the southern border of the SBA, just west of the SBA, south, and west are very supersaturated (0.600 to 0.800). The rest of the study area is in the fairly supersaturated state (0.400 to 0.600).

The 601 to 800 feet quartz saturation index distribution range is between -0.199 to 0.800 (Figure 36h). A small zone in the northwest is saturated with respect to quartz (-0.199 to 0.199). Large areas in the midsouth and southeast are very supersaturated (0.600 to 0.800). Areas along the western, southern, and northeastern borders and just west of the SBA are in the slightly supersaturated state (0.199 to 0.400). The remainder of the study area has fairly supersaturated concentrations of 0.400 to 0.600.

The uppermost 801 feet and greater quartz SI distribution diagram has a range of -0.199 to 0.800 (Figure 36i). Two zones in the south and two zones along the northern border are in equilibrium with respect to quartz (-0.199 to 0.199). Numerous zones in the south and areas along the northern border are in the slightly supersaturated state (0.199 to 0.400). Areas in the southeast and southwest are very supersaturated (0.600 to 0.800). The rest of the northern and southern groundwaters are fairly supersaturated with respect to quartz (0.400 to 0.600).

APPENDIX B

IDRISI MODULES' FUNCTION AND DESCRIPTION

Image and Vector Layers

The operation of the IDRISI spatial analysis program was performed through the use of image and vector layers. Image layers describe a region of space by means of a fine matrix of cells. These cells each contain numeric values that express the nature of the land at that location. Image layers are excellent for describing spatially continuous data such as elevation or in this study for the different depth intervals and aquifer units for the variables in the groundwater system.

Vector layers, on the other hand, are useful for describing distinct features in the landscape. These include features such as the borders and roads. To do so, vector layers store a set of points (each referenced by a pair of location coordinates) that describe either the locations of the features (if they are points), or their course or boundary by means of a sequence of points that are joined by a straight line. Although IDRISI for Windows is adept at the input and display of both image and vector layers, analysis is primarily oriented towards the use of image layers. As a result, it is commonly described as a raster system (i.e., one that describes space by means of raster images) (Eastman, 1995). Vector layers were initially composed through the importation of a space delimited text file through the XYZIDRIS module. In this importation of data, the relevant file was set up in separate columns as such: X, Y, variable (ion concentration or saturation index of a mineral).

INTERPOL Module

In order to compose the image layers from vector files, the INTERPOL module was used. INTERPOL first requires that you specify the interpolation procedure. The digital elevation model was then selected to calculate a potential surface. This option interpolates a Digital Elevation Model by means of a distance-weighted average. The next step requires the input of the name of the vector file containing the point data and a name for the output image to be created (Eastman, 1995). A distance weight exponent was set at two (the default setting), which is commonly chosen, yielding a weight equal to the reciprocal of the distance squared. Then it was indicated that the heights at the control points be specified by using the ID's in the vector file (Eastman, 1995). The interpolation was limited to a 6-point search radius about each interpolated point, and the default was set to use this specified radius.

INTERPOL next required the specification of a data type and file type for the output image and was set to binary. The number of columns and rows was then indicated and used for the region specified in the vector documentation file. This study used 316 for columns and 366 for rows. The minimum and maximum X and Y coordinates then needed input into the file. As the columns and rows were set to maintain consistency in this study, the same coordinates were used: 280,000 (X_{min}), 64,9600 (X_{max}), 89,000 (Y_{min}), and 552,395 (Y_{max}). Finally, through a number of passes performed by the module, an image layer is constructed.

RESAMPLE Module

Due to lack of consistency in the coordinate system for the Marshall aquifer images, the RESAMPLE module was brought into use to reformat the coordinate system. RESAMPLE took a well-distributed set of points about their position in the "old" X-Y coordinate system to take on the "new" UTM system. This information was stored as an ASCII correspondence file (*.cor) in which the first line indicates the number of control points (50) for which the data are being supplied. There then follow as many lines of data as there are points. Each line contains four numbers, separated by spaces. The first two indicate the X and Y coordinates of a point in the old reference system while the last two indicate the coordinates of that same point in the new reference system, i.e. UTM.

In use, RESAMPLE required the input vector file to be resampled (or transformed) and its name. The new name, the reference system (UTM), and the reference units (m) for the output file, as well as the unit distance (the default was set to 1) were indicated. A new background was also instituted into the module; the default was set to 0. This background was used to flag cells in the output file where no corresponding cell was found in the input file. The first order (linear) mapping function was then entered, i.e. the order of polynomial fit desired. This was chosen on the basis that the lowest order of polynomial provides a reasonable solution since the effect of poor control point specification gets dramatically worse as the order of equation used increases. The new minimum and maximum UTM X and Y coordinates of the final output map were then introduced: 280,000 (X_{min}), 649,600 (X_{max}), 89000 (Y_{min}), and 552395 (Y_{max}). Again, these UTM values are the same minimums and maximums used throughout the construction of every map. The process works by moving through each output cell and determining its position within the input vector file to establish an appropriate output value. Once the new vector files for the Marshall aquifer were made, the interpolation process was induced to provide an image file relevant to the new coordinate system.

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