

THESIS



This is to certify that the

thesis entitled

FIELD EVIDENCE FOR SHALE MEMBRANE FILTRATION OF GROUNDWATER, SOUTH-CENTRAL MICHIGAN

presented by

David F. Slayton

has been accepted towards fulfillment of the requirements for

Masters degree in Geology

Grahame J. hannen Waid Rhong Major professor

Date May 21, 1982

O-7639

MSU is an Affirmative Action/Equal Opportunity Institution



FIELD EVIDENCE FOR SHALE MEMBRANE FILTRATION OF GROUNDWATER, SOUTH-CENTRAL MICHIGAN

*

by

David F. Slayton

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Geology

ABSTRACT

FIELD EVIDENCE FOR SHALE MEMBRANE FILTRATION OF GROUNDWATER, SOUTH-CENTRAL MICHIGAN

By

David F. Slayton

Shale membrane filtration is the process that controls the groundwater geochemistry of part of the Saginaw Formation aquifer in south-central Michigan. This process purports that certain rock types such as shales act as semi-permeable membranes which can selectively retard the movement of dissolved ions in a water migrating through the membrane. Based on the recharge information and surficial bedrock lithology, two study areas were chosen in south-central Michigan to test the occurrence of shale membrane filtration in the Saginaw Formation. Tritium analysis of selected wells, in one area, supports the presence of local "point recharge" through sands and gravels to sandstone at the surface of the Saginaw Formation. The other area, based on tritium analysis, does not show the presence of local point recharge.

Ion ratios from bedrock waters in the two study areas were found to increase or decrease relative to each other as would be predicted by shale membrane filtration theory, laboratory experiments, and field studies. Water/rock interactions and mixing with other chemically different waters do not correctly explain the observed ion ratios, or can not explain all the ratios as does shale membrane filtration. Shale membrane filtration best explains the observed geochemistry of Saginaw Formation's waters from the study area where conditions are favorable for the occurrence of membrane filtration.

ACKNOWLEDGEMENTS

Ι wish thesis to thank my master's committee chairmen, Dr. Grahame Larson and Dr. David Long, who gave freely of their time throughout the course of this investigation and were a constant source of encouragement. I also wish to thank Dr. James Trow for serving on my thesis guidance committee and critically reviewing this manuscript. Thanks is offered also to Jim Vanderkloot who helped with sampling and spent many hours assisting me with computer programs. I would also like to thank Mr. Lloyd Ness for collecting rock samples of the Saginaw Formation from Lansing Board of Water and Light water wells.

unise Prozol di estimatione de la servici de la servici

TABLE OF CONTENTS

LIST OF FIGURES	iv
LIST OF TABLES	v
INTRODUCTION	1
Purpose and Scope	1 2
GEOLOGY AND HYDROGEOLOGY OF THE STUDY AREA	6
Coology of the Study Area	,
A guifor Characteristics	0
Aquiter Characteristics	7
Recharge to the Saginaw Pormation	10
Source of Dissolved Solids in Groundwater.	
	4
	16
Interpretation of Tritium Data	6
SHALE MEMBRANE FILTRATION	20
Previous Works - Theoretical	20
Previous Works - Experimental	23
Previous Works - Field Study Example	25
Test of Shale Membrane Filtration Hypothesis in the	
Tri-County Area	77
	-/
METHOD OF ANALYSIS	29
RESULTS AND DISCUSSION	32
Results of Chemical Predictions	36
SO,/HCO,	40
CI/HCO	+2
CI/SO.	13
Ca/Md	14
	15 15
	5)
	10
	¥7
$TDS \dots \dots$	F7
Summary \ldots \ldots \ldots \ldots Summary \ldots \ldots \ldots Summary S	+7
Conclusion	19
BIBLIOGRAPHY	52
APPENDIX	56

LIST OF FIGURES

Figure 1:	Location of Study Area	7
Figure 2:	Generalized Surficial Bedrock Lithology	11
Figure 3:	Location of Study Areas A and B	13
Figure 4:	Wells Analyzed for Tritium Content	15
Figure 5:	Wells Analyzed for Water Chemistry	30
Figure 6:	Generalized Piper Diagram	33

LIST OF TABLES

Table 1:	Tritium Content (T.U.) of Water Wells	17
Table 2:	Water Analysis of Drift and Rock Wells	66
Table 3:	Average Ion Ratios for Drift and Saginaw Fm	37
Table 4:	Average Ion Ratios for Study Areas A and B	38
Table 5:	Comparison of Study Area A and B Ratios	39
Table 6:	Comparison of Another Field Study to This Study	41
Table 7:	Ion Ratios of All Drift and Rock Wells	73
Table 8:	Wells from Study Areas A and B Used for Ion Ratio Comparisons	80

INTRODUCTION

Purpose and Scope

This research tested the hypothesis that shale membrane filtration controls the groundwater geochemistry of the Saginaw Formation in south-central Michigan. Shale membrane filtration (reverse osmosis) is the process whereby certain rock types can selectively remove or retard the movement of ions in water migrating through the formation (White, 1965; Berry, 1969; Hanshaw and Coplin, 1973; Kharaka and Berry, 1973).

The theory of shale membrane filtration states that some geologic formations such as clay and shale can act as semi-permeable membranes. Specifically, if water is forced through the membrane, selective retardation of dissolved ions can occur. However, due to various factors discussed later, certain ions are filtered out or have their movement through the membrane retarded more with respect to other ions. As a result, water on the "input" side would eventually become more concentrated than water on the "output" side in ions that are retarded or could not pass through the membrane. Hence, waters on opposite sides would be chemically different. The working hypothesis of this study is that these differences in chemistry are predictable from experiments, field data, and the general theory of shale membrane filtration. These experimental and field data will be compared with groundwater chemistry data from the Tri-County study area to see if shale membrane filtration can account for the observed groundwater quality.

Previous Investigations

The geology of the Saginaw Formation in the Tri-County area has been described in detail by Kelly (1936), and by Mecenberg (1963). The hydrology of the Saginaw Formation has been studied by Stuart (1945), Firouzian (1963), Wheller (1967), Vanlier and Wheeler (1968), Radfar (1979), and Ritter (1981). In addition, a report by Vanlier (1964) contains a general discussion of the geology, hydrology, and water quality of the Tri-County area. A similar but more detailed report was also done by Vanlier, et al., 1973.

Previous work on the geochemistry of the groundwater in the Saginaw Formation has suggested shale membrane filtration (reverse osmosis) as the best explanation for the observed difference in water chemistry between the bedrock Saginaw Formation and the overlying glacial drift (Wood, 1969, 1976; Vanlier, et al., 1973). Another study by Radfar (1979) studied potential recharge areas using water quality data and concluded that shale membrane filtration was not the controlling process on groundwater chemistry in the Saginaw Formation.

Wood (1976) proposed ion filtration as the explanation for the observed distribution of dissolved solids in the Saginaw Formation aquifer. The 1976 paper hypothesized that shale beds in the Saginaw Formation act as ion filters that allow water of lower dissolved-solids content to pass through, into sandstone of the aquifer. Although the Kharaka and Berry (1973) paper was cited, the retardation sequences presented are not used, and Wood assumed all ions are filtered nearly the same. As well, when comparing chemical data, Wood does not use ion ratios, only individual ions total dissolved amount. The comparisons were only between drift water and Saginaw Formation water (in which only 4 of 9 parameters measured to test the hypothesis were accepted at 10% level of significance), and between wells cased in sandstone versus wells cased in shale (in which comparison only 3 of 9 hypothesis were accepted at 10% level of significance). Additionally, the retardation sequences quoted by Wood (1976) from Kharaka and Berry (1973) are general sequences, not specific for membrane composition. Wood also states that point recharge is not likely to control the water composition. However, tritium analyses for this study, and Ritter's (1981) indicate that point recharge areas exist, and therefore cannot be ruled out as a control of bedrock water chemistry. Thus, if Wood makes comparisons by averaging all Saginaw Formation wells regardless of location, point recharge and shaley areas are mixed, potentially masking any filtering in the shaley areas. Nevertheless, the data collected can be interpreted to indicate that the groundwater chemistry of the Saginaw Formation is controlled by shale membrane filtration.

This study goes farther since two distinct study areas were chosen in the bedrock, one favorable for filtration, and the other not favorable (point recharge areas). These two distinct areas were compared as well as drift to bedrock water. It is better to compare a dominantly shaley area to a dominantly sandstone area. Secondly, ion ratios were used for comparisons, otherwise a simple dilution model could explain the lower dissolved-solids content of the bedrock. These ratios are a more sensitive measure of a change in chemistry. This study used retardation sequences with ions being "filtered" or retarded to different degrees, not all the same. Additionally, this study used retardation sequences specific for the membrane composition (shale) found in the Saginaw Formation aquifer.

This research is important because shale membrane filtration has not been verified in this or any other shallow aquifer system. The research will be presented along the following lines.

The first section of this study will look at the geology and hydraulics of sandstone and drift in the study area, and will attempt to confirm suspected

recharge areas within the Tri-County region. For example, previous studies (Larson, 1979; Ritter, 1980) have suggested areas where recharge is likely to occur to the bedrock Saginaw Formation. In this study, measurement of tritium levels will be used to substantiate Larson's study (1979), and to confirm suspected recharge into the bedrock. Obviously these areas would not be good for shale membrane filtration since the presence of shales is a prerequisite for filtration. High rates of recharge would imply no shales at the surface of the bedrock acting as aquitards.

The second section will present the theory of shale membrane filtration. Previous field and experimental data regarding shale membrane filtration will be discussed, and predictions concerning groundwater chemistry will be made. A field example of possible shale membrane filtration will also be discussed to see how it compares with experimental lab data, and to determine if experimental predictions might be modified under actual field conditions.

The third section will detail what analysis procedures were used to analyze groundwater samples for various ions. Also explained is the computer modeling done to describe the groundwater chemistry. These data are then compared with theoretical predictions using chemical equilibrium analysis of groundwater from the Saginaw Formation and from the glacial overburden. The chemical compositions of waters from the input (drift) and output side (Saginaw Formation) will be determined, and computer compilation and data reduction processes will be done to determine dissolved ion ratios and equilibrium conditions. Selected ratios will be compared to trends based on shale membrane filtration lab experiments and field data. For example, the following ratios should increase in groundwater if shale membrane filtration is occurring: SO_{μ}/HCO_{3} , Cl/HCO₃, Ca/Na.

The fourth section will present the results of the computer modeling and one other water analysis procedure, the Piper diagram. The data will be presented and compared to the predictions from shale membrane filtration theory, lab experiments, and field studies.

GEOLOGY AND HYDROGEOLOGY OF THE STUDY AREA

The study area shown in Figure 1 is located in the Michigan Basin, slightly south of the center of the basin. This basin contains about 14,000 feet of Paleozoic age sediments at the deepest point, plus some thin and scattered sediments of Mesozoic age. All periods of the Paleozoic are represented in the basin with the exception of the Permian. The sedimentary rocks forming the basin have the characteristic outcrop pattern, with beds dipping toward the center of the basin at about one degree. The bedrock in most places is also covered by drift of Pleistocene age, ranging from a few feet to over 1,000 feet thick.

Geology of Study Area

The surficial deposits in the study area consist of unconsolidated glacial deposits of Pleistocene age. These deposits are generally 50 to 200 feet thick (Vanlier, et al., 1973), and are very complex. They fall into three broad categories: 1) outwash, kames, eskers, 2) glacial lake deposits, and 3) till. The outwash, kames, and eskers are composed of well-sorted mixtures of sand, silt, and gravel. This type of deposit is the best and most widely used as a water source of the glacial deposits. The glacial lake deposits are generally layered sequences of sand, silt, and clay. The glacial till, on the other hand, consists mostly of unsorted and unstratified mixtures of sand, silt, clay, and gravels.

Except for southwestern Eaton County where Mississippian sediments occur, and in northern Clinton County where the younger Pennsylvanian age Grand River Formation is present, the bedrock directly underlying the study area is the Pennslyvanian age Saginaw Formation (Kelly, 1936). The Grand River

£



FIGURE 1: LOCATION OF STUDY AREA IN CLINTON, EATON, AND INGHAM COUNTIES

7

LOWER PENNINSULA OF MICHIGAN

Formation is primarily a sandstone and apparently was deposited on an erosional surface of the Saginaw Formation. It is usually distinguished from the Saginaw Formation by its red color. The Grand River and Saginaw Formation are considered one complex aquifer (Vanlier, et al., 1973).

The Saginaw Formation, the principal aquifer in the area, consists predominantly of sandstone and shale beds, but also includes minor coal and limestone beds. Both the sandstone and shale beds tend to be non-persistent and lenticular, and most layers are generally no more than 20 feet thick. However, in the Lansing area, some of the sandstone beds are as much as 300 feet thick (Kelly, 1936). The sandstones are composed chiefly of fine grained quartz grains, with abundant light colored mica, and are cemented with silica and calcium carbonate. Many of the sandstones also contain minor beds of coal and fossil plant fragments.

The term shale seems to be used by drillers in the area for anything they do not consider sandstone, coal, or limestone (Wood, 1969). Thus "shale" may signify in some cases siltstone or underclay as well as shale. Wood (1969) analyzed two samples of shale taken from a quarry in Grand Ledge where the Saginaw Formation crops out. Results of examination of the clay fraction in the samples (less than 2 microns) showed that they are composed primarily of three types of clays. Sample A was a black fissile shale with a cation exchange capacity of 67.7 meq/100 gr. for calcium/magnesium, and 52 meq/gr. for K/NH₄. Sample B was a light brown siltstone to shale with a cation exchange capcity of 65.5 meq/100 gr. for Ca/Mg, and 48 meq/100 gr. for K/NH₄. The sample's clay fraction consisted of the following:

<u>A</u>		<u>B</u>
59%	Kaolinite	42%
30%	Illite	46%
11%	Vermiculite	12%

Coal was the main reason that the Saginaw Formation was first studied, but it is rarely reported in well logs in the Tri-County area. Limestone occasionally appears on well logs, but it is usually quite thin (less than 2 feet thick).

Aquifer Characteristics

The origin of the water in the drift and Saginaw Formation is precipitation, which averages about 31 inches per year. According to U.S.G.S. records (1968), stream runoff averages about 7.6 inches per year. Wood (1969) states that the difference, about 23.4 inches, is the approximate loss per year to evapotranspiration. Of the 7.6 inches that comprises stream runoff, it was found by graphical methods that 58%, or 4.1 inches, was derived from groundwater sources (Wood, 1969).

Pump tests and water level data from wells throughout the study area indicate that the Saginaw Formation acts as a leaky artesian system over most of the area. Wheeler (1967) estimated the average value of leakage between the drift and the Saginaw Formation to be approximately 0.0012 gpd per square foot under existing head conditions. This value represents leakage before extensive pumping in the Lansing Metropolitan area. The many pumping tests indicate the sandstone of the Saginaw Formation has a permeability of about 100 gpd per square foot, and that the shales are more variable with permeabilities ranging from 0.01 to 1.0 gpd per square foot (Wood, 1969). The transmissibility of the formation is about 23,000 gpd/ft (Stewart, 1945; Firouzian, 1963).

Assuming steady-state groundwater conditions, Wood (1969) estimated that one-seventh (1/7) of the water in a stream under base flow is from the Saginaw Formation, with the remaining water coming from the overlying drift. Also, the piezometric surface of the Saginaw aquifer seems to be a smoothed reflection of the surface topography, suggesting a hydrologic connection between the glacial drift and bedrock.

The Saginaw Formation is confined below by the Bayport Formation which is a dense limestone approximately 40 feet thick. This formation acts as a base to the flow system in the Saginaw Formation; it also prevents all but small quantities of water from entering the Saginaw Formation from below (Wood, 1969). Some contamination of the Saginaw aquifer, however, has been documented from water originating in underlying formations, but it usually is associated with abandoned, poorly cased and sealed mineral water wells that allow leakage of salt water from lower formations (Wood, 1969). The Bayport Formation directly underlies the glacial drift in southwestern and extreme western Eaton County. Since the aquifer in this area is composed almost entirely of limestone, it was not considered in this study.

In summary, precipitation is the source of water for the Saginaw Formation which receives recharge water through the overlying drift. The pattern of flow is dependent on topography, formation thickness, and permeability contrasts (Wood, 1969). The Bayport limestone acts as a base to the Saginaw system, retarding flow into, and out of the Saginaw Formation from below.

Recharge to the Saginaw Formation

Figure 2 is a bedrock map of the southeast part of the Tri-County area. The map shows that eastern Ingham County is underlain predominantly by shale, whereas western Ingham and eastern Eaton County is underlain predominantly by sandstone. Figure 2 also shows various areas which are favorable for rapid recharge to Saginaw Formation sandstone through sands and gravels in the drift. All of these areas occur in western Ingham and eastern Eaton Counties (Larson, 1979; Vanlier, et al., 1973), and would indicate areas where shale membrane filtration would not be operating. Therefore, on the basis of lithology, two study





SHALE

RECHARGE AREA

areas were selected (Figure 3). One area (study area A) is assumed to have slow recharge rates and to favor shale membrane filtration, and the other (study area B) is assumed to have high recharge rates and be an area where filtration would not occur.

Source of Dissolved Solids in Groundwater

The water chemistry of the Saginaw aquifer is dependent on the source, distribution, and movement of water. Thus to understand the water chemistry, the source of recharge water must be identified, the chemistry of the recharge water should be known, the source of dissolved ions should be determined, and the interaction between the water and aquifer materials should be understood.

According to Wood (1969), precipitation is not a major source of dissolved solids in the water from the Saginaw aquifer. The only ion that precipitation may contribute in significant quantities is chloride. Other ions are present in precipitation, but their very low concentration cannot account for the observed concentrations found in groundwater from the Saginaw Formation and glacial drift.

Since recharge to the Saginaw Formation is through the overlying drift, the drift would be the next obvious potential source of dissolved solids. According to an experiment by Wood (1969), water leached from samples of soil-glacial material after standing 5 to 7 days was similar to the ion composition of water obtained from the drift and Saginaw Formation. The results of the experiment showed that most of the dissolved ions probably were dissolved from glacial drift, and that much of the calcium and sulphate was probably derived from solution of detrital gypsum in the drift. Wood also states that the sulphate is not due to the oxidation of sulfide minerals because there is a one-to-one relationship between sulphate and non-carbonate hardness, and that the major source of calcium, magnesium, and bicarbonate appears to be from the reaction



Point Recharge model study area B

of carbonic acid with limestone and dolomite in the drift. Chloride and sodium probably come from the solution of halite, with some sodium contributed by ion exchange with clay minerals.

Leaching experiments were also performed by Wood (1969) on rock samples of the Saginaw Formation, and produced very small concentrations of dissolved solids in the leachate. The results of the experiments show that some sodium, however, might be contributed by the Saginaw Formation through cation exchange in shales. Also, the underlying Michigan Formation does not appear to contribute dissolved solids, as the formations (Michigan and Bayport) do not seem to be hydraulically connected to the Saginaw aquifer. This is also supported by chemical analyses of the Saginaw and Michigan Formations' waters since they are chemically different. If water from the Michigan Formation did migrate into the Saginaw and contribute dissolved ions, it would change the chemistry or composition of the Saginaw, and this phenomenon is not observed.

Tritium in the Groundwater

By analyzing for tritium content of water from the Saginaw Formation, the relative age of the water can be determined, and can provide an estimate of the rate of recharge to the bedrock. Groundwater samples were collected from domestic water supply wells in the drift and bedrock aquifers. One set of samples came from study area "B" near Eaton Rapids where a study by Larson (1979) located several potential recharge areas to the bedrock aquifer through sands and gravels. Other samples from wells came from study area "A" near Williamston, and a shaley area in Clinton County where recharge to the bedrock may pass through a shale. Figure 4 shows the location of wells sampled for tritium content.



FIGURE 4: LOCATION OF WELLS SAMPLED FOR TRITIUM STUDY

• ROCK WELL

[•] DRIFT WELL

Tritium Data

The tritium content of groundwater analyzed for this study ranged from 0.0 T.U. to 118 T.U. Two samples were analyzed three times to check reproducability. One of the samples (Avery) averaged 60.8 T.U. with a standard deviation of 5.04, while the other (Herriff) averaged 71.6 T.U. with a standard deviation of 3.61 (see Table A, Appendix). The results of tritium analyses are summarized in Table 1. "T.U." stands for tritium unit, a standard unit of measure for tritium content where 1 T.U. = 1 tritium atom for every 1 x 10¹⁸ hydrogen atoms.

Interpretation of Tritium Data

The average tritium content of water from 23 wells tapping the bedrock Saginaw Formation is about 18 T.U., while water from 7 drift wells averaged about 25 T.U. Thus, the water from the drift seems to contain more tritium, and hence appears to be relatively younger. This would be expected since the drift receives recharge directly from precipitation, which today contains approximately 20-45 T.U.

There appears to be no apparent correlation between tritium content and depth of well; this probably reflects the complexity of both the drift and bedrock aquifers. It appears that the tritium content depends on the aquifer's complexity, depth, and degree of interconnection with surface or rain water recharge. One area that directly shows younger drift water over older bedrock water, separated by shale, is in Bath (05N01W). Here a drift well 79 feet deep contained 17 T.U., whereas three nearby rock wells completed below the shale in sandstone (200, 260, and 425 feet deep, respectively) all contained 0.0 T.U. Other pairs of wells (drift and rock well close together) in the study area also indicate that water in the drift is relatively younger than in the bedrock. One pair, 01N03W27CC (drift) and 01N03W28DD (rock) contained 14 T.U. and 6 T.U.,

TABLE 1: Location number consists of township, range, section, and quarter, with the largest quarter given first. The quarters are divided with A = northeast, B = northwest, C = southwest, and D = southeast.

TRITIUM DATA

Precipitation				
Date	<u>T.U.</u>			
Dec. 1979	42.9 ± 8.4	4		
Jan. 1980	43.1 ± 6.	2		
Mar. 1980	34-4 ± 7-	- 7		
Apr. 1980	22.8 ± 8.9	9		
May 1980	26.3 ± 5.	6		
Surface Water				
Grand River	54.9 ± 5.0	9		
Red Cedar	47.0 ± 6.	5		
Groundwater		Depth		
Drift Wells	Location	(feet)	<u>T.U</u>	<u>.</u>
Bath	05N01W28CA	79	17.6 ±	7.4
Wilson	01N03W27CC	121	14.2 ±	8.8
Maxev	02N03W12CC		68.2 ±	9.1
Iverson	03N01E33AB	25	21.5 ±	5.1
Roadside park	04N01E29BC	-	52.2 ±	5.5
Smithville dam	01N03W02DB	-	1.2 ±	6.5*
Geyer	04N01E26AA	-	1.9 ±	4.9*
Rock Wells				
Bath townhall	05N01W20AC	425	0.0 ±	6.3
Bath	05N01W28BA	200	0.0 ±	7.1
Bath	05N01W20BB	260	0.0 ±	5.6
Johnson	02N02W30BC	196	3.4 ±	7.2
Avery	02N02W06BD	-	57.1 ±	8.6
Herriff	02N02W20AB	150	69. 1 ±	8.2
Listing	02N02W20DC	139	6.7 ±	9.3
Hartenburg	01N02W06BC	115	64.3 ±	8.6
Topliff	02N02W20BB	-	27.1 ±	8.4
Allen	02N02W18CC	216	4.0 ±	7.2
M.S.U. tap water	04N01W	-	8.9 ±	7.6
Maxey	02N03W12CC	-	118.2 1	= 15.7
Church	02N03W27DA	100	2.0 4	6.9
Kowalski	02N03W12AD	120	0.0 ±	8.5
SR 8	03N01W06BD	89	19.2 ±	7.9
Battley	01N03W28DD	137	5.9 ±	6.7
Ness (Ĺ.)	03N03W34CC	155	2.6 ±	5.4
Ness (R.)	03N03W30CC	60	18.4 ±	5.3
Iverson	03N01E33AB	186	1.9 ±	3.8
Williamston. citv	03N01E02	200	7.7	3.3
Chubb	03N01E33AB		0.4	3.9
Hayes	04N01E27BA	-	13.1 4	2.8
Shaulis	04N01E26AA	240	4.2	2.9

* May be rock wells, no logs available, assumed to be drift.

respectively. Another pair (03N01E33AB) separated by shale showed 21.5 T.U. in drift water, and 1.9 T.U. in bedrock water.

Four of the bedrock wells tested contained 0.0 T.U.'s, and three contained 2.0 T.U.'s or less. All of these wells were either deep, or in areas where the surface of the bedrock contained shale. The highest values of tritium came from wells in areas where the geologic conditions favor rapid recharge to the bedrock aquifer (study area B). Figure 4 shows the location of wells sampled for tritium, and Figure 3 shows the location of areas where conditions are favorable for rapid recharge. Comparison of the two figures clearly shows that the proposed rapid recharge area (study area B) has the highest tritium levels in the bedrock. Bedrock wells from study area "A" averaged 5.5 T.U., and bedrock wells from study area "B" averaged 35.2 T.U.

Ritter (1980) also analyzed the tritium content of water samples from wells in Meridian Township, which is thought to be a recharge area to the Saginaw Formation. Ritter's study generally shows higher tritium content in rock wells close to where sands and gravels directly overlie sandstone than in wells further distant. This suggests that areas where the drift consists chiefly of sand and gravel in contact with sandstone of the Saginaw Formation do indeed transmit water readily to the bedrock.

Some rock wells in shaley areas near Williamston contain some tritium, but generally in very low levels. These wells tap sandstones below a layer of shale that acts as an aquitard. Thus, descending water must pass either through the shale or fractures in the shale. This is probably the path of recharge to the bedrock since there are no areas characterized by sand and gravel lying directly over sandstone. In addition, tritium values in the aquifer are low, which does not support the occurrence of rapid recharge. The presence of some tritium, however, suggest slow leakage downward through the shale. In conclusion, tritium levels suggest that select areas located by lithologic considerations do seem to be rapidly recharging water to the Saginaw Formation since wells in these areas (particularly study area B) are relatively higher in tritium content. On the other hand, in the shale membrane filtration area (study area A), tritium levels and subsurface geology do not indicate any rapid recharge system and thus recharge to the Saginaw Formation is probably slow through the shales present at the surface of the bedrock. The levels of tritium in study area A, however, do suggest some recharge is occurring, although it is much slower than in study area B.

SHALE MEMBRANE FILTRATION

Previous Works - Theoretical

The process of osmosis occurs when two chemically different solutions are separated by a semi-permeable membrane which allows the passage of water. A chemical potential difference across the membrane is created. The net movement of water will be from the low concentration side to the high concentration side. This water movement causes an increase in pressure on the high concentration side, with the pressure differential across the membrane known as the osmotic pressure. When the osmotic pressure equals the chemical potential difference, the flow of water will cease.

The process of reverse osmosis occurs if a hydraulic pressure greater than the osmotic pressure is applied to the high concentration side of a membrane. Water will then be forced through the membrane in the direction opposite to osmosis flow.

Reverse osmosis is called shale membrane filtration when the semipermeable membrane involved is shale (Toerell, 1935; Meyers and Sievers, 1936). Other early papers suggesting that clays and shales act as membranes include Schlumberger, et al., 1933; Russell, 1933; Mackay, 1946; De Sitter, 1947; Korzhinskii, 1947; Wyllie, 1948, 1949, 1951, 1955; White, 1957; and others. An extensive review on the subject is found in Berry, 1969.

There is substantial evidence that clays and shales act as semi-permeable membranes, due to the negative electric charges on the clay particles (Kharaka and Berry, 1973). The negative electrical sites on the surface and edges of clay particles are caused by 1) substitution of lower valence cations for higher valence cations such as Al^{+3} and Si^{+4} , 2) broken bonds along clay particle edges,

3) removal of the hydrogen from an exposed hydroxyl group and its replacement by an exchangeable cation, and 4) under certain conditions, structural cations other than H^+ become exchangeable (Kharaka and Berry, 1973).

Hanshaw and Coplin (1973) demonstrated that anions, such as CI^- and SO_4 , are excluded from passing through a clay by a layer at the surface of the clay particle known as the Gouy-Chapman double layer. Electrostatic forces attract cations to the negatively charged clay platelet, and repel anions. This forms a "diffuse layer" between the clay platelet and the equilibrium solution in which the concentrations of cations is higher than in the equilibrium solution. The diffuse layer and the negatively charged clay surface form the Gouy-Chapman double layer. With compaction of a clay sediment, the particles of clay are brought closer together, which causes the double layers of the particles to overlap. This lowers the concentration of the anions in the pore solution since they are repelled by the negative charge on the clay surface. This anion exclusion is responsible for the membrane properties of clays and shales (Kharaka and Berry, 1973).

The flow of ions through a geologic membrane is a function of the following: 1) the concentration of the ion in the pore solution, 2) the water velocity through the membrane, 3) the electrical interaction of the ion with the negative sites on the clay particles, and 4) the electrical interaction of the ion with the "streaming potential". The streaming potential is caused by the displacement of the double layer (composed mostly of cations) by water movement through the membrane. Since the cations are displaced, some negative sites on clay particles would be exposed, and cations that were associated with the negative sites would be displaced toward the direction of water flow. The effect is the retardation of cation flow within the membrane due to attraction with exposed negative sites on clay particles and repulsion by

the cations previously associated with the negative sites. The same phenomena causes the acceleration of the flow of anions within the membrane. An overall effect of this potential is to cause the concentration of anions and the concentration of solutes to be greater in the effluent solution than its concentration in the pore fluid (Kharaka and Berry, 1973).

The efficiency of a geologic membrane in retarding the flow of dissolved 1) the temperature of surrounding solutions, 2) the ions is dependent on: composition of the membrane, 3) water velocity through the membrane, and 4) the ionic strength of the solution. Membrane efficiency decreases with higher temperature of the solutions, and is attributed to two factors. The first is that flow rates are higher because of lower water viscosity, and higher flow rates cause a decrease in efficiency (Milne, et al., 1964) since ions are propelled through the membrane faster. The second reason is that ionic association usually increases at higher temperatures, and complexing may affect the charge and hydrated radius of ions which in turn primarily control selective adsorption of cations by clays. Increasing ion complexing would mean more neutral ion complexes in the solution which would decrease the liklihood that the ion complex would be adsorbed. McKelvey and Milne (1962), Milne, et al. (1964), and Kharaka (1973) show that the geologic membrane's efficiency increases as the hydraulic-pressure gradient decreases. This is important since hydraulicpressure gradients ued in the experiments are much higher than those found in field situations. Thus the lower hydraulic-pressure gradient in the field should mean an increase in a geologic membrane's efficiency over laboratory experiments. In summary, low temperature, low flow rate, low ionic strength, and high cation exchange capacity increases the efficiency of the membrane.

Kharaka and Berry (1973) predicted a retardation sequence for ions based on ionic charge, hydrated radii, and hydraulic drag. Higher ionic charge and larger hydrated ionic radii should increase the degree of electrical interaction between ions and the membrane which would increase retardation of the Ion. Hydraulic drag is the force flowing water has on dissolved ions in solution, propelling them in the direction of flow. Increasing hydraulic drag should decrease retardation on an ion because the ion would be propelled through the membrane faster. The retardation sequences as a function of increasing retardation by a membrane predicted by Kharaka and Berry (1973) were as follows:

monovalent cations	Li < Na < K < NH ₄ < Rb < Cs
divalent cations	Mg < Ca < Sr < Ba
anions	HCO ₃ < I < B < SO ₄ < Cl < Br

The sequences mean, for example, that for anions the HCO_3 ion is retarded the least from flowing through the membrane in comparison with other anions.

Previous Works - Experimental

Evidence that shales could act as semi-permeable membranes was presented by Wyllie (1948), who measured the electric potential developed across a shale separating NaCl solutions of unequal concentrations. Osmotic pressures were measured across compacted shale samples separating different solutions by Kemper, 1961, and young and Low, 1965.

The first filtration experiments using geologic membranes were conducted by McKelvey and Milne (1962) who forced different concentrations of NaCl solution through bentonite and shale under 10,000 psi compaction pressure. The ratio of input to output concentration of ions, called the filtration ratio, was reported as high as 8 with bentonite, and 1.7 with shale. McKelvey and Milne (1962), and Milne, et al. (1964) further showed that the filtration ratios increased (membrane efficiency increased) with a decrease of the input fluid pressure. Hanshaw (1962), and Hanshaw and Coplen (1973) also studied the filtration of NaCl solutions by using montmorillonite and illite membranes, and reported a good agreement between the filtration ratios and those ratios predicted from experimental studies, with filtration ratios increasing with solutions of lower salinity. Kharaka and Berry (1973) studied the flow of artificial sea water and chloride solutions of alkali and alkaline earth metals through compacted bentonite, illite, and shale samples. These are important studies in that Kharaka and Berry first used solutions similar to what may be expected in the field, not just NaCl solutions. The investigations by Kharaka and Berry (1973) confirmed trends established in previous works, confirmed their own theoretical predictions, showed that the efficiency of a membrane increased with increased compaction pressure, and that geologic membranes are specific in that the retardation sequences of dissolved species are different depending on the experimental conditions (temperature, pressure) and the composition of the membrane.

The experimental filtration ratios obtained in the study by Kharaka and Berry (1973) generally are the same as the qualitative predictions, and also about the same as filtration ratios from field studies. The retardation sequence obtained for monovalent cations in the 1973 study by Kharaka and Berry using bentonite is:

$$Li < Na < NH_{\mu} < K < Rb < Cs$$

This means that Cs is retarded the most, and would be depleted in the effluent solution. The positions of NH_4 and K are interchanged when shale and illite membranes are used.

For divalent cations the retardation sequence obtained from the lab experiment is:
except in the illite sample where it is:

Ca < Mg

Monovalent cations are generally retarded with respect to divalent cations except for Li. Hydraulic drag seems to be a significant factor in controlling the order of retardation between monovalent and divalent cations. A high flow rate would cause a high drag component and might cause the monovalent cations to be retarded with respect to divalent cations. A low flow rate, and consequently an absence of a significant drag component could cause divalent cations to be retarded with respect to monovalent cations. Higher water drag favors the retarded with respect to monovalent cations. Higher water drag favors the retardation of monovalent cations since the hydrated radii are smaller and would not be affected as much as larger ions by hydraulic drag, and thus the monovalent cations would interact with the membrane by being absorbed on negative sites on the clay particles.

For aninons, the retardation sequences obtained by Kharaka and Berry (1973) in their lab experiment are different for different clays:

bentonite	$HCO_3 < B < I < SO_4 < CI < Br$
shale	$HCO_3 < I < CI < SO_4 < Br < B$
illite	$HCO_3 < Cl < l < Br < B < SO_4$

The above results for anions are for conditions at laboratory or ambient temperature. At 70^oC, the retardation sequence changes to:

$$HCO_3 < I < B < SO_h < CI < Br$$

Previous Works - Field Study Example

Some investigators have explained chemical composition, salinity, and pressure anomalies of formation waters in various locales using the theory of reverse osmosis or shale membrane filtration (Berry, 1959; Berry and Hanshaw, 1960; Hill, et al., 1961; Bredehoeft, et al., 1963; White, 1965; Graf, et al., 1966; Kharaka and Berry, 1974). The study in 1974 by Kharaka and Berry was carried

out at Kettleman North Dome oil field in California. Subsurface formation waters were indicated to be principally meteoric in origin, and their concentration relative to meteoric water was attributed to shale membrane filtration as well as to water/rock interactions. Kharaka and Berry's 1973 experimental lab investigation showed Ca is retarded by a geologic membrane with respect to Mg, and the field data from Kettleman North Dome show the same effect. The 1973 experimental results also showed that Na was retarded with respect to Ca, but the opposite was found in the data from Kettleman North Dome. The difference is attributed to the much higher hydraulic gradients used in the lab. The results for anions in terms of being filtered at Kettleman North Dome can also be explained by shale membrane filtration. For example, the HCO₃ increase and SO₄ depletion with respect to Cl can be explained by shale membrane filtration.

The only major differences were with the Ca/Na and Na/K ratios. The field data from Kettleman North Dome indicates that Ca is retarded with respect to Na, which is opposite of the experimental lab results. Kharaka and Berry (1973), and White (1965) indicate that at hydraulic pressure gradients similar to field conditions, Ca was retarded strongly with respect to Na. A higher pressure gradient would cause higher flow velocities, resulting in higher water drag which favors the retardation of monovalent cations. Thus the lab experiments using high pressure gradients show that Na is retarded with respect to Ca, when actually under field conditions and lower gradients, Ca is retarded with respect to Na.

The retardation sequence for monovalent cations as developed from lab experiments should also be obtained in the field, except that temperature dependent water/rock interactions also affect the Na/K ratio. This ratio showed no zonal separation, but a general increase with depth. Temperature controlled exchange reactions may also modify the Rb/Na (general increase with depth) and Li/Na ratio trends caused by filtration.

Test of Shale Membrane Filtration Hypothesis in the Tri-County Area

The first assumption is that there are areas in the Tri-County region where shale membrane filtration is occurring. These areas would be a function of the presence of shales in the upper portions of the bedrock to act as membranes to filter the water. Two study areas were chosen, and are shown in Figure 3. It is assumed that study area "A" will show the affects of shale membrane filtration in water analyses, while study area "B" would not.

These study areas were chosen on the basis of surficial bedrock geology and glacial drift lithology. Areas with sand and gravel in the drift directly overlying sandstone in the bedrock are favorable areas for rapid recharge since no shales or clays are evident. Thus in these areas (Figure 3), shale membrane filtration will not occur. Study area "B" was chosen as the study area representing the aquifer where water analyses would show no filtrations affects. The assumption that area "B" is a rapid recharge area to the bedrock is supported by the tritium data presented earlier. Study area "A", on the other hand, has no areas of sand and gravel over sandstone evident in addition to abundant shale in the upper bedrock. Thus any recharge to the bedrock likely has to pass through the shale, which can act as a membrane that filters the water passing through. Tritium data also supports area "A" as an area of slower recharge than area "B", which would be expected if the water passes through shale.

Once the locations have been defined in the Tri-County area where geologic conditions occur that are necessary for shale membrane filtration, water quality analyses from this area can be compared to water analyses from the area where filtration is not occurring. Three basic tests will be employed. Ratios of dissolved ions from groundwater in the study areas will be compared to predictions based on shale membrane filtration theory, lab experiments, and other field data from previous studies.

The three comparisons made are: 1) drift water versus bedrock water from area "A" below shale, 2) bedrock water from area "A" where filtration is thought to occur versus bedrock water from area "B" where no filtration is occurring, and 3) drift water versus bedrock water from area "B" where filtration is not occurring. The important one is the bedrock comparison, since the water quality should be different in the two areas since different mechanisms are assumed to be controlling the water chemistry.

As in previous studies, ratios of ions are used to determine if membrane filtration is occurring in the Saginaw Formation. Earlier it was noted that the retardation sequence for anions obtained in experimental studies depended on the composition of the membrane. Shale samples from the bedrock Saginaw Formation consist of 30-46% illite, hence retardation sequences for illite membranes were used for comparative purposes. Thus, the important retardation sequences (Kharaka and Berry, 1973) are as follows:

monovalent cations	Li < Na < K < NJ ₄ < Rb < Cs
divalent cations	Ca < Mg < Sr < Ba
anions (illite)	$HCO_3 < Cl < l < Br < B < SO_4$
anions (shale)	HCO ₃ < I < Cl < SO ₄ < Br, B

From the above retardation sequences, it is predicted that where shale membrane filtration is occurring the ratios SO_4/HCO_3 , CI/HCO_3 , and Ca/Na will decrease compared to non-filtered groundwater. On the other hand, CI/SO_4 , Ca/Mg, CI/Ca, and Na/K ratios should increase in "filtered" water.

METHOD OF ANALYSIS

Samples of water were collected from 27 wells and analyzed for Ca, Mg, Na, K, Fe, HCO_3 , SO_4 , and Cl (Table 2 in Appendix). Samples were taken in prewashed polyethylene bottles (two 500 ml and one 125 ml). Temperature and pH were recorded in the field at the time of collection. One of the 500 ml samples was filtered and acidified with concentrated HNO_3 . This sample was used to measure Ca, Mg, Na, K, and Fe. The other 500 ml sample was used for the determination of HCO_3 and Cl. The sulfate ion was measured in the 125 ml sample. This sample had been pretreated in the field with formaldehyde to prevent biologic reduction of the sulfate ion.

A Perkin Elmer model 560 adomic absorption unit was used for the determination of Ca, Mg, Na, K, and Fe. Sulfate was measured indirectly by atomic absorption (Dunk, et al., 1969), alkalinity by potentiometric titration, and chloride by the Mohr titration using silver nitrate.

The data from water analyses was reduced by computer using a modified version of the WATEQ program of the United States Geological Survey (Truesdall and Jones, 1973; Long and Angino, 1977; Kharaka, et al., 1973). The final computer printout provided molalities, epm-cation and emp-anion values, ionic strength, total dissolved solids, distribution of ionic species, ion ratios, and saturation indices for selected minerals. The ion ratios and saturation indices were used to compare with trends predicted by shale membrane filtration, and to test for the contributions due to reactions with the aquifer material to the water chemistry.

Table 7 in the Appendix is a listing of ion ratio data from all wells analyzed by the computer program, and Figure 5 shows the locations of the wells



ANALYZED FOR GEOCHEMISTRY ION RATIO STUDY

O DRIFT WELL

• ROCK WELL

analyzed. Table 8 in the Appendix is a list of the specific wells from each of the two study areas used in ion ratio comparisons.

Not all wells listed from the two study areas were used due to possible contamination with salt, or very unusual chemical composition as compared to other wells. Wells were not used in comparing the two study areas if the chloride content was greater than 25 mg/l, or the total dissolved solids content was greater than about 650 mg/l since these were unusual as compared to the rest of the wells, and may represent brine or salt contamination. Two other wells were not used due to unusual chemical composition. One has the cations composed almost entirely of Na, and the other being hit in SO₄ and total dissolved solids.

RESULTS AND DISCUSSION

The chemical data from the Saginaw Formation and drift water was plotted on a Piper diagram (Figure 6). The Piper Diagram (Piper, 1944) is a way of semiquantitatively representing the 6 major chemical components by one point on a graph. Construction is by the combination of trilinear diagrams for the cationic and anionic components of a water sample. Most of the water wells analyzed plot in the left "corner" of the diamond-shaped field. Thus, the Saginaw Formation water is a Ca-Mg-HCO₃ type water, since those are the dominant ions. However, there are two trends in the data distribution in the diamondshaped field, and are labeled Trend 1 and Trend 2 on Figure 6.

Trend 1 is caused by the distribution of points in the anion trilinear graph. In this trilinear graph, some wells contain more SO_4 thus plotting toward the SO_4 corner. This is where most drift water plots. Trend 2 is caused by the distribution of points in the cation trilinear graph where some of the water analyzed is enriched in Na. Therefore, the higher Na content is not a function of Saginaw Formation water mixing with a brine because there is no corresponding Cl trend in the anion trilinear graph.

According to Piper (1944), if a water composition is the result of mixing between two chemically different waters, the resulting mixture would plot on a straight line between the positions of the two parent waters. Since the wells plot along a curved line, conservative mixing of drift water and Saginaw Formation water does not explain the chemistry of study groundwaters. A chemical evolution of the water between the drift and the Saginaw Formation is suggested.



All drift wells plotted in or close to Trend #1. This results from drift water having higher concentrations of SO_4 relative to HCO_3 . This shows up in the anion trilinear graph where the drift wells plot toward the SO_4 corner.

Bedrock wells from study area "B", where shale membrane filtration probably does not occur, plotted in the same area as the drift wells (Trend #1). This is expected, since the drift and bedrock aquifers in study area "B" are most likely directly connected, and the chemistry of the drift would control the chemistry of bedrock water. Thus, in direct recharge areas like study area "B", the drift and bedrock water would be similar. Since water from drift and bedrock aquifers water from wells in study area "B" plot in the same area, it suggests that shale membrane filtration is not occurring in that area.

The distribution of wells as plotted on the Piper diagram does not support a dilution model explanation for the observed water chemistry of the bedrock aquifer except in study area "B". When dilution of a parent water is the mechanism that produces a different water, the water plots in the same area as the parent water since the relative percentages of ions remain similar. The water simply has less of all dissolved constituents. Other wells from different areas do not plot with drift wells. Bedrock wells from study area "A" do not plot in the same area as drift wells and wells from study area "B". All bedrock wells from study area "A" do not plot in the same area as drift or other bedrock water. As well, no bedrock wells plot between the position of Michigan Formation water on the graph and any other water. If drift water and Michigan Formation waters were mixing to produce the observed Saginaw Formation water, the Saginaw water would plot on a straight line between drift and Michigan Formation waters. Thus Saginaw Formation water is not a dilution or mixture involving the lower Michigan Formation's water.

The theory of shale membrane filtration can explain the distribution of wells as plotted on a Piper diagram. The theory predicts that SO_4 ions are retarded relative to HCO_3 by clays and shales acting as membranes. Thus water in the bedrock where filtration is occurring would be depleted in SO_4 . A majority of Saginaw Formation wells plotted closer to the Ca-Mg-HCO₃ corner of the diamond shaped field than drift wells, which is a result of drift wells having more SO_4 relative to HCO_3 . Bedrock water depletion with regard to SO_4 in study area "A" can be explained by filtration.

The fact that wells from study area "A" (Trend #2) are enriched with Na relative to Ca and Mg can also be explained by shale membrane filtration. Ca and Mg are retarded with respect to Na from passing through a clay or shale membrane. Thus the bedrock, or output side of any membrane should be enriched in Na. Cation exchange, where Na is released and Ca and Mg preferentially absorbed, is a major factor causing the retardation of Ca and Mg with respect to Na along with hydraulic drag considerations. Thus a shale membrane may impede Ca and Mg from passing, as well as contribute Na by cation exchange.

Although not conclusive in itself, the distribution of wells on the Piper diagram suggests chemical evolution is taking place. The distribution can be explained by predictions based on shale membrane filtration theory, and the distribution relative to bedrock lithology (study area A and B wells different plotting position) is consistent with filtration theory. The increased Na in the bedrock could be explained by contribution from the lower Michigan Formation which is rich in Na, but that could not explain why no Cl comes with the Na. No corresponding Cl trend is observed with the increased Na, so contamination or mixing with a brine is unlikely as a cause for the observed chemistry. The shale membrane filtration theory best explains the Na increase relative to other cations while at the same time reducing the SO_4 content relative to HCO_3 without increasing CI in bedrock water. Bedrock surface lithology seems to be a controlling factor since wells form the two study areas delineated by lithology differences plot in two separate areas on the Piper diagram in a manner consistent with shale membrane filtration theory.

Results of Chemical Predictions

The averages of ion rates SO_4/HCO_3 , CI/HCO_3 , CI/SO_4 , Ca/Mg, Na/K, Ca/Na, CI/Ca, and TDS were computed for the overall drift water, overall bedrock Saginaw Formation water, the direct recharge study area "B", and the shale membrane filtration study area "A". These ratios are summarized in Tables 3 and 4. The data used to calculate the ion ratios comes from 27 water wells analyzed for this study, as well as 87 analyses of water wells from a previous work by Vanlier, et al., 1973. When comaprisons were made to drift water, an average value computed from 42 drift well analyses from all across the Tri-County study area was used. This was done because of the scarcity of drift wells within the smaller study areas "A" and "B", it was assumed this average was more representative of typical drift water, and was better statistically.

Table 5 is a comparison of the ion ratios of the two study areas "A" and "B". Study area "A" is favorable for the occurrence of shale membrane filtration, and study area "B" is an area where shale membrane filtration most likely does not occur. Thus the comparison is between bedrock water that may have been filtered and bedrock water that was not filtered. The first column is the prediction of whether a ratio should increase or decrease if the water was filtered. In other words, if the ratio is predicted to increase, non-filtered water would have a lower ratio that filtered water. The next two columns list the average ion ratios of rock wells from the two study areas. The following column

	,	DRIFT	SAGINAW Fm.			
	x	S	Ν	x	S	Ν
so ₄ /hco3	.08522	.08161	42	.05596	.08451	155
CI/HCO3	.09948	.18488	42	.02295	.04513	155
CI/SO4	.91627	1.16613	39	.70216	.94602	147
Ca/Mg	1.7913	.43910	42	1.8920	.44823	155
Na/K	14.5052	11.9797	42	9.1364	14.5984	155
Ca/Na	7.4575	9.9409	42	7.4760	7.4032	155
Cl/Ca	.22244	.34745	42	.08733	.25316	155
TDS (mg/1)	588.59	112.67	42	548.45	113.39	155
Tritium (T.U.)	25.2	25.4	7	18.8	30.0	23

=

TABLE 3: Average ion ratios from all wells.

S = standard deviation

N = number of samples

	Stuc	ly Area B	Study Area A Saginaw Fm. Water			
	Saginav	v Fm. Water				
	X	S	Ν	X	S	Ν
so ₄ /hco3	.04143	.03494	25	.01384	.01628	20
CI/HCO3	.01622	.01784	25	.01265	.01836	20
CI/SO4	.61146	.84242	24	1.0454	.62573	20
Ca/Mg	1.8031	.2366	25	2.0110	.4501	20
Na/K	7.0032	2.8610	22	9.4730	7.2018	20
Ca/Na	9.3434	4.5341	25	3.9570	2.9784	20
TDS (mg/1)	516.88	50.26	25	512.54	68.55	20
Tritium (T.U.)	29.7	36.5	13	5.5	5.1	5

TABLE 4: Average ion ratios from respective study areas.

X = average of samples

S = standard deviation

N = number of samples

TABLE 5: Comparison of study areas ion ratios of Saginaw Aquifer water trends are based on filtration model as developed in text. between direct recharge study area "B" and suspected shale membrane filtration study area "A". Predicted

Level of Significance	58%	5%	95%	85%	%66	%66	92%	70%
Observed Trend	decrease	decrease	increase	increase	increase	decrease	decrease	increase
K WELL RATIO Area "A"	.01384	.01265	1.0454	2.0110	9.4730	3.9570	512.54	.0566
ROC ION Area "B"	.04143	.01622	.61146	1.8031	7.0032	9.3434	516.88	.0453
PREDICTION comparing Direct Recharge area "B" to Hyperfiltration area "A" rock wells. Ratios should:	decrease	decrease	increase	increase	increase	decrease	decrease	increase
	so ₄ /HCO ₃	cl/HC03	CI/SO ₄	Ca/Mg	Na/K	Ca/Na	TDS (mg/1)	CI/Ca

lists the observed trend, and the last column shows the level of significance as calculated from a "t" test.

Table 6 compares a field example discussed earlier of possible shale membrane filtration (Kharaka and Berry, 1974) and theoretical/laboratory predictions to the results of this study. The results contained in Tables 5 and 6 are significant since the ion ratios behave as predicted by theory, while at the same time comparing favorably to the field study by Kharaka and Berry (1974). All ratios increase or decrease as predicted when comparing the two study areas. The levels of significance are low in several cases, but this is most likely due to the leaky artesian system present in the Saginaw aquifer. The levels of significance are low in several cases, but this is most likely due to the leaky artesian system present in the Saginaw aquifer. Not all water is filtered in the Tri-County region, such as in study area "B", and mixing with filtered water in the Saginaw Formation would reduce the observable effects of filtering. Secondly where there is shale, the water may recharge to some extent through cracks and fissures in the shale, thus diluting the filtration effect.

The following is a more detailed discussion of the individual ion ratios with any other controlling factors addressed besides filtration. The discussion is based on the data in Table 5 which is a comparison of Saginaw Formation water between study areas "A" and "B".

SO4/HCO3

Since SO_4 is retarded relative to HCO_3 , the SO_4/HCO_3 ratio should be lower in water that has been filtered as compared to non-filtered water. Therefore, if shale membrane filtration is occurring, as water moves from the drift to the bedrock through clays and shales, the ratio should decrease in the effluent or bedrock water (study area "A") relative to the non-filtered bedrock water (study area "B") and the drift water. Saginaw Formation water from the TABLE 6: Comparison of field example from California study to observed trends found in Saginaw Formation water. "A" would be non-filtered, and "B" filtered in this case.

COMPARISON OF KHARAKA'S FIELD DATA TO PRESENT STUDY



OUTPUT

	A to B KHARAKA <u>FIELD</u>	A to B PRESENT <u>STUDY</u>	GENERALLY** PREDICTED
Ca/Na	decreased	decreased*	either
TDS	decreased	decreased*	decrease
Cl	decreased	decreased*	decrease
нсо ₃ /сі	increased	increased	increase
Na/K	increased	increased*	increase
HCO3/SO4	increased	increased*	variable
so ₄ /CI	decreased	decreased*	variable

* Significant at greater than 10% level.

** Based on previous studies experimental and field data. For this study, A = drift, b = Saginaw Formation.

. .

shale membrane filtration study area "A" does indeed have a smaller ratio than bedrock water from study area "B", or water from the drift (Table 5).

A comparison of the average drift water ratio to bedrock water from the shale membrane filtration study area "A" shows a significant decrease or lower ratio in the bedrock water as predicted. The bedrock SO_{4}/HCO_{3} ratio from study area "B" is also less than drift water. This means that the lower ratio of bedrock water could be explained by dilute water recharging the bedrock through "clean" sands and gravels without filtration. However, a comparison of the two study areas "A" and "B" shows that study area "A" has an even lower ration than area "B". This can best be explained by shale membrane filtration where SO_{4} is retarded from passing through a membrane relative to HCO_{3} .

Computer analysis of the water data indicates that calcite is supersaturated in bedrock water. If calcite did precipitate, then the effect would be to increase the ratio. However, shale membrane filtration theory predicts a decrease in the ratio, and that is observed. If precipitation of calcite is tending to increase the ratio in the bedrock versus the drift, it is not a strong enough effect to overcome the apparent effect of filtration that decreases the ratio.

CI/HCO3

This ratio should decrese or be smaller in water that has been filtered. A comparison of drift water to Saginaw Formation water from study area "A" shows a significantly lower ratio in the bedrock as would be predicted by shale membrane filtration. The bedrock water from study area "B" is also much lower than drift water. As well, the bedrock water from area "A" is lower than area "B" when comparing this ratio. The ratio behaves as would be predicted in all three cases.

Less salt or NaCl in clean sands and gravels could account for the lower ratio since it is easily dissolved and would be "washed" out rapidly. Thus direct recharge could explain the lower ratio in the bedrock as compared to the drift, but does not explain why study area "A" has a lower ratio than area "B".

If calcite was precipitating and removing CO_3 from the system, it would have the effect of increasing the ratio. This is not observed, or may not cause enough increase to counter a decrease caused by filtration. If calcite was precipitating, Ca would also be removed, affecting the Ca/Mg and Ca/Na ratios. Calcite precipitation does not seem to affect these ratios, however, as the discussion later suggests.

CI/SO4

Determining whether this ratio should increase or decrease depends on the composition of the membrane and temperature. At 70°C, the SO₄ ion is retarded with respect to Cl. However, at room temperature, the retardation sequences obtained for anions were variable depending on membrane composition, except that HCO₃ was always least retarded. The Saginaw Formation shales clay fraction is composed of kaolinite, illite, and vermiculite. Since kaolinite has a low cation exchange capacity, and the properties that create cation exchange also create the filtering effect, this clay probably has minor effects on filtration. Any membrane properties in the Saginaw Formation likely result from illite and vermiculite. In experiments, an illite sample retards SO₄ with respect to Cl (Kharaka and Berry, 1973). Therefore, the Cl/SO₄ ratio should increase in any filtered water with respect to non-filtered water.

A comparison of drift water to study area "A" bedrock water shows the bedrock water indeed does have a larger ratio as predicted. However, when drift water is compared to bedrock water from study area "B", the bedrock water ratio is lower than drift water. Thus filtration does not seem to occur in study area "B". The lower bedrock ratio in area "B" may be due to less NaCl present in recharging waters and the bedrock. A comparison of bedrock water from the two study areas "A" and "B" shows that the Cl/SO_4 ratio is larger or increases in area "A" relative to area "B". Thus the lower Cl/SO_4 ratio in bedrock water from direct recharge areas such as area "B" as compared to drift ratios can be explained by little NaCl present in recharging waters from the drift, but the increase of the ratio in study area "A" over both drift and study area "B" becrock water can only be explained by shale membrane filtration.

Ca/Mg

In terms of ion exchange, Ca is preferentially absorbed over Mg (Kharaka and Berry, 1973), and therefore the Ca/Mg ratio would decrease if ion exchange were occurring as water passed through a clay or shale. The other major controlling factor in shale membrane filtration for cations is hydraulic drag, and this consideration suggests that the Ca/Mg ratio should decrease in water passing through a clay since Mg has a greater hydraulic drag and would be propelled through the membrane faster than Ca. Most clays, considering absorption and hydraulic drag, retard the movement of Ca more than Mg, and thus the Ca/Mg ratio should be smaller or decrease in filtered water.

However, the 1973 study by Kharaka and Berry showed the clay illite to be one of the exceptions. That study showed that an illite sample retarded Mg more than Ca. Thus, the Ca/Mg ratio should increase in filtered water. Water from study area "A" bedrock has a higher ratio than drift water. Water from study area "B" bedrock wells is nearly identical to drift water, and this would be expected since in direct recharge areas such as area "B" the drift and bedrock are directly connected. Study area "A" bedrock water, where conditions are favorable for filtration, has a higher ratio than study area "B" bedrock water as predicted by shale membrane filtration theory. The only possible water/rock interaction that might affect this ratio in the Saginaw Formation system would involve calcite or limestone and dolomite. Equilibrium data show that the drift and bedrock are both supersaturated with calcite. Thus calcite would tend to precipitate and remove Ca from the water, which in turn would have the effect of decreasing the Ca/Mg ratio. But this is not observed as the ratio shows an increase as predicted by filtration theory, and calcite precipitation may only serve to lessen any increase caused by filtration. Calcite precipitation would only cause a difference if precipitation occurred in only one of either drift or bedrock aquifers. Since calcite is supersaturated in both aquifers it makes no difference.

Na/K

According to the given retardation sequence, K is retarded with respect to Na. Thus the ratio should increase in waters that have been filtered. However, drift water or "unfiltered" water has a larger ratio than bedrock water from either study area "A" or "B". This is possibly due to less NaCl in the bedrock, and was mentioned earlier in connection with the Cl/HCO_3 and Cl/SO_4 ratios. The decrease from drift to bedrock may also be due to K being released in a cation exchange process as well as Na. Illite is a potassium rich clay, and therefore K may be released. One or both of the above reasons may account for the lower ratio in the bedrock relative to drift water.

However, when comparing bedrock water in the two study areas, the ratio behaves as predicted by filtration theory. Saginaw Formation water from study area "A" has a larger ratio of Na/K than bedrock water from study area "B". Going from drift to bedrock the ratio is smaller which is the opposite of filtration theory, so some other mechanism controls that decrease. Yet when comparing filtered and non-filtered bedrock water, there is a noticeable change in the ratio in the direction predicted by shale membrane filtration theory.

Ca/Na

This ratio has been used in the past as an important test to distinguish between effluent (filtered) and membrane concentrated waters (Kharaka and Berry, 1973). Field investigations have indicated that Ca is retarded with respect to Na. However, experimentally obtained results are the opposite, and this discrepancy is attributed to the much higher pressure gradients used in the lab studies. According to field studies, Ca is retarded with respect to Na, and the ratio would decrease in filtered water.

The Ca/Na ratio does decrease from drift to bedrock water in study area "A". The Ca/Na ratio increases from drift to bedrock water in study area "B" however. And the ratio decreases significantly from study area "B" to study area "A" bedrock water.

The increase from drift to bedrock in area "B" may also be due to less NaCl again in "clean" sands and gravels in the drift and bedrock. With less Na, the ratio would increase in the bedrock water compared to other drift water.

Supersaturation of the bedrock water with certain minerals as indicated by the computer analyses may also affect this ratio. If Ca were being removed by calcite precipitation, this would cause the ratio to decrease. This could account for the decrease observed in study area "A" over study area "B" bedrock water instead of shale membrane filtration. But that would require that calcite not be precipitating in area "B", otherwise the effect would be the same in both study areas. The analyses show that CaCO₃ is supersaturated over the entire Saginaw Formation aquifer in both study areas. So if precipitation of calcite is occurring, it is occurring in both areas, and cannot account for the Ca/Na ratio decrease only in one of the study areas.

Cl/lCa

Since the data comparing anions to cations are scarce, this ratio is included only as another indicator that filtration may be occurring. This ratio should increase or be larger in water tha has been filtered (Van Everdingen, 1968). When comparing study area "A" to area "B", the ratio is larger as predicted in area "A" bedrock water. The bedrock water ratio is smaller than the drift water, however, and may be due to less NaCl in the bedrock again, or much more Ca relative to Cl since the bedrock aquifer cement is silica and calcite, and the water is supersaturated with calcite. Regardless, some proces increased the ratio as predicted in bedrock water from study area "A" relative to area "B" water, and filtration can account for it.

TDS

Water from the Saginaw Formation aquifer in both study areas "A" and "B" has less total dissolved solids (TDS) than drift water. As well, study area "A" bedrock water has slightly less TDS than bedrock water from study area "B". Both comparisons are consistent with predictions bsed on filtration. Direct or point recharge to sandstone of the bedrock through sand and gravels, such as in area "B", could provide recharge water lower in TDS relative to most drift water, and shale membrane filtration also could provide lower TDS recharge water to the bedrock. Although both processes appear to be occurring, shale membrane filtration can further reduce the TDS content of bedrock water in study area "A". It would be difficult to say at this point which process, direct recharge or shale membrane filtration, is dominant in controlling the TDS levels in the bedrock water.

Summary

When comparing drift water to bedrock water from study area "A" where shale membrane filtration is thought to occur, 6 of the 8 parameters (ratios)

discussed behave as predicted by filtration theory. When comparing bedrock water from study area "A" to study area "B" (proposed non-filtration area), all 8 parameters or ratios behave as predicted by filtration theory. In study area "B", where shale membrane filtration is not thought to occur, 5 of the 8 ratios do not behave as would be expected were filtering to be occurring, suggesting that filtration does not occur in this area.

Another possible mechanism to control the chemistry of the Saginaw Formation aquifer's chemistry is mixing with the lower Michigan Formation waters. However, water data as plotted on a Piper Diagram do not support that hypothesis, and mixing in this manner cannot account for all the ratio changes. Thus, mixing with Michigan Formation waters is ruled out as a major control on the chemistry of groundwater in the Saginaw aquifer.

The fact that some ratios change slightly is probably due to two effects: 1) some ions are retarded nearly the same by a membrane, thus any ratio comparing two similarly retarded ions would not show much change, and 2) the Saginaw Formation aquifer is a leaky artesian system having shale aquitards that may not be very efficient in all cases at preventing water from migrating through fissures and cracks. Direct recharge also seems to be occurring to the Saginaw aquifer providing water that is not filtered to mix with any filtered water. The water chemistry in the bedrock is most likely due to both shale menbrane filtration and direct recharge systems operating simultaneously in the Tri-County region.

Further evidence supporting shale membrane filtration may be provided by pairs of wells, one completed in the drift and one in the Saginaw Formation, in close proximity. A well pair such as this in shaley areas on the Saginaw Formation should show filtering affects in the bedrock water. The following is a list of some "well pairs". <u>05N01W28</u>: In this section, a drift well shows a static water level of 830 feet elevation near a rock well completed below shale with a static water level of 820 feet. Thus, any water movement between drift and bedrock would be downward through the shale. All ratios except Cl/Ca increase or decrease as predicted, including TDS.

<u>03N01E02</u>: This well pair in Ingham County from Vanlier (1973) is located in an area that has been noted before for its "naturally" softened bedrock water. All ratios increase or decrease as predicted, except TDS was higher in the bedrock well than in the drift well.

<u>01N03W27</u>: A well pair in this section showed all ratios except Na/K behaving in the predicted manner, with a well log showing the rock well completed below 44 feet of shale.

<u>02N03W12CC</u>: This well pair is in study area "B", the direct recharge area. Predictably, only 3 of the 8 ratios increased or decreased as would be expected if the bedrock water was filtered. Most ratios show no filtering, and this seems to confirm that shale membrane filtration is not occurring in this area.

<u>03N01E34</u>: A drift well water elevation is about 895 feet near a rock well completed below shale with a water elevation of 880 feet. Thus the water movement if occurring is downward which is required for filtration here in study area "A".

Conclusion

Two study areas were chosen based on surficial bedrock lithology and location of probable recharge areas. One represents and area where conditions are favorable for the occurrence of shale membrane filtration (study area "A"), and the other an area where shale membrane filtration is not occurring (study area "B").

Tritium analyses of water from drift and bedrock aquifers showed that Saginaw Formation waters from study area "B" have the highest tritium content relative to bedrock water from study area "A". This suggests faster recharge to the Saginaw Formation in study area "B", supporting the existence of direct recharge in this area. Water from the Saginaw Formation in study area "A" show low levels of tritium. This suggests some water is recharging through shales in the bedrock from the drift. Tritium data show that direct recharge systems are found in the Tri-County area, and that a "point recharge" model is a valid explanation of how water is recharged to the bedrock. In direct recharge areas such as study area "B", shale membrane filtration could not occur.

Water composition data of drift and bedrock wells were plotted on a Piper Diagram, and the wells were distributed in a distinct pattern that suggests some sort of chemical change or evolution is taking place. Wells from study areas "A" and "B" plotted in specific, different locations of the graph, which can be explained by shale membrane filtration of waters recharging the Saginaw Formation.

Experimental and field studies have shown that clays and shales behave as semi-permeable membranes, selectively filtering out ions in water flowing through the membrane. Membrane composition is important in determining which ions are filtered the most. Retardation sequences have been developed in previous investigations allowing prediction of whether certain ion ratios would increase or decrease if the water were being filtered.

Ion ratios were used in three basic tests to determine if shale membrane filtration was occurring. First, drift water was compared to bedrock water from study area "A"; second, drift water was compared to bedrock water from study area "B"; and finally, bedrock water from study area "A" was compared to bedrock water from study area "B". Ion ratio variations predicted by shale membrane filtration theory are observed in bedrock water from the shale membrane filtration study area "A", and are not observed in bedrock water from the direct recharge study area "B". This study's results also compared favorably with previous field investigations.

The theory of shale membrane filtration best explains the observed groundwater chemistry of the Saginaw Formation in study area "A", and accounts for the difference with bedrock water from area "B". Shale membrane filtration does not seem to be occurring in study area "B". It would appear that both recharge processes proposed to explain the observed water chemistry, direct recharge and shale membrane filtration are occurring in the Tri-County study area.

BIBLIOGRAPHY

- Berry, F. A. F., 1959. Hydrodynamics and geochemistry of the Jurassic and Cretaceous Systems in the San Juan Basin, northwestern New Mexico and southwestern Colorado. Standord University, Ph.D. dissertation.
- Berry, F. A. F., 1969. Relative factors influencing membrane filtration effects in geologic environments. Chem. Geol. 4, p. 295-301.
- Berry, F. A. F. and Hanshaw, B. B., 1960. Geologic evidence suggesting membrane properties of shales. 21st International Geologic Congress, Copenhagen, 1960.
- Bredehoft, J. D., Blyth, C. R., White, W. A. and Maxey, G. B., 1963. Possible mechanism for concentration of brines in subsurface formations. Bull. Amer. Assoc. Petrol. Geol. 47, p. 257-269.
- DeSitter, L. V., 1947. Diagenesis of oil-field brines. Bull. Amer. Assoc. Petrol. Geol., v. 31, p. 2030-2040.
- Dunk, R., Mostyn, R. A., and Hoare, H. C., 1969. The Determination of Sulfate by Indirect Atomic Absorption Spectroscopy. Atomic Absorption Newsletter, v. 8, no. 4, July-August.
- Firouzian, A., 1963. Hydrological studies of the Saginaw Formation in the Lansing, Michigan, area. Michigan State Univ., Unpub. M.S. Thesis.
- Graf, D. L., Meets, W. F., Friedman, I., and Shimp, N. F., 1966. The origin of saline formation water, 3, Calcium chloride waters. Ill. State Geol. Surv. Circ. 397, 60p.
- Hanshaw, B. B., 1962. Membrane properties of compacted clays. Harvard University, Unpub. Ph.D. dissertation.
- Hanshaw, B. B. and Coplen, T. B., 1973. Ultrafiltration by a compacted clay membrane - II. Sodium ion exclusion at various ionic strengths. Geochim. Cosmochim. Acta 37, p. 2311-2327.
- Hanshaw, B. B. and Hill, G. A., 1969. Geochemistry and hydrodynamics of the Parados Basin region, Utah, Colorado, and New Mexico. Chem. Geol. 4, p. 264-294.
- Hill, G. A., Colburn, W. A., and Knight, J. W., 1961. Reducing oil-finding costs by use of hydrodynamic evaluation. Economics of Petroleum Exploration, Development and Property Evaluation. Prentice-Hall, Englewood Cliffs.
- Kelly, W. A., 1936. The Pennsylvanian system in Michigan. Michigan Dept. of Conservation, Geol. Surv. Div. Pub. 40, Geol. Ser. 34.

- Kemper, W. D., 1961. Movement of water as affected by free energy and pressure gradients - II. Experimental and analysis of porous systems in which free energy and pressure gradients act in opposite directions. Soi. Sci. Soc. Amer. Proc. 25, p. 269-265.
- Kharaka, Y. K., 1971. Simultaneous flow of water and solutes through geologic membranes: experimental and field investigations. Univ. of California, Unpub. Ph.D. dissertation.
- Kharaka, Y. K. and Berry, F. A. F., 1973. Simultaneous flow of water and solutes through geologic membranes, I. Experimental Investigations. Geochim. Cosmochim. Acta 37, p. 2577-2603.
- Kharaka, Y. K. and Berry, F. A. F., 1974. The influence of geologic membranes on the geochemistry of subsurface waters from Miocene sediments at Kettleman North Dome in California. Water Resources Reserach, v. 10, no. 2.
- Kharaka, Y. K. and Smalley, W. C., 1976. Flow of water and solutes through compacted clays. Bull. Amer. Assoc. Petrol. Geol., v. 60, p. 973-980.
- Korzhinskii, D. S., 1947. "Filtration effect" in solutions and its role in geology. Bull. Akad. Sci. U.S.S.R., Geol. Ser., 2:35-48.
- Larson, G., 1979. Study for Tri-County Regional Planning Commission.
- Long, D. T. and Angino, E. E., 1977. Chemical speciation of Cd, Cu, Pb, and Zn in mixed freshwater, seawater, and brine solutions. Geochim. Cosmochim. Acta 41, p. 1183-1191.
- McKelvey, J. G. and Milne, I. H., 1962. The flow of salt through compacted clay. Clay Minerals 9, p. 248-259.
- Mackay, R. A., 1946. The control of impounding structures on ore deposition. Econ. Geol., 41, p. 13-46.
- Mencenberg, F. E., 1963. Ground-water geology of the Saginaw group in the Lansing, Michigan, area. Michigan State Univ., Unpub. M.S. Thesis.
- Meyer, K. H. and Sievers, J. F., 1936. Helv. Chim. Acta 19, 649, 665, 987.
- Milne, I. H., McKelvey, J. G., and Trump, R. P., 1964. Semi-permeability of bentonite membranes to brines. Bull. Amer. Assoc. Petrol. Geol. 48, p. 103-105.
- Piper, A. M., 1944. A graphic procedure in the geochemical interpretation of water-analysis. Transactions, Amer. Geophysical Union - Hydrology papers--1944.
- Radfar, S., 1979. Determination of recharge areas from groundwter quality data, Ingham County, Michigan. Michigan State Univ., Unpub. M.S. Thesis.
- Russell, W. L., 1933. Subsurface concentration of chloride brines. Bull. Am. Assoc. Petrol. Geologists, 17, p. 1213-1228.

- Ritter, M. H., 1980. The use of tritium for confirming areas of groundwater recharge, meridian Township, Michigan. Michigan State Univ., Unpub. M.S. Thesis.
- Schlumberger, C., Schlumberger, M., and Leonarden, E., 1933. Electrical coring: a method of determining bottom-hole data by electrical measurements. Trans. A.I.M.E., 110, p. 237-272.
- Stuart, W. T., 1945. Ground-water resources of the Lansing area, Michigan. Michigan Geol. Survey Prog. Report 13.

Toerell, T., 1935. Proc. Soc. Exptl. Biol. Med., v. 33, p. 282.

- Truesdell, A. H. and Jones, B. F., 1973. Wateq: A computer program for calculating chemical equilibria of natural waters. U.S.G.S. Pb220-464, 73p.
- VanEverdingen, R. O., 1968. "Mobility of pair ion speciation reverse osmosis and the modification of subsurface brines. Canadian Journal of Earth Sciences, v. 5, no. 5, October.
- Vanlier, K. E., 1964. Groundwater in the Tri-County region, Michigan, Chapter 1 of Natural resources problem study: Lansing, MI, Tri-County Reginal Planning Comm., p. 122.
- Vanlier, K. E., Wood, W. W. and Brunett, J. O., 1973. Water-supply development and management alternative for Clinton, Eaton, and Ingham Counties, Michigan. U.S.G.S Water-Supply Paper #1969.
- Vanlier, K. E. and Wheeler, M. L., 1968. Ground-water potential of the Saginaw Formation in the Lansing Metropolitan area, Michigan. Tri-County Regional Planning Commission, Lansing, Michigan.
- Walton, H. F., 1958. Principles of osmosis applicable to oil hydrology. Unpub. research report, Petrol. Reserach Corp., Denver, CO, 66p.
- Wheeler, M. L., 1967. Electric analog model study of the hydrology of the Saginaw Formation in the Lansing, Michigan, area. Michigan State Univ. Unpub. M.S. Thesis.
- White, D. E., 1957. Magmatic, connate and metamorphic waters. Bull. Geol. Soc. Am., 68, p. 1657-1706.
- Wood, W. W., 1969. Geochemistry of groundwater of the Saginaw Formation in the upper Grand River basin, Michigan. Michigan State Univ. Geology Dept., Unpub. Ph.D. dissertation.
- Wood, W. W., 1976. A hypothesis of ion filtration in a potable water aquifer system. Groundwater, v. 14, no. 4, p. 233-244.
- Wyllie, M. R. J., 1948. Some electrochemical properties of shales. Science 108, p. 684-685.

Young, A. and Low, P. F., 1965. Osmosis in argillaceous rocks. Bull. Amer. Assoc. Petrol. Geol. 49, p. 1004-1007. APPENDIX

Tritium Analysis

Ideally, a tracer used for groundwater studies should accurately describe water flow through the groundwater system under investigation for the duration of the study. This requires that the presence of a tracer in the water does not change the properties of groundwater or the transmission characteristics of the medium through which the flow is being traced. In particular, hydrogen isotopes serve as excellent tracers because they are incorporated directly into the water molecule, and at concentrations most often used do not change the water properties. Since tritium is also a naturally occurring isotope, artificial introduction of the tracer is not necessary. In addition, tritium is radioactive and can be detected at very small concentrations. It has a half-life of 12.35 years, and therefore is particularly useful to date recent water movement in recharge areas.

Tritium is continuously being produced in the upper atmosphere by interaction of cosmic radiation with nitrogen atoms. The reaction is:

$$^{14}N + n^{\circ} \rightarrow ^{3}H + ^{12}C$$

This cosmicly produced tritium eventually reaches the earth's surface through precipitation. Early 1950's and 1960's thermonuclear bomb tests in the atmosphere also injected large quantities of artificially produced tritium into the atmosphere, and hence into the hydrologic cycle. This spike of artificial bomb tritium from thermonuclear events supplies a means to "date" the relative age of recharging groundwater from its tritium content.

Analysis for tritium is based on detection of the Beta radiation that accompanies radioactive decay of tritium $({}^{3}H)$ to helium $({}^{3}He)$. There are two types of Beta decay: negatron and positron. Tritium Beta decay involves negatron (electron) decay. The decay scheme is:

$$^{3}H \rightarrow ^{3}He + e^{-1}$$

neutron
$$\rightarrow p^+ + e^- + v_e$$

A tritium neutron decays into a proton, electron, and energy. The energy (Beta radiation) produced by this type of tritium decay can be emitted over a continuous range from essentially 0.0 MeV to 0.019 MeV.

Tritium Analysis Procedure

The most common type of radiation detection device requires radiation to pass through a window of a detection device. Once inside, the radiation ionizes certain gases in the chamber, generating an electric current which in turn can be detected and counted. However, since tritium is a very low energy Beta emitter, all or most of the Beta particles would be absorbed by the window of such a detector. Also, the Beta particles have small mass and are easily detected, particularly low energy Beta particles.

Because of the inherent difficulty in detecting weak Beta radiation, special techniques were developed to measure soft Beta raidation. This method utilizes liquid scintillation, a technique which involves mixing the radioactive sample in a detecting medium such as a fluorescent organic solution. The radiation from tritium decay causes the organic solution to emit light, which can be converted to photoelectrons in a photomultiplier tube, and measured as an electric pulse. In theory, this method assumes that each tritium disintegration produces a pulse of light which can be more easily detected and counted than the radiation itself, and therefore it is much more sensitive in the detection of low energy Beta radiation than other methods. The liquid scintillation counter is set up to count the number of light pulses, and thus the number of disintegrations. The maximum efficiency using the counter available for this study is approximately 60% of all decays detected.

The procedure for sample preparation prior to liquid scintillation counting is relatively simple. Care must be used at all stages not to contaminate the

samples, as even atmospheric moisture could add tritium to a sample. Samples of well water, precipitation, and river water were collected in 500 ml prewashed plastic bottles and labeled. Each water sample was then distilled to remove suspended solids and dissolved minerals. Next an electrolysis process resulting in isotropic fractionation, facilitated by the addition of an electrolyte after distillation, is used to concentrate the naturally occurring tritium to levels that are more easily detected. After electrolysis, the water samples are distilled out of the electrolysis cells for two reasons. First, the post-distillation removes the electrolyte added beforehand. Second, the water sample is removed from the cumbersome electrolysis cell into a smaller weighing bulb to ease the measurement of the final volume of sample left after electrolysis. After postdistillation, a measured amount of water is placed in a boro-silicate scintillation vial, mixed with a fixed amount of scintillation fluid, and measured in a liquid scintillation counter when a sufficient number of samples have been processed. The Appendix contains a more detailed analysis procedure.

Tritium Lab Set-up

The four basic steps of tritium analysis are: 1) predistillation, 2) electrolysis, 3) post-distillation, and 4) liquid scintillation counting.

Pre-distillation consists of a three unit glass vacuum system mounted on an aluminum lattice rack, with boiling flask, Kjeldahl bulb, condenserto, and receiving flask. The system uses cooling water, vacuum, electric heating elements, and dried air. The electrolysis system consists of a low temperature chamber, thermostat, Ostlund electrolysis cells, and adjustable power supply, and a vacuum exhaust line. The low temperature chamber is an open top freezer containing water and anti-freeze, a circulation pump, and a plexiglass rack to hold the electrolysis cells. A vacuum switch was installed on the power line to the electrolysis cells to authomatically cut off power in the event of failure in
the vacuum exhaust lines, minimizing the danger of explosion due to a concentration of explosion due to a concentration of explosive gases in the cells. The post-distillation is a three unit glass system mounted on an aluminum lattaice rack. Electric heating elements, liquid nitrogen, vacuum, and dried air are used in this system. It is designed to distill the water sample out of an Ostlund electrolysis cell into a weighing bulb.

This study used a Beckman LS 8100 liquid scintillation counter. This as an ambient temperature, soft beta counting spectrometer provided with digital readout and printout for data recording. This unit automatically counts to a preset error or time, and calculates counts per minute.

Laboratory Procedures

Prior to distillation, all units are dried under vacuum before adding a water sample to the boiling flask, and each cooling water circulation is checked for leakage. When dry, the water sample is added to the boiling and immediately placed under vacuum. After the sample stops degassing, the vacuum is turned off and heat is applied to the flask. At this time, dry air can be readmitted to the boiling flask to avoid excess bumping and to reduce the danger of implosion, however, distillation is generally more rapid under vacuum. Each distillation unit is normally connected to a baloon to indicate pressure within. If during distillation a balloon indicates excess pressure, momentary vacuum is applied to a unit or heat reduced. Just before dryness, the heat is removed from the boiling flask to allow any water in the Kjeldahl bulb to drain, and flame is applied to the bulb and connecting glass of the condenser to thoroughly dry them. Heat is then reapplied to the flask, and distillation taken to dryness, with a heating of several minutes past dryness to dehydrolyze salts. In a glass vacuum system, there is danger of implosion, therefore, it is recommended that a face shield be used at all times.

In the electrolysis step, normally two volumes are used for enrichment, 100 ml and 500 ml, although this is not a restriction. The electrolyte used is NaOH in pellett form added to the electrolysis cells with the water sample and allowed to dissolve before electrolysis begins. Up to 10 cells are placed in the cooling bath where a temperature is maintained at 1° or 2° C. Vacuum exhaust lines to remove hydrogen and oxygen are then connected to the electrolysis cells which are connected in series to a variable power supply. The initial current applied to the cells is 6 amps, but is gradually reduced as sample volume decreases. The final current is 0.5 to 1 amp to reduce the danger of arcing in the cell. At times an initial current of 4.0 amps can be used to improve the electrolysis efficiency slightly, and to produce a more consistent final volume of sample left in the cells. The electrolysis efficiency (how much tritium in the original volume of sample is concentrated in the final volume) using an initial current of 6.0 amps is about 74%, meaning that 74% of the original tritium in a sample is concentrated in the final volume left after electrolysis. This efficiency is determined by running a standard of known activity with each set of samples. A blank, or sample containing no tritium, is also run with each set of samples to provide the background radiation count.

The next step, post-distillation, commences when the electrolysis step is completed. Each electrolysis cell is removed from the cooling bath, and a distillation head is placed on top of the cell effectively sealing it from the atmosphere. The cells then are immediately placed on the post-distillation system, put under vacuum, and heat is applied. The water from each cell is condensed in a separate weighing bulb cooled by liquid nitrogen. When distillation is complete, the weighing bulb is weighed to determine the final volume of water left after the electrolysis step. A measured amount, as close to 5.0 grams as possible in this study is then placed in a scintillation vial. "Instagel" scintillation fluid is added, 6 ml to each vial, after which the vials are store in a dark area until ready for counting.

Measuring the activity of the samples is the last step. The Beckman scintillation counter used in this study is equipped with pre-programmed "Library Programs for various isotopes". Library program #5 with modifications was used for this study, a program set to count tritium. The Beckman counter has two adjustable channels or detectors. Channel 1 was "optimized to reduce the background noise or radiation to approximately 6 or 7 counts per minute instead of 18 to 20 counts per minute with the channel wide open. On the Beckman scale, channel 1 was set at 125 for the lower end, and 225 for the upper limit of the detection window. Channel two was left wide open, from 0 to 397, for comparison, and encompasses the entire tritium decay energy range.

The amount of quenching in each sample was determined separately using a built in feature of the Beckman liquid scintillation counter that calculates an "H" number. The "H" number, which is a function of the quenching within a sample, is related to the liquid scintillation counting efficiency using prepared standards containing variable amounts of quenching agent. As a result, counting efficiency for each sample can be calculated.

The H number is a method of quench monitoring that is done automatically by the Beckman LS counter. A graph of counting efficiency versus H number was developed using a set of standards with varying quench. How much a sample is quenched determines how efficiently the LS counter can detect the bursts of light produced th bye radiations interaction with the scintillation fluid. Since all samples cannot be produced exactly alike, the quench varies slightly, and therefore the counting efficiency varies. An H number is calculated for each sample by the LS counter, and this number is converted to counting efficiency by linear interpolation of the nearest two bracketing points on the graph of H number versus counting efficiency. The counting efficiency for the samples was usually between 13% and 14% with channel 1 set at 125 and 225.

In each set of samples there was a counting standard used to determine electrolysis efficiency, plus a blank used to indicate the background radiation. Both standard and blank went through the same electrolysis conditions (electrolyzed in same set as samples) and were counted on the LS counter with each sample set.

Thus, for each sample, the counting efficiency of the LS counter and the electrolysis efficiency are calculated. Finally the actual activity of the sample can be determined from the equations given in the following "calculation" section of the appendix. Once the activity is expressed in dpm/gm, it is converted to tritium units (T.U.) by the conversion factor of 1 TU = 0.0071 dpm/gm. The results in this study are given in TU's.

Tritium Calculations

In order to calculate the final activity of a sample, the electrolysis efficiency must be calculated using a standard of known activity. The electrolysis efficiency of the standard is calculated as follows:

$$EE_{es} = \frac{(V_f)(A_{es})}{(V_o)(A_{oes})}$$

 V_f = final volume of electrolysis standard

- V_{0} = initial volume of electrolysis standard
- A_{ac} = final activity of electrolysis standard

A es = initial activity of electrolysis standard

Initial and final volume refer to the amount of standard before electrolysis and the amount remaining after electrolysis. The initial activity of the standard of course takes into account decay that has taken place since the standard was prepared. The final activity of the electrolysis standard (A_{es}) is calculated as follows:

cpm = counte per minute

bkgd cmp = badkground counts per minute

mass = mass of electrolysis standard counted

efficiency = counting efficiency (from H number)

Once the electrolysis efficiency of the standard is known, it can be applied to calculate the electrolysis efficiency of each sample. The comparison between the standard and the samples is done using what is called the Electrolysis Fractionation Factor "Beta" (B). The electrolysis efficiency of each sample may vary because during electrolysis gases bubbling through the samples carry away water vapor and spray. Although the electrolysis cells are connected in series, slight differences in vapor loss will occur due to non-uniform temperatures in the water bath, slight variation in amount of electrolyte added, and differences between electrodes (area, spacing, etc.). Therefore, each sample has a slightly different final volume, and therefore a slightly different electrolysis efficiency from the standard. The calculation of the electrolysis efficiency for each sample is made using the Electrolysis Fractionation FActor "Beta" (B).

$$B = \frac{\ln (V_0/V_f)_{es}}{-\ln EE_{es}}$$

 $EE_s = (V_o/V_f)^{-1/B}$ $EE_s = electrolysis efficiency of sample$ $V_o = initial volume of sample$ $V_f = final volume of sample$ B = Electrolysis Fractionation Factor

When the electrolysis efficiency for each sample is known, then the activity of each sample can be determined by:

 $dpm/gm = \frac{cmp - bkgd cpm/mass}{(EE_s)(V_o/V_f)(counting eff.)}$

dpm/gm = disintegrations per minute per gram

cmp = counts per minute of the sample

bkgd cmp = background counts per minute

mass = mass of sample counted

 EE_s = electrolysis efficiency of sample

 V_0/V_f = samples initial volume/samples final volume

counting eff. = efficiency of LS counting (from H number)

The average electrolysis efficiency of the standards during the study was 74.25%, meaning 74.25% of the tritium originally in the sample remained after electrolysis. The average Electrolysis Fractionation Factor "Beta" was 9.27, and the average value for background radiation was 6.68 counts per minute.

Error for the samples were calculated from the following equation

$$2 \operatorname{sigma} \% = \sqrt{\frac{((\operatorname{cpm}_{s+b})(2\sigma_{s+b}\%)^2 + ((\operatorname{cpm}_b)(2\sigma_b\%))^2}{\operatorname{cpm}_{s+b} - \operatorname{cpm}_b}}$$

$$\operatorname{cpm}_{s+b} = \operatorname{counts} \operatorname{per} \operatorname{minute} \operatorname{of} \operatorname{sample} + \operatorname{background}$$

$$\operatorname{cpm}_b = \operatorname{counts} \operatorname{per} \operatorname{minute} \operatorname{of} \operatorname{background}$$

$$2 \operatorname{s+b} \% = 2 \operatorname{sigma} \% \operatorname{error} \operatorname{of} \operatorname{sample} + \operatorname{background}$$

$$2 \operatorname{b} \% = 2 \operatorname{sigma} \% \operatorname{error} \operatorname{of} \operatorname{background}$$

Cpm, or counts per minute, and 2 sigma % error for both sample and background are automatically calculated and recorded by the LS counter and are read directly from the printout.

TABLE A.*

Well	<u>Run 1</u>	Run 2	<u>Run 3</u>	Mean	Standard Deviation
A ver y	66.60	57.10	58.90	60.86	5.046
Herriff	69.99	69.1	75.76	71.61	3.625

*Values given in Tritium Units (T.U.)

TABLE 2

(mg/1)
WELLS
DRIFT
Slayton

Location	Ca	Mg	Na	×۱	리	S 1	HCO ₃	Чe	됩
D5N01W28CAA	85	37	7.0	1.2	5.3	71	37.5	1.3	7.2
J3N01E33ABC	89	51	23.6	1.8	22.5	12.7	438	3.2	6.9
04N01E26AA	89	26.5	0.8	0.7	4.0	26.7	311.5	2.4	7.25
04N01E29BCC	66	53.2	28.5	3.8	107.0	31.5	470	3.6	7.2
01N03W02DBB	145	25	22.0	2.2	22.7	183.0	367	0.7	7.5
01N03W27CCB	88	30	4.9	1.9	8.4	5.6	406.5	4.0	7.55
12N03W12CC	124	43	24.0	1.3	0.06	19.4	429	0.9	7.3
			Slayton F	ROCK WELI	LS (mg/1)				
15N01W20ACD	75	15	14.0	3.9	1.5	139	259	0.2	7.0
15N01W28BAA	48	14	19.0	2.9	0.5	0	288	0.0	7.4
01N02W06BCB	110	86	21.0	0.7	70.0	43.5	396	0.9	7.6
D2N02W06BDC	110	39	6.2	1.2	27.5	38	438	1.5	7.55
12N02W18CCD	78	30	5.3	1.3	2.7	1.0	385	0.3	7.55
D2N02W20ABA	74	27	4.3	0.9	12.3	65	269	2.3	7.2
J2N02W20BBc	66	36	5.3	1.3	13.7	9.9	60†	0.1	7.3
D2N02W20DCD	84	31	4.6	0.9	2.3	18	370	0.6	7.9
12N02W 30BCC	17	28	6.2	2.2	0.9	1.0	401	0.7	7.5
3001E33ABB	43	17	13.9	5.2	1.0	4.2	343	0.0	7.55
J3N0IE33ABC	74	25	17.7	4.6	1.0	1.5	390.7	0.4	7.35
J3N02W34ADD	84	32	4.3	1.0	3.3	0	396	0.6	7.6
04N01E26AA	8	00	10.5	4.7	8.5	17	327.4	0.0	7.85
04N01E27BAA	74	17.5	15.3	4.6	1.9	5.6	348.5	0.0	7.4
01N03W28DDA	82	29	5.6	3.1	3.3	0	385	0.6	7.45
12N03W12ADD	85	29	5.6	2.0	1.6	0	393	0.5	7.8
12N03W12CC	85	59	2.9	0.8	2.5	19.4	350	1.1	7.35
J2N03W36CC	8	28	3.2	1.2	4.0	0	398	0.2	7.75
J3N03W30CCC	78	26	3.7	1.1	2.5	0	370	0.6	7.4
13N03W 34CCD	65	27	6.6	2.3	0.7	0	354	0.5	7.4

(Continued)
E
(mg/
WELLS
DRIFT
Slayton

됩	7.92	7.15	7.62	7.25	7.52	7.57	7.4	7.75	7.4	7.6	7.3	7.6	7.7	7.45	7.4	7.7	7.5	7.44	7.5	7.4	7.4	7.4	7.48	7.7	7.4	7.3	7.3	7.4	7.5
Fе	4.4	3.8	7.2	1.3	2.3	13.0	1.7	1.2	3.2	3.0	6.0	0.34	0.9	1.8	0.4	0.7	0.0	0.83	0.89	1.7	1.4	0.0	1.4	2.2	0.1	0.0	2.5	3.3	1.2
HCO.	395	354	307	351	394	482	494	361	436	512	484	261	420	546	364	296	290	419	330	325	339	264	347	365	350	308	256	347	340
S 1	27	81	37	17	24	12	17	13	22	22	76	12	57	37	18	47	120	13	69	58	71	143	2	45	16	73	93	52	7
리	2.5	48.0	2.0	1.5	5.0	3.4	16.0	2.0	7.1	2.0	23.0	1.7	0.46	2.0	1.4	21.0	18.0	3.4	11.0	4.0	12.0	150.0	2.6	6.0	108.0	23.0	0.6	1.6	0.1
⊼	1.4	1.6	4.2	3.7	1.3	1.4	1.7	1.8	1.8	2.0	1.6	1.8	1.3	2.6	1.2	1.6	2.0	2.3	1.4	0.5	1.0	2.0	1.4	1.7	2.5	2.5	1.2	0.9	1.0
Na	6.5	25.0	12.0	12.0	7.5	12.0	15.0	16.0	16.0	11.0	26.0	40.0	10.0	26.0	8.0	23.0	5.8	14.0	4.1	4.1	3.5	81.0	13.0	5.0	42.0	14.0	6.6	3.0	12.0
Mg	28	34	18	21	28	32	36	26	35	41	46	12	43	64	26	26	32	35	25	26	31	30	22	27	35	30	22	27	26
Ca	85	106	76	80	80	102	92	65	86	92	111	35	130	88	75	64	110	70	98	87	96	112	6 6	85	120	84	86	83	64
Location	05N02W09BBC	05N02W27CAAA	05N02W27CCAB	05N02W27CDBA	06N01W12BDBD	06N02W24ADDC	06N02W29BAAA	06N03W08BAB	06N04W05AAAA	06N04W25ACB	07N02W15CBAB	07N03W13ADDD	07N04W08DDCC	07N04W24DDDB	07N04W30BAD	08N01W13BCC	08N01W13BDC	08N01W19DADD	08N01W24ADD	08N01W27DDC	08N01W35ADD	08N03W08BAB-1	08N04W06ADDD	08N04W11BBC	02N01W08AACD	02N01W09CBBB	03N01E02BBA	03N02W02DACC	04N02E16DDD

됩	7.71	\$.0 8.0	7.69	3 7.6	7.5	7.7	7.62	7.75	7.55	7.7 6	7.19	7.19	7.1	7.56	7.12	7.23	5 7.2	7.18	7.2	3 7.5	7.28	7.4	7.22	7.72	3 7.4	7.52	7.5	7.22	5 7.78	7.35
Fe	3.5	0.16	2.5	0.38	0.9	1.0	0.4	0.9	0.6	64.0	0.1	2.4	0.8	2.0	3.0	0.7	64.0	1.2	4.5	0.73	0.6	1.8	0.47	0.6	0.43	1.8	2.5	1.6	0.9 5	0.79
HCO3	386	260	06†	744	425	410	305	310	313	312	308	290	385	329	417	346	317	361	519	351	461	454	405	00†	386	318	635	434	380	412
ୢୠୗ	19	58	56	99	23	17	6	3.2	2.4	∞	19	13	ø	94	140	170	22	340	240	11	ø	6	6	6.8	6	42	4 4	12	11	11
리	3.6	5.5	8.5	3.0	3.0	5.0	3.2	2.0	1.5	1.3	5.9	1.5	1.2	4.3	6.7	1.9	1.4	7.5	25.0	1.2	1.3	1.1	1.0	2.0	1.6	1.9	3.0	1.1	1.7	1.2
×۱	1.0	5.2	1.2	1.0	0.8	1.0	4.9	4.2	3.1	3.2	3.6	4.4	3.0	2.0	1.8	4.4	2.3	7.2	2.5	1.9	1.5	2.2	2.1	4.3	4.8	1.8	2.2	1.6	1.2	1.8
Na	3.0	6.8	7.1	4.2	5.8	8.3	18	20	18	6	20	21	6	6	7.5	∞	∞	14	10	14	4	9.5	5.5	14	15	4	12	7.5	9	9.5
Mg	30	23	8	42	\$	32	14	14	19	20	22	13	25	24	38	34	20	42	51	26	33	32	77	26	25	22	53	32	28	28
Ca	86	68	112	103	88	84	67	55	58	68	62	57	83	93	129	127	74	184	178	60	100	90	82	70	77	93	115	82	78	78
Location	02N03W32DDD	02N04W19CBBC	03N05W29BAB	03N06W 34BC	03N06W28BAA	04N06W02CADB	05N01W18CBC	05N02W16AAAA	05N02W18DCD	05N02W22DCDA	05N02W22DCDC	05N02W27CBDB	05N02W27CCAD	05N02W28BBDA	05N02W28DCAC	05N02W33ABAB	05N02W33ACB	05N02W33BAAA	05N02W33CDDB	05N03W05CCDD	05N03W15BBCC	05N03W 18AABB	05N03W18CCAA	05N03W21BBB	05N03W23BABB	05N03W27BCBB	05N04W12DDD	05N04W16ACBA	05N04W18CBDA	05N04W21ADCD

(Continued)
1
(mg/
WELLS
DRIFT
Slayton

핍	7.62	7.6	7.6	7.46	7.47	7.39	8.0	7.8	7.2	7.7	8.05	7.8	7.6	7.6	7.6	7.8	7.8	7.51	7.4	7.5	7.75	7.3	7.32	7.93	7.45	7.6	7.73	7.65	7.45	7.75
н Ч	0.79	0.2	0.31	1.2	0.51	0.44	0.1	0.34	0.0	1.3	0.77	2.0	0.6	0.0	0.65	0.8	0.84	0.53	0.3	0.37	1.8	0.96	1.2	1.6	0.38	0.15	0.35	1.2	1.1	0.7
HCO ₃	405	316	394	462	398	390	507	380	370	410	272	330	360	228	329	434	324	295	374	376	370	414	396	380	398	427	444	405	445	346
<u>S</u>	4 6	6	m	16	4	23	70	12	15	38	m	51	125	108	16	11	m	7	9	0	42	58	19	41	14	17	Ś	9	2	m
리	2.8	1.5	1.2	2.2	1.8	9.1	23.0	5.0	4.0	21	0.5	3.9	2.0	6.0	1.0	3.2	0.9	0.9	••	1.1	14	1.7	2.4	12	1.5	7.0	1.8	0.8	1.6	1.3
⊻I	1.2	2.6	2.0	2.7	2.6	4.0	2.0	1.1	1.3	0.8	4.6	0.7	1.2	1.1	2.1	6.8	1.1	1.8	1.0	7.4	1.5	1.2	1.2	1.0	2.2	6.2	7.8	1.6	4.0	1.5
Na	7	30	6.5	18	13	55	210	11	12	5.3	6.6	3.3	5.7	6.1	3.3	20.0	6.0	7.5	4.6	32.0	5.6	5.5	4.0	5.7	7.0	117.0	90.06	7.9	7.5	9.5
Mg	30	18	28	%	30	21	5.4	32	32	35	14	26	23	22	21	25	23	18	27	22	28	36	28	30	8	10	12	8	8	25
Ca	86	62	74	80	62	53	18	70	99	106	59	85	130	85	74	87	60	57	80	54	100	95	90	94	80	34	47	80	90	65
Location	05N04W24ABBB	06N02W24ACCD	06N02W29BAAA	06N04W23BABB	07N02W15CBAA	07N03W14BBBB	07N04W11DACD	08N01W2IBCCD	08N01W29CDCD	01N01E23DDDD	01N01W02CAAA	01N01W17BBBB	01N01W28AADD	01N02E19ADC	01N02W29CAAC	02N01E15DDBB	02N01E25CDDA	02N01E28DACC	02N01W05ACCC	02N01W13BCBB	02N01W18DCCC	02N01W26BDBB	02N01W28CBBB	02N02E02ACDD	02N02W 19AABA	03N01E02AAAA	03N01E08ABAB	03N01E08DDCC	03N01E12BCC	03N01E22BAAD

됩	7.51	8.03	7.32	7.29	7.45	7.75	7.33	7.25	7.2	7.83	7.5	7.65	7.4	7.9	7.4	7.7	7.3	7.51	7.6	7.1	7.5	7.51	7.55	7.2	7.5	7.2	7.8	7.71	7.5	7.4	7.4
Fe	0.57	0.35	2.4	0.77	0.44	0.4	0.37	0.63	0.77	0.8	1.1	0.68	0.6	1.9	4.1	0.92	0.61	0.7	2.2	0.6	0.95	0.78	0.46	2.0	0.4	2.9	0.3	1.2	0.7	0.4	0.8
HCO ₃	378	376	373	423	390	385	436	441	414	354	395	334	432	386	384	382	344	289	370	390	368	292	302	390	388	462	320	317	350	360	365
S 10	2	9	61	23	15	∞	Ś	11	18	73	64	79	7	ø	1.6	25	2	26	34	55	4	180	13	108	45	130	7	7	0	35	70
리	1.0	1.1	2.9	1.2	2.8	0.8	1.0	1.5	1.1	5.1	5.9	5.7	0.9	0.7	1.0	16	0.9	3.1	7	4	1.0	1.7	1.5	15	4.0	13	0	1.5	0	7	12
×۱	1.6	7.4	1.6	2.6	2.0	4.0	6.0	5.6	1.6	1.4	0.8	0.6	3.1	2.2	8.5	8.4	0.9	1.2	0.6	0.9	5.2	5.4	4.3	1.4	0.0	2.3	1.0	1.6	1.3	2.2	1.2
Na	10	65	Ś	4	Ś	13	8.5	11	7.5	Ś	Ś	Ś	6	4.9	6.1	90	2.5	7	2.9	3.2	62	20	11	9.2	13	12	11	•0	7.6	15	18
Mg	28	15	27	30	28	29	77	8	32	80	80	8	31	77	23	10	25	21	80	õ	18	24	14	%	30	43	24	23	19	77	32
Ca	72	44	94	91	82	75	88	90	90	64	96	86	85	84	83	46	75	65	87	94	68	124	74	114	80	120	54	62	70	76	86
Location	03N01E32BBCC	03N01E34ADDD	03N01W17BBBC	03N01W03BABB	03N01W07AAA	03N01W10ABBC	03N01W15BBDA	03N01W23DCCC	03N01W25ADAA	03N01W29CCAA	03N01W31BBAA	03N01W32ABAA	03N02E04ACCC	03N02E12BCAD	03N02E15ABBC	03N02E17ADDD	03N02W11ADAD	03N02W18DCB	03N02W23ADBB	03N02W23CBAD	04N01E08DADA	04N01E13CCAA	04N01E20CCA	04N01W07CACD	04N01W07DBBC	04N01W08CCCA	04N01W10BADA	04N01W11CDD	04N01W11CDDC	04N01W17ABAA	04N01W18BAD

됩	8.2	7.3	7.6	7.4	8.0	7.5	7.5	7.6	7.4	7.1	7.4	7.6	7.6	7.4	7.3	7.9	7.0	7.8	7.5	6.9	7.2	7.4	7.29	7.65	7.65	7.5	7.62	7.3	7.55	7.4
Чe	0.15	3.0	0.34	1.6	3.6	6.0	2.3	1.0	0	0.28	0.2	0.2	0.25	2.0	0.55	0.8	16.0	0.3	0.4	1.1	0.44	0.5	0.88	2.5	2.7	0.3	2.4	0.87	2.5	4.1
HCO ₃	327	396	290	320	266	398	370	356	374	348	364	354	439	340	400	904	550	375	364	378	394	368	417	434	322	315	298	346	472	525
<u>[0</u>	9	38	83	20	22	Ś	92	13	31	4.6	44	7	44	22	24	19	270	78	10	7.1	35	16	23	1	01	35	32	53	4	120
히	1.0	2.5	Ś	4	0	0	15	0	10	1.2	9	Ś	Ś	4	2	0	15	90	0	0.9	3.9	1.0	2.8	1.4	1.9	2	2.9	4.2	0.9	40
∠	0.0	1.4	4.4	3.7	0.7	1.2	1.2	3.7	4.1	2.0	1.7	1.5	0.0	2.0	2.5	0	1.6	2.4	0.8	1.6	1.3	0	1.2	13.0	2.4	1.8	I.9	1.0	1.4	1.1
Na	Ś	4.5	10	30	3.7	5.1	8.3	23	149	8.1	11	13	ø	8.7	6.5	12	11	46	5.7	5.6	4	7	3.5	60	6.0	3.5	7	m	3.9	12
Mg	28	8	10	12	24	Z	33	21	1.4	25	28	25	39	25	32	30	62	%	24	27	30	24	59	20	20	21	23	27	31	48
S	58	90	72	6 6	54	84	104	68	4.4	69	82	9 9	94	75	83	80	188	110	76	79	6	80	64	56	85	80	76	98	100	158
Location	04N01W18CCA	04N01W19CCAA	04N01W24DAAD	04N01W26BCA	04N01W27BABB	04N01W28DAB	04N01W29BBBB	04N01W35BBBB	04N02E33CDDD	04N02W04DDCC	04N02W05CCCC	04N02W05DCDC	04N02W08BCDC	04N02W09BDAD	04N02W09CBCA	04N02W11DBDD	04N02W12CCD	04N02W16DAA	04N02W18BDAB	04N02W24ADDD	04N02W25AABA	04N02W27CDA	04N02W36DAAD	01N04W13ABA	02N03W30DAB	02N03W34ACAB	02N04W04CBBC	02N04W10ABCC	02N05W23ACDC	02N05W25ADDA

71

Location	Ca	Mg	Na	×۱	리	<u> S</u>	HCO ₃	Fe	핍
02N05W26CCB	96	32	4	1.2	3.7	15	447	2.7	7.3
02N05W30DADD	100	8	5.6	2.1	0.9	Ś	450	0.16	7.7
02N05W33DCCD	96	32	4.5	0.7	8.2	39	413	1.1	7.34
03N03W35BAB	84	28	3.5	1.2	1.2	2	402	1.5	7.73
03N04W09DCCD	74	26	3.7	2.4	2	23	337	1.6	7.55
03N04W23DDB1	116	39	12	1.2	25	85	074	2.3	7.3
03N04W23DDB2	92	32	4.6	0.8	7	38	400	0.7	7.5
03N04W26BBBB	102	35	5.5	1.3	6.6	33	448	1.6	7.55
03N05W23AAA	80	30	9.5	2.5	1.2	10	407	3.0	7.62
03N05W25CBB	86	33	7.5	1.7	2.2	13	425	1.1	7.55
04N03W07ABBB	75	32	11	2.1	1.3	6	421	0.55	7.5
04N03W13ADD	80	24	13	2.8	0	4	400	0.6	7.4
04N03W14DAB	62	26	31	3.0	Ś	ø	390	0.4	7.4
04N04W02AACD	80	29	1	1.5	Ś	18	385	0.5	7.5
04N04W10BBBA	72	32	12	1.9	2	23	400	6.0	7.68
04N04W11DCAD	80	80	9	0.8	m	43	364	2.0	7.5
04N04W14ABAA	93	31	6.9	1.0	3.5	31	406	0.83	7.3
04N04W23DDC	76	32	6.6	1.8	1.5	26	373	0.95	7.67
04N05W03CDC	38	24	49	3.4	1.2	10	378	0.5	8.03
04N06W28CDC	80	26	3.5	1.2	0.9	•0	385	2.9	7.65

TABLE 7

Slayton DRIFT WELL Ratios

SO,/HCO		cı/HCO,	CI/SO,	Ca/Mg	Na/K	Ca/Na	CI/Ca	TDS mg/1	epm cat.	epm an
.12026 .02432 0.20	.02432 0.20	0.20	7 2	1.393	9.921	6.965	0.704	582.8	7.238	7.373
.01839 .08831 4.80	.08831 4.80	4.80	04	1.054	22.300	2.163	.2858	642.5	9.552	7.860
.04258 .39190 9.20	.39190 9.20	9.20	39	1.128	1.745	1.992	1.2219	796.5	6.004 10.375	11.044
.31673 .10645 0.33	.10645 0.33	0.33	61	3.518	17.008	3.780	.1769	767.6	9.375	9.527
.00875 .03556 4.06	.03556 4.06	4.06	643	1.779	4.386	10.301	.1079	549.3	7.000	6.855
.02872 .36106 12.57	.36106 12.57	12.57	00	1.749	31.400	2.963	.8205	731.6	10.533	9.692
			Slayt	on ROCK	WELL Rat	ios				
.34089 .00996 0.02	.00996 0.02	0.02	92	3.032	6.105	3.072	.0226	507.6	5.211	6.705
.00000 .00298 1.45	.00298 1.4E	1.4E	3+25	2.079	11.143	1.449	.0117	372.4	4.391	4.678
.06977 .30423 4.30	.30423 4.36	4.3	502	1.755	51.025	3.004	.7194	680.1	9.192	9.008
.05510 .10806 1.96	.10806 1.96	1.96	60	1.710	8.787	10.176	.2826	661.4	8.668	8.400
.00164 .01207 7.31	.01207 7.31	7.31	58	1.577	6.934	8.441	.0391	503.6	6.489	6.269
.15348 .07869 0.51	.07869 0.51	0.51	27	1.662	8.126	9.871	.1879	454.8	5.859	5.811
.01537 .05765 3.74	.05765 3.74	3.74	96	1.668	6.934	10.714	.1564	574.3	7.969	7.098
.03090 .01069 .03	.01069 .03	0	3462	1.643	8.693	10.474	.0309	511.4	6.740	6.278
.00158 .00386 2.4	.00386 2.4	2.4	386	1.668	4.793	7.123	.0132	517.0	6.347	6.486
.00777 .00501 0.64	.00501 0.61	0.61	451	1.534	4.546	1.774	.0262	427.5	4.200	5.659
.00243 .00440 1.80	.00440 1.80	1.80)64	1.795	6.544	2.398	.0152	514.9	6.524	6.344
.00000 .01434 9.35	.01434 9.31	9.3I	3+25	1.592	7.313	11.205	.0444	521.2	6.894	6.434
1	1	I		ı	ı	I	I	I	2.233	5.959
.01020 .00938 0.91	.00938 0.91	0.91	93	2.565	5.657	2.774	.0290	467.4	5.806	5.772
.00000 .01475 9.3E	.01475 9.3E	9.3E	+25	1.715	3.072	8.399	.0454	508.6	6.683	6.278
.00000 .00700 4.5E	.00700 4.5E	4.5E	:+25	1.777	4.762	8.706	.0212	516.7	6.772	6.333
.03520 .01229 0.34	.01229 0.3	<u>.</u> .0	161	1.777	6.165	16.812	.0332	490.7	6.598	6.020
.00000 .01729 1.1	.01729 1.1	1.1	E+25	1.949	4.535	16.132	.0502	524.6	6.807	6.477
.00000 .01162 7.0	.01162 7.0	7.0	E+25	1.819	5.721	12.092	.0362	481.9	6.114	6.021
.00000 .00340 1.9	.00340 1.9	1.9	E+25	1.460	4.880	5.649	.0121	456.1	5.716	5.720

Ratios
WELL
RIFT
(69) 10
r (196
Vanlie

								TDS	epm	epm
<u>Location</u>	SO,/HCO3	CI/HCO3	<u>CI/50</u>	Ca/Mg	Na/K	Ca/Na	CI/Ca	mg/1	cat.	an.
5N02W09BBC	.04341	.01089	0.2508	1.841	7.896	7.500	.0332	549.8	6.624	6.861
5N02W27CAAA	.14534	.23337	1.6057	1.891	26.576	2.432	.5119	653.4	8.816	8.387
5N02W27CCAB	.07655	.01121	0.1464	2.561	4.859	3.632	.0297	463.4	5.768	5.661
5N02W27CDBA	.03076	.00735	0.2390	2.310	5.516	3.823	.0211	487.5	6.199	5.993
6N01W12BDBD	.03869	.02184	0.5644	1.733	9.812	6.118	.0706	542.1	6.467	6.886
6N02W24ADDC	.01581	.01214	0.7677	1.933	14.579	4.875	.0376	657.8	8.191	8.031
6N02W29BAAA	.02327	.05934	2.5502	1.550	15.007	3.518	.1966	643.4	8.033	8.173
6N03W08BAB	.02287	.00953	0.4168	1.516	15.119	2.330	.0347	486.0	5.973	6.086
6N04W05AAAA	.03205	.02802	0.8744	1.490	15.119	3.083	.0933	607.1	7.716	7.568
6N04W25ACB	.02729	.00672	0.2463	1.361	9.354	4.797	.0245	685.0	8.226	8.611
17N02W15CBAB	42660.	.08178	0.8199	1.463	27.639	2.448	.2342	773.6	10.050	9.638
17N03W13ADDD	.02920	.01121	0.3838	1.769	37.796	0.501	.0549	363.8	4.452	4.505
17N04W08DDCC	.08620	.38519	4.4684	1.833	13.083	7.456	.8174	756.2	10.023	10.246
7N04W24DDB	.04304	.00630	0.1464	1.089	17.008	1.941	.0256	752.4	9.268	9.402
17N04W 30BAD	.03141	.00661	0.2107	1.749	11.339	5.377	.0211	0.464	6.093	6.208
8N02W13BCC	.10085	.12210	1.2106	1.493	24.450	1.596	.3709	494.3	6.137	6.181
8N01W13BDC	.26284	.10683	0.4064	2.085	4.932	10.878	.1849	583.8	7.818	7.152
BN01W19DADD	.01970	.01396	0.7086	1.213	10.353	2.867	.0549	557.5	6.865	7.049
8N01W24ADD	.13281	.05736	0.4319	2.329	4.981	13.430	.1295	537.4	6.696	6.781
8N01W27DDC	.11336	.02118	0.1868	2.029	13.947	12.171	.0519	506.3	6.376	6.331
8N01W35ADD	.13303	.06092	0.4579	1.878	5.952	15.732	.1413	554.9	7.138	6.976
8N03W08BAB-1	.34406	.97788	2.8422	2.264	68.884	0.793	1.5141	794.0	10.980	10.885
8N04W06ADDD	.00366	.01289	3.5224	1.819	15.794	2.912	.0445	455.4	5.620	5.702
8N04W11BBC	.07830	.02829	0.3612	1.909	5.002	9.751	.0798	536.9	6.448	6.797
2N01W08AACD	.16515	.53107	3.2157	2.079	28.574	1.638	1.0175	748.6	10.232	10.151
2N01W09CBBB	.15055	.12852	0.8536	1.698	9.524	3.441	.3095	534.5	6.976	6.851
3N01E02BBA	.23075	.06050	0.2622	2.371	9.354	7.474	.1183	485.3	6.050	5.984
3N02W02DACC	.09518	.00793	0.0833	1.864	5.669	15.869	.0217	517.8	6.262	6.520
4N02E16DDD	.01307	.00050	0.0387	1.493	20.410	3.059	.0017	451.3	5.772	5.600
2N03W 32DDD	.03126	.01605	0.5133	1.738	5.102	16.443	.0473	532.1	6.728	6.613

									,	2
-								SOI	epm	epm
ation	<u>50,/HCO3</u>	CI/HCO3	<u>CI/50</u>	Ca/Mg	Na/K	Ca/Na	<u>ci/ca</u>	mg/1	<u>cat.</u>	- la
W19CBBC	.14170	.03640	0.2569	1.793	2.224	5.735	.0914	438.0	5.426	5.352
W 29BAB	.07259	.02985	0.4112	1.787	10.063	9.048	.0857	715.3	8.618	8.983
W 28BAA	.03437	.01214	0.3534	1.570	12.331	8.702	.0385	595.5	7.227	7.285
W 34BC	.09442	.01162	0.1231	1.487	7.143	14.066	.0329	663.6	8.336	8.266
W02CADB	.02633	.02098	0.7960	1.592	14.117	5.805	.0672	575.3	6.998	6.995
W18CBC	.01874	.01805	0.9633	2.903	6.248	2.135	.0539	421.5	5.302	5.171
W16AAAA	.00655	.01110	1.6935	2.383	8.099	1.577	.0411	410.1	4.795	5.162
W18DCD	.00487	.00824	1.6935	1.851	9.875	1.848	.0292	415.6	5.240	5.136
W 22DCDA	.01628	.00717	0.4403	2.062	ı	t	.0216	413.0	5.006	5.199
22DCDC	.03918	.03296	0.8413	1.709	9.449	1.778	.1075	440.6	5.732	5.474
27CBDB	.02847	.00890	0.3126	2.659	8.117	1.556	.0297	402.3	4.883	4.974
2W27CCAD	.01319	.00536	0.4064	2.013	5.102	5.298	.0163	515.0	6.539	6.370
2W28BBDA	.18148	.02249	0.1239	2.350	7.653	5.927	.0522	557.3	6.625	7.019
W28DCAC	.21325	.02765	0.1296	2.059	7.086	9.865	.0587	743.0	9.203	9.160
W 33ABAB	.31209	.00945	0.0302	2.265	3.092	9.105	.0169	692.0	8.745	8.403
W 33ACB	.04408	.00760	0.1724	2.244	5.916	5.305	.0213	445.2	5.596	5.537
W 33BAAA	.59824	.03575	0.0597	2.657	3.307	7.538	.0460	956.9	11.642	11.402
W33CDDB	.29373	.08290	0.2822	2.117	6.803	10.210	.1587	1030.0	12.201	12.767
W05CCDD	.01990	.00588	0.2955	1.399	12.533	2.458	.0226	465.8	5.665	5.882
W15BBCC	.01102	.00485	0.4403	1.838	4.535	14.339	.0146	609.4	7.728	7.561
W18AABB	.01259	.00417	0.3311	1.706	7.344	5.434	.0138	599.6	7.423	7.467
W18CCAA	.01411	.00424	0.3010	1.842	4.454	8.551	.0137	532.1	6.469	6.699
W21BBB	.01079	.00860	0.7969	1.633	5.537	2.868	.0323	523.7	6.200	6.599
W 23BABB	.01481	.00713	.04817	1.868	5.315	2.944	.0234	518.8	6.533	6.412
W 27BCBB	.08389	.01028	0.1225	2.564	3.779	13.336	.0230	484.5	6.428	5.878
W12DDDD	.04401	.00813	0.1847	1.316	0.927	5.496	.0294	886.5	10.717	10.915
W16ACBA	.01756	.00436	0.2483	1.554	7.972	6.271	.0151	571.8	6.932	7.211
W18CBDA	.01838	.00769	0.4187	1.689	8.504	7.456	.0246	506.9	6.313	6.326
W21ADCD	.01695	.00501	0.2955	1.689	8.976	4.709	.0173	542.3	6.500	6.850
W2IBDAC	.06736	.05215	0.7741	1.455	10.742	4.588	.1648	676.1	8.291	8.612

								TDS	epm	epm
<u>Location</u>	SO /HCO3	CI/HCO3	<u>c1/so</u>	Ca/Mg	Na/K	<u>Ca/Na</u>	CI/Ca	mg/1	<u>cat.</u>	. an
05N04W24ABBB	.07214	.01189	0.1649	1.738	9.921	7.047	.0368	578.8	6.786	7.359
06N02W24ACCD	.01809	.00816	0.4515	2.089	19.625	1.185	.0273	439.3	5.837	5.298
06N02W29BAAA	.00483	.00524	1.0838	1.603	5.527	6.530	.0183	509.0	6.192	6.413
06N04W23BABB	.02199	.00819	0.3725	1.348	11.339	2.549	.0310	618.1	7.597	7.744
07N02W15CBAA	.00638	.00778	1.2193	1.253	8.504	2.735	.0328	511.9	6.067	6.524
07N03W14BBBB	.03746	.04015	1.0720	1.530	23.387	0.552	.1941	555.5	6.716	6.971
07N04W1IDACD	.08769	.07807	0.8902	2.022	17.859	0.049	1.4445	835.5	10.373	10.260
08N01W21BCCD	.02055	.02264	1.1290	1.326	17.008	3.650	.0807	511.4	6.448	6.433
08N01W29CDCD	02575	.01860	0.7225	1.251	15.700	3.154	.0685	500.3	6.320	6.328
01N01E23DDDD	.05887	.08815	1.4974	1.837	11.268	11.471	.2239	617.4	8.092	7.766
01N01W02CAAA	00700	.00316	0.4519	2.556	2.440	5.127	.0095	360.5	4.406	4.44]
01N01W17BBBB	.09816	.02034	0.2072	1.983	8.018	14.774	.0518	501.9	6.245	6.275
01N01W28AADD	.22055	.00956	0.0433	3.428	8.079	13.082	.0173	647.5	7.988	7.884
01N02E19ADC	.30087	.04529	0.1505	2.343	9.431	7.992	.0798	456.2	5.892	5.702
01N02W29CACC	.03089	.00523	0.1693	2.137	2.672	12.862	.0152	447.1	5.472	5.602
02N01E15DDBB	.01609	.01269	0.7882	2.110	5.002	2.495	.0415	587.8	7.242	7.228
02N01E25CDDA	.00588	.00478	0.8128	1.582	9.277	5.735	.0169	418.8	5.071	5.289
02N01E28DACC	.00430	.00525	1.2193	1.920	7.086	4.359	.0178	382.7	4.627	4.825
02N01W05ACCC	.01019	.03681	3.6127	1.797	7.823	9.975	.1130	500.9	6.304	6.341
02N01W13BCBB	.0000	.00503	3. IE+25	1.488	7.355	0.967	.0230	492.9	5.995	6.09
02N01W18DCCC	07210	.06512	0.9031	2.166	6.349	10.242	.1582	562.9	7.272	7.020
02N01W26BDBB	.08898	.00706	0.0794	1.600	7.795	9.907	.0202	612.4	7.606	7.662
02N01W28CBBB	.03047	.01043	0.3422	1.949	5.669	12.905	.0301	541.8	6.814	6.752
02N02E02ACDD	.06853	.05435	0.7930	1.900	9.694	9.459	.1443	565.3	7.107	7.093
02N02W 19AABA	.02234	.00648	0.2903	1.617	5.411	6.555	.0211	533.1	6.642	6.674
03N01E02AAAA	.02528	.02821	1.1157	2.062	32.097	0.166	.2327	625.3	7.663	7.444
03N01E08ABAB	.00715	.00697	0.9754	2.375	19.625	0.299	.0432	608.0	7.340	7.322
03N01E08DDCC	.00941	.00339	0.3612	1.617	8.397	5.808	.0113	523.5	6.689	6.619
03N01E12BCC	.00285	.00618	2.1676	1.819	3.189	6.883	.0200	581.2	7.239	7.219
03N01E22BAAD	.00550	.00646	1.1741	1.577	10.772	3.924	.0226	452.0	5.635	5.649

*								TDS	epm	epm
L ocation	SO ₄ /HCO ₃	CI/HCO3	CI/SO4	Ca/Mg	Na/K	Ca/Na	CI/Ca	<u>mg/1</u>	cat.	ar.
03N01E32BBCC	.00840	.00455	0.5419	1.559	10.630	4.129	.0157	496.2	6.242	6.191
03N01E34ADDD	.01013	.00503	0.4967	1.779	14.940	0.388	.0282	514.9	6.328	6.200
03N01W03BABB	.00345	.00488	0.1413	1.840	2.616	13.049	.0149	575.6	7.031	7.217
03N01W07AAA	.02443	.01235	0.5057	1.776	4.252	904.6	.0386	525.2	6.487	6.601
03N01W10ABBC	.01319	.00357	0.2709	1.568	5.527	3.309	.0120	515.2	6.629	6.330
03N01W15BBDA	.00437	.00394	0.9031	1.977	2.409	5.938	.0128	569.9	6.991	7.087
03N01W17BBBC	.10388	.01338	0.1288	2.111	3.189	17.972	.0348	564.9	6.764	7.114
03N01W23DCCC	.01584	.00585	0.3694	1.819	3.340	4.693	.0188	590.7	7.403	7.313
03N01W25ADAA	.02761	.00457	0.1655	1.706	7.972	6.883	.0138	565.0	7.294	6.983
03N01W29CCAA	.13099	.02479	0.1893	1.900	6.074	10.783	.0613	563.3	6.987	7.038
03N01W31BBAA	.07879	.02570	0.3262	1.941	6.378	18.355	. 0694	580.8	7.088	7.327
03N01W32ABAA	.15024	.02937	0.1955	1.738	8.504	16.443	.0749	539.0	6.499	6.868
03N02E04ACCC	.00147	.00358	2.4386	1.663	4.937	5.417	.0119	562.6	7.120	6.977
03N02E12BCAD	.01316	.00312	0.2370	1.887	3.788	9.833	4600.	514.7	6.504	6.331
03N02E15ABBC	.00264	.00448	1.6935	2.189	1.220	7.804	.0136	511.3	6.450	6.238
03N02E17ADDD	.04156	.07208	1.7341	2.790	18.223	0.293	.3932	578.3	ı	ı
03N02W11ADAD	.00369	.00450	1.2193	1.819	4.724	17.207	.0135	450.9	5.833	5.599
03N02W18DCB	.05714	.01846	0.3230	1.877	9.921	5.326	.0539	413.0	5.153	5.205
03N02W23ADBB	.05836	.03256	0.5578	1.759	8.220	17.207	6060.	547.7	6.711	6.710
03N02W23CBAD	.08957	.01765	0.1970	1.900	6.047	16.849	.0481	590.7	6.992	7.312
04N01E08DADA	.00690	.00467	0.6773	2.291	9.485	1.344	.0166	494.2	6.171	6.034
04N01E13CCAA	.39156	.01002	0.0255	3.134	6.299	3.556	.0154	647.9	8.339	7.742
04N01E20CCA	.02734	.00854	0.3126	3.206	4.351	3.858	.0229	420.3	5.317	5.142
04N01W07CACD	.17590	.06619	0.3763	1.920	11.177	7.107	.1487	675.6	8.513	8.461
04N01W07DBBC	.07366	.01774	0.2408	1.617	ı	3.529	.0565	560.4	6.739	7.118
04N01W08CCCA	.17873	.04842	0.2709	1.692	8.874	5.735	.1224	785.2	9.405	9.902
04N01W10BADA	.00396	.00000	0.0000	1.364	18.709	2.815	.0000	412.3	5.071	5.183
04N01W11CDD	.01402	.00814	0.5806	1.635	8.504	4.445	.0273	421.3	5.268	5.268
04N01W11CDDC	00000	.00000	0.000	2.234	9.943	5.283	0000.	466.6	5.334	5.643
04N01W17ABAA	.06175	.00956	0.1548	1.707	11.597	2.906	.0297	529.6	6.495	6.454

								TDS	epm	epm
<u>Location</u>	SO /HCO3	CI/HCO3	<u>CI/SO4</u>	Ca/Mg	Na/K	Ca/Na	<u>CI/Ca</u>	<u>mg/1</u>	cat.	ar.
04N01W18BAD	.12182	.05658	0.4644	1.630	25.513	2.740	.1577	599.0	7.365	7.396
04N01W18CCA	.01165	.00526	0.4515	1.256	1	6.653	.0194	436.2	5.239	5.337
04N01W19CCAA	.06095	.01086	0.1782	1.819	5.467	11.466	.0314	565.4	6.597	7.078
04N01W24DAAD	.18180	.02967	0.1632	4.367	3.865	4.129	.0785	474.7	4.657	6.314
04N01W26BCA	.03969	.02151	0.5419	3.336	13.791	1.261	.0685	466.3	5.572	5.645
04N01W27BABB	.05253	.00000	0.0000	1.364	8.990	8.371	.0000	390.0	4.706	4.680
04N01W28DAB	.00797	.00000	0.0000	1.887	7.228	9.447	.0000	535.2	6.526	6.478
04N01W29BBBB	.15794	.06977	0.4417	1.911	11.764	7.187	.1630	640.8	7.812	7.894
04N01W35BBBB	.02319	.00000	0.0000	1.964	10.573	1.695	.0000	495.7	6.082	5.963
04N02E33CDDD	.05264	.04601	0.8740	1.906	51.811	0.016	2.5693	573.9	6.881	7.017
04N02W04DDCC	.00839	.00593	0.7068	1.674	6.888	4.886	.0196	470.2	5.799	5.724
04N02W05CCCC	.07678	.02836	0.3694	1.776	11.005	4.275	.0827	545.0	6.645	6.776
04N02W05DCDC	.01256	.01458	1.1612	1.601	14.741	2.912	.0513	478.2	5.826	5.902
04N02W08BCDC	.06366	.01960	0.3079	1.462	3.4E+26	6.739	.0601	631.7	7.891	7.915
04N02W09BDAD	.04110	.02024	0.4926	1.819	7.398	4.944	.0602	490.7	6.078	5.968
04N02W09CBCA	.03811	.00860	0.2258	1.573	4.422	7.324	.0272	564.9	6.907	6.906
04N02W11BDBD	D .02972	.00000	0.0000	1.617	5.2E+25	3.823	.0000	551.3	6.747	6.824
04N02W12CCD	.31182	.04693	0.1505	1.839	11.693	9.803	.0902	1130.8	13.588	13.402
04N02W16DAA	.13212	.41306	3.1264	1.853	32.599	1.371	.9249	746.1	10.017	9.813
04N02W18BDAB	.01745	.00000	0.0000	1.920	12.118	7.647	.0000	496.3	5.894	6.049
04N02W24ADDD	.01193	.00409	0.3434	1.774	5.952	8.091	.0128	515.5	6.334	6.247
04N02W25AABA	.05642	.01703	0.3019	1.819	5.233	12.905	.0489	558.6	6.911	7.035
04N02W27CDA	.02761	.00467	0.1693	2.022	3.0E+26	6.555	.0141	499.5	6.110	6.226
04N02W 36DAAD	.03503	.01155	0.3298	1.966	4.960	15.405	.0336	571.4	7.043	7.164
01N04W13ABA	.00146	.00555	3.7934	1.698	7.850	0.535	.0282	587.9	7.289	7.060
02N03W 30DAB	.07890	.01015	0.1287	2.578	4.252	8.125	.0252	480.0	5.990	5.923
02N03W34ACAB	.07057	.01092	0.1548	2.310	3.307	13.110	.0282	468.6	5.705	5.732
02N04W04CBBC	.06820	.01674	0.2455	2.004	1.790	21.796	.0431	438.2	5.640	5.431
02N04W10ABCC	.09729	.02089	0.2147	2.201	5.102	18.737	.0484	533.1	6.956	6.569
02N05W23ACDC	. 00538	.00328	0.6096	1.956	4.738	14.707	.0101	615.7	7.578	7.652

								TDS	epm	epm
Location	SO ₄ /HCO ₃	CI/HCO3	<u>CI/SO4</u>	Ca/Mg	Na/K	Ca/Na	CI/Ca	mg/1	<u>cat.</u>	an.
02N05W25ADDA	.14519	.13113	0.9031	1.996	18.555	7.552	.2862	908.2	11.588	11.385
02N05W26CCB	.02131	.01424	0.6683	1.819	5.669	13.766	.0435	601.6	7.450	7.529
02N05W 30DADD	.00705	.00344	0.4877	2.022	4.535	10.242	.0101	593.8	7.552	7.300
02N05W33DCCD	.05998	.03417	0.5697	1.819	10.934	12.236	.0965	594.5	7.352	7.513
03N03W35BAB	.00316	.00513	1.6257	1.819	4.960	13.766	.0161	523.4	6.533	6.510
03N04W09DCCD	.04335	.01021	0.2356	1.726	2.622	1.147	.0305	469.7	5.886	5.875
03N04W23DDB1	.12271	.09778	0.7969	1.804	17.008	5.544	.2436	735.5	9.041	9.148
03N04W23DDB2	.02034	.03011	0.4991	1.743	9.779	11.471	.0860	590.1	7.158	7.251
03N04W26BBBB	.04678	.02535	0.5419	1.767	7.195	10.637	.0731	633.0	7.944	7.903
03N05W23AAA	.01560	.00507	0.3151	1.617	6.463	4.830	.0169	543.2	6.788	6.738
03N05W25CBB	.01942	.00890	0.4585	1.580	7.503	6.577	.0289	569.5	7.183	7.094
04N03W07ABBB	.01357	.00531	0.3913	1.421	8.909	3.910	.0195	552.0	6.740	6.951
04N03W13ADD	.00635	.00000	0.0000	2.022	7.896	3.529	.0000	534.6	6.477	6.515
04N03W14DAB	.01303	.02206	1.6935	1.446	17.575	1.147	.0911	534.7	6.529	6.581
04N04W02AACD	.02969	.02235	0.7526	1.673	12.473	4.171	.0706	543.2	6.706	6.642
04N04W10BBBA	.03652	.00860	0.2356	1.364	10.742	3.441	.0314	543.8	6.581	6.870
04N04W11DCAD	.07503	.01418	0.1890	1.617	12.756	7.647	.0423	546.1	6.488	6.686
04N04W14ABAA	.04850	.01583	0.3059	1.819	12.736	7.731	.0425	589.3	7.269	7.144
04N04W23DDC	.04427	.00692	0.1563	1.440	6.236	6.605	.0223	517.9	6.537	694.9
04N05W03CDC	.01680	.00546	0.3151	0.960	24.512	0.444	.0357	504.1	5.948	6.297
04N06W28CDC	.01319	.00402	0.3048	1.866	4.960	13.110	.0127	507.5	6.183	6.348

TABLE 8: Rock wells from the Saginaw Formationused for ion ratio comparison from study areas.

STUDY AREA A

03N01E33ABB	03N01E02AAAA	03N02E04ACCC
03N01E33ABC	03N01E08ABAB	03N02E12BCAD
04N01E27BAA	03N01E08DDCC	03N02E15ABBC
02N01E15DDBB	03N01E12BCC	03N02E17ADDD
02N01E25CDDA	03N01E22BAAD	04N01E08DADA
02N01E28DACC	03N01E32BBCC	04N01E20CCA
02N02E02ACDD	03N01E34ADDD	

STUDY AREA B

02N02W20ABA	03N02W23ADBB	04N02W11DBDD
02N02W20BBC	03N02W23CBAD	04N02W18BDAD
04N02W20DCD	04N02W04DDCC	04N02W24ADDD
02N02W30BCC	04N02W05CCCC	04N02W25AABA
02N03W12ADD	04N02W5DCDC	04N02W27CDA
02N03W12CC	04N02W08BCDC	04N02W36DAAD
02N02W19AABA	04N02W09BDAD	02N03W30DAB
03N02W11ADAD	04N02W09CBCA	02N03W34CAB
03N02W18DCB		

