QUALITATIVE ESTIMATE OF RECHARGE IN AN UNCONSOLIDATED

GLACIAL AQUIFER IN FULTON COUNTY, OHIO

A Thesis

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AKNOWLEDGEMENTS

INTRODUCTION

The purpose of this study is to describe the source and process of recharge in an unconsolidated glacial aquifer in Fulton County, Ohio. This is done both by analysis of local hydrogeology and of the chemistry of surface and ground water samples taken from the area. Water well logs were used to model the geologic and hydraulic properties of the aquifer. Water samples were analyzed for major cations and anions and for stable isotopes. The results were then synthesized to help determine surface-ground water interaction and ground water flow direction and processes.

STUDY AREA

The study area (see Figure 1) is about 5 square kilometers in Fulton Township of Fulton County, State of Ohio, approximately 4 kilometers northeast of the town of Delta, Ohio and centered near the intersection of township roads HJ and 5. It is an exclusively agricultural area with very flat topography and is sparsely populated. Water wells in this area are used exclusively for domestic supplies of water and not for agriculture/irrigation. According to the Ohio Department of Natural Resources the average annual precipitation rate here is about 84 centimeters, the average annual evapotranspiration rate is about 58 centimeters, and the average annual temperature is about 9.5 degrees Celsius.

METHODS

Surface water and ground water samples were collected for determination of dissolved major cation and anion concentration and for stable isotopic composition of the water. Two samples (one sample for ions, one for isotopes) were taken from each of five surface water sites (s1-s5) and five domestic water wells (g1-g5). The approximate location of each sampling was then plotted on a U. S. Geological Survey topographic map of the area (Figure 1). Precleaned 125 mL HDPE Nalgene bottles were used to collect ion samples and precleaned 63 mL glass

Qorpak wide-mouth square bottles were used to collect the isotope samples. Each bottle was rinsed twice with the sample water before filling and cap was double-checked for tight seal. Bottles were then stored at approximately 7 degrees Celsius in a dark environment until analysis. Major ions measurement was performed approximately seven weeks after collection and isotope testing approximately 11 weeks after collection.

The major cations (Na, K, Mg, and Ca) and anions (Cl, SO_4, NO_3, F, and Br) were measured using a DX120 Dionex Ion Chromotograph. All ion water samples were filtered with a 0.4 micrometer Nucleopore filter before being analyzed. Dilutions were carried when necessary using our cleanest water (Millepore Milli-Q Academic Water System). After filtration, the cation samples were acidified to a pH of 2.0 using Ultrex HNO_3. A detailed procedural discussion of the analytical technique can be found in Welch, et al. (1996). Precision of these measurements is $\pm 5\%$ or better.

Isotopic analysis was performed at Dr. J. White's laboratory at the University of Colorado at Boulder. The samples were analyzed for δD (Deuterium or ^2H) and $\delta^{18}O$, which are values of the isotopic ratios compared to a known standard. The formula used to calculate δD and $\delta^{18}O$ is:

$$\delta^{18}O \text{ (or } \delta D) = \frac{(^{18}O/^{16}O) \text{ sample } - (^{18}O/^{16}O) \text{ standard}}{(^{18}O/^{16}O) \text{ standard}} \times 1000$$

Results are presented in units of parts per mil ($^o/_{oo}$), which means parts per thousand. The standard used is Standard Mean Ocean Water (SMOW).

Area hydrogeology was characterized by collaborative use of water well logs, a topographic map, a bedrock topography map, hydrogeologic maps, literature review, and comparison with ionic and isotopic data. Two hydrogeologic cross-sections were prepared of the study area (see Figures 2 and 3 for cross sections A-A' and B-B'). Data were compiled primarily from specific water well logs from the Ohio Department of Natural Resources. These data were compared to and supplemented by data from other nearby water well logs, bedrock topography

data from ODNR Open-File Map #BT-D4E8, and by well depth and static water level measurements taken from two of the test wells (g1 and g5).

RESULTS

Hydrogeologic Setting

Bedrock Hydrogeology

The study area is underlain by gray to black, fissile shale of the Upper Devonian Ohio Shale, Antrim member. This shale is approximately 49 meters thick in the study area (based on well logs) and dips generally about 3.75 meters per kilometer towards the northwest in the Lake Plains region (Reimann, 1979). The regional bedrock trend is controlled by the Findlay Arch and strikes generally north-northeast and dips 1-3 degrees northwest.

The Ohio Shale has poor vertical and horizontal hydraulic conductivity, ranging from 10^{-8} to 10^{-6} m/day (G. D. Casey, in Eberts and George, 2000). This produces well yields of 3.5 to 19.0 liters per minute in general. Because of this, wells that are developed in the Ohio Shale typically serve only as a secondary aquifer to the glacial sediments. Some wells in the area are developed into only the first meter of the shale. This is done for one or both of the following two reasons: older drilling rigs made it difficult to set a screen in glacial sediments at such large depths (30 meters) so the casing was set shallow into the bedrock instead of screening to prevent glacial sediment fines from being drawn into the casing; and the upper surface of the shale is often highly fractured and transmits water better than the rest of the rock unit, and therefore can contribute additional water to the well.

Glacial Hydrogeology

This area is part of the geographic Lake Plains area and contains glacial deposits ranging from 18 to 46 meters thick. Glacial deposits overlay the Ohio Shale and serve as the primary aquifer for domestic water supplies. These glacial deposits thicken towards the northwest so that

bedrock highs and topographic highs trend in nearly the exact opposite direction. Much of the thinning of glacial deposits towards the southeast is thought to be caused by erosion by successive proglacial lake stages after glacial deposition (Angle, 1987, Forsyth, 1959).

The Lake Plains was named for the extensive lacustrine clays and associated sandy beach ridges and terraces deposited in the area by proglacial lakes at the end of the Wisconsinan glacial stage. These lake deposits were the final seal on the thick, extensive layers of glacial till deposited earlier by successive Wisconsinan continental ice sheets. Wisconsinan ice sheets existed intermittently in the Lake Plains area beginning around 70,000 years before present (B.P. hereafter) and the final ice sheet left the area by about 15,000 BP (Dreimanis and Goldthwait, 1973). End moraines mark the final existence of the glacier margin in the Lake Plains, while the beach ridges record the glacier's retreat out of the rest of the Lake Erie basin.

Crossing the surface of the study area is the thin, sandy ridge referred to as the Lake Whittlesey beach ridge. It averages about 30 meters wide and about 4 meters thick. It is comprised of a moderately sorted sand with a median phi size of 2 (medium grained), and a porosity of 31% (Table 1). Most of the homes and structures in the area are built upon the beach ridge but no wells are developed in it, only through it.

Associated with the beach-ridge is a thin layer of lacustrine clay and silt lying adjacent and below the beach ridge. Due to the erosional nature of the pre-Whittlesey proglacial lake stages, most or all of the lacustrine clays and silts northwest of the Whittlesey beach ridge were eroded, so that only the southeast half of the study area contains extensive lacustrine mud (M. Angle, personal communication). Lake plain lacustrine muds are commonly laminated and sometimes covered by marl and peat and were laid during the successive proglacial lake stages between about 14,500 and 12,750 years before present (Forsyth, 1960; Goldthwait and others, 1961). During the period between glaciation and colonization by Europeans in the early 1800's this area was part of an extensive swamp that covered most of the same area as the Lake Plains. Before being ditched and drained for agriculture this area was called the "Great Black Swamp"

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by early settlers. This explains the presence of at least some of the peat and marl in the lacustrine deposits. Hydraulic conductivity of lacustrine clays and silts in the Lake Plains is very low, ranging from about 2.0×10^{-5} m/day to 1.0×10^{-3} m/day (Eberts and George, 2000).

Lying below the lacustrine deposits is a layer of compacted clayey till ranging from about 15 to 37 meters thick. Tills in this area are generally about 80-95 percent silt and clay and so hydraulic conductivity is in the low range for glacial till (Angle, M., 1987; Steiger & Holowaychuk, 1971). Vertical ground-water flow velocities through clayey tills in this area have been determined to be between 12 and 24 meters per 10,000 years (Eberts and George, 2000). This corresponds with the lower estimates of hydraulic conductivity for glacial till of 10^{-7} to 10^{-3} m/day (Domenico & Schwartz, 1990). Thin, discontinuous layers of sand and gravel are distributed throughout the till and probably contribute much of the transmissivity of the till. The high clay and silt content of the glacial deposits as a whole form a rather restricted and static groundwater setting.

The principle aquifer in the glacial till is a lenticular sand and gravel outwash layer at the base of the till, sandwiched between the more clayey till above and the Ohio Shale below. Well logs indicate that this outwash layer ranges from 0.5 to 5.0 meters thick and covers roughly an 8 square kilometer area, pinching out at its edges. The confining pressure of the clayey till above creates a hydraulic head as much as 17 meters above the outwash layer (Figures 2 and 3). Hydraulic head does not vary much horizontally across the aquifer, and therefore there is little, if any force outside of pumping to drive horizontal recharge of the sand and gravel aquifer. Also, the small increase in hydraulic head moving southeast to northwest is likely offset by the bedrock dip in the same direction (see Figure 2). Well yields in the study area range from 19 to 114 liters per minute (based on well log data), depending on the thickness and fines content of the outwash.

Major Dissolved Ions

Ionic data were reported in milligrams per liter and was then placed in Microsoft Excel spreadsheet format (see Table 2 below). Concentrations were then converted into millimoles per liter by dividing sample concentrations by the corresponding molar weight in grams, with the exception that nitrate (NO_3) is actually reported as nitrogen, and so was divided by the molar weight for nitrogen (Table 2). Total Dissolved Solids (TDS) was calculated simply by adding the concentrations (in milligrams per liter) of all nine dissolved species plus the estimated concentration of bicarbonate (Table 2).

An ion balance of each sample was calculated in order to estimate the concentration of bicarbonate in the samples. It was assumed that the molar amounts of cations and anions balance exactly (Welch and others, 1996). Ion balance was calculated for each sample by first multiplying the molar concentration of each ion by its valence (+1 for Na and K; +2 for Mg and Ca; -1 for F, Cl, Br, and NO_3; -2 for SO_4) and then adding all categories for each sample. This yielded positive values for all samples, as expected, and the bicarbonate concentration is assumed to be roughly equal in molar concentration to the ion balance. Therefore, the ion balance value (in millimoles per liter) for each sample was then multiplied by the molar weight of bicarcarbonate (in grams) to obtain the apparent concentration of bicarbonate in milligrams per liter (Table 2).

Ionic data were then plotted on a trilinear diagram to assist with analysis of the samples (figure 4). The AquaChem trilinear program was used, which automatically converts concentrations from milligrams per liter to milliequivalents per liter and then to percentage of total milliequivalents per liter. Results on the diagram are in units of percent-milliequivalents per liter (%meq/L). AquaChem also computes Total Dissolved Solid (TDS) and results are reported in parts per million or equivalently, milligrams per liter. To find the TDS for each sample, compare the radius of the sample's corresponding circle with the chart at the upper left corner of the diagram (Figure 4).

Stable Isotopes

$\delta^{18}O$ and δD were computed as described above in the Methods section and are reported

in Table 3 in units of parts per mil (i.e. parts per thousand). δD was plotted against $\delta^{18}O$ for all 10

samples on a Meteoric Water Line graph (Figure 5). A Meteoric Water Line graph contains a

strait line of slope: $\delta D = 8(\delta^{18}O) + 10$ (see Figure 5: "meteoric water line") that represents the

approximate ratio of δD to $\delta^{18}O$ in meteoric (atmospheric) waters (Craig, 1961). Samples

plotting along or astride the meteoric water line are considered to be meteoric in origin, and those

plotting significantly off of the line should be analyzed closer for possible non-meteoric origin,

interaction with carbonate aquifer material, or significant evaporation (Drever, 1982).

DISCUSSION

Major Dissolved Ions

The ground water geo-chemistry in the study area is strikingly different from surface

water geo-chemistry. All surface water samples (s1 - s5) contain significant concentrations of

sulfate (>44.0 mg/L) and all but one (s3) have significant concentrations of nitrate (>20.0 mg/L).

However, none of the ground water samples (g1 – g5) contain any detectable sulfate or nitrate

(Table 2). The high levels of nitrate in surface samples s1, s2, s4, and s5 is not surprising, given

that the study area is an exclusively agricultural area where nitrogen fertilizers are used

abundantly. Sample s3 however, is an anomaly, containing no detectable amount of nitrate. The

pond that s3 was taken from is quite different from the other pond sample s1. The s3 pond sits on

a topographic high, astride the Whittlesey beach ridge and thus does not receive runoff from the

surrounding corn and soybean fields. The s1 pond however, has banks about 2.5 meters high and

sits below the surrounding fields, receiving farm runoff both from the fields and an adjacent

stream overflow pipe. Also, the s3 pond was human-made only 6 years ago while the s1 pond

was human-made about 45 years ago. The lack of nitrate in s3 suggests that there is little or no

fertilizer input and/or there is rapid biological uptake of nitrogen by the aquatic ecosystem in the pond (W.B. Lyons, personal communication).

The absence of sulfate and nitrate in the ground water samples indicates that chemically, this glacial aquifer has highly reductive, anoxic environments within it (Hem, 1985). When a subsurface environment with low hydraulic conductivity has been depleted of molecular oxygen, it becomes dominated biologically by certain species of bacteria that only use oxygen bound in compounds such as nitrate and sulfate. The bacteria accomplish this by sequentially reducing all of the nitrate and then all of the sulfate present in their environment (Berner & Berner, 1996).

Denitrification, or in other words, the separation of nitrogen and oxygen by chemical reduction of nitrate, occurs in a complex series of reactions. Nitrate-reducing bacteria can only survive in anoxic or suboxic conditions (oxygen < 2%). They can then use the oxygen that is liberated by reduction of nitrate to oxidize organic carbon into carbon dioxide (Chapelle, 1993). A simple stoichiometric model for this reaction is:

$$5CH_2O \ + \ 4NO_3^- \ >>>> \ 2N_2 \ + \ CO_2 \ + \ 4HCO_3^- \ + \ 3H_2O$$
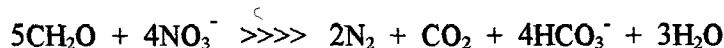
The complete absence of nitrate in the groundwater samples is consistent with the slow, low hydraulic conductivity setting described in HYDROGEOLOGIC SETTING above. If recharge from rain and surface water runoff is very small, and if little or no circulation of the groundwater occurs, then over time the O_2 concentration would become depleted and suboxic conditions would persist. Also, since bicarbonate (HCO_3^-) is a byproduct of denitrification, one would expect to find high concentrations of bicarbonate in groundwater where denitrification has occurred. This is precisely what we find in all five groundwater samples, with bicarbonate concentrations range from 218 – 675 milligrams per liter (Table 2).

Sulfate is one of the most common dissolved species in natural waters, occuring in virtually all natural water (Hem, 1985). As with nitrate, sulfate can also be removed by

bacterially-mediated reduction in ground water if conditions are favorable. Sulfate-reducing

bacteria are commonly found in deep subsurface environments, existing in a symbiotic

relationship with fermentative bacteria (Chapelle, 1993). The fermentative bacteria produce

simple organic compounds such as lactate that sulfate-reducing bacteria need to survive. Under

anoxic conditions, bacteria then reduce sulfate and oxidize these organic compounds for energy

(Chapelle, 1993). The generalized stoichiometry of the reaction is:

$$2CH_2O + SO_4^{2-} >>> H_2S + 2HCO_3^-$$
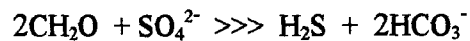
This would explain the complete absence of sulfate in the ground water samples as well as the

high levels of bicarbonate, especially when considered in conjunction with nitrate reduction.

Eberts and George (2000) also found that groundwater from glacial aquifers in the Lake Plains

area were depleted in sulfate.

The dissolved ion data indicate that the aquifer is a very anoxic environment, with little

or no supply of fresh, oxygenated water from the surface. Many of the wells in the study area

also have methane that occurs naturally in the water. Methane is also a common indicator of

strongly reducing environments (Hem, 1985). The data are indicating a hydrologic environment

that is isolated, with very little circulation or flushing occurring and long residence times for

groundwater in the aquifer.

Stable Isotopes

Isotopes are considered "stable" if they do not undergo radioactive decay. Deuterium

(^2H) and Oxygen-18 (^{18}O) are both stable isotopes. Stable isotopes are used to help identify the

source of a water and the natural and/or anthropogenic processes that have affected it since its

"formation" or infiltration into an aquifer (Drever, 1982). Because isotopes of the same element

have a different number of neutrons they also have different masses. The mass difference is most

profound among the lighter elements like hydrogen and oxygen since a single neutron makes up a

greater proportion of their total mass. This difference in mass causes isotopic *fractionation* in

nature. Any process that causes the isotopic ratios to differ from another in nature, whether physical or chemical, is called fractionation (Drever, 1982). For example, rainwater has a different ratio of $^{18}O/^{16}O$ than Pacific ocean water. The standard for $^{18}O/^{16}O$ and for $^{2}H/^{1}H$ is the mean of ocean water (SMOW).

When ocean water evaporates to form clouds, fractionation occurs where the lighter isotopes (^{16}O and ^{1}H) evaporate more easily and the vapor becomes "lighter" than the ocean water with lower ratios of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ (Drever, 1982). When cloud vapor condenses to form rainwater or snow the reverse fractionation process occurs, with ^{18}O and ^{2}H condensing more rapidly than ^{16}O and ^{1}H and the precipitation becoming "heavier" than the cloud vapor. As a cloud moves inland precipitation becomes progressively more depleted or "lighter" in ^{18}O and ^{2}H. Also, greater fractionation occurs at colder temperatures than at warmer temperatures so that δD and $\delta^{18}O$ values decrease with a decrease in temperature (Eberts and George, 2000). Therefore, lower δD and $\delta^{18}O$ values may correspond to greater altitudes or greater distance inland from sea, or possibly to a past glacial period when temperatures where lower.

Stable isotope concentrations are very different when comparing the surface water and ground water samples. As seen in Table 3, δD (Deuterium) and $\delta^{18}O$ values for the ground water samples are more negative than for surface water. A glance at the meteoric water line (Figure 5) shows the nice grouping of surface and ground water samples, as well as how closely the samples fit on the meteoric water line [*]. For the ground water samples (g1, g2, g3, g4, and g5) one can conclude that the water is meteoric in origin based on their plot on the meteoric water line. However, their smaller δD and $\delta^{18}O$ values (in comparison with surface water samples) needs some further explanation.

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[*] Only samples s3 and s1 (very slightly) plot off of the meteoric water line, however this is to be expected from water from closed basins where evaporation is higher (Drever, 1982). As discussed above, s1 is from a pond with banks 2.5 meters high, while s3 is from a pond on a topographic high that does not have an effective bank and therefore has higher evaporation rates. This explains the trend of s1 and s3 away from the meteoric water line.

δD and $\delta^{18}O$ values for all five groundwater samples (see Table 3) correspond to values typically found around the southern end of Hudson Bay in central Canada ($-120 \leq \delta D \leq -80$ and $-16 \leq \delta^{18}O \leq -12$). However, typical meteoric water from northern Ohio would have a δD value of about -50 and a $\delta^{18}O$ of about -7.5 (compare Ohio prediction to stream water samples: s2, s4, and s5 in Table 3) (Drever, 1982). These groundwater samples are "out of place" and indicate that some "abnormal" or additional fractionation has occurred, producing these light values.

As described above, a decrease in temperature causes greater fractionation of ^{18}O and ^2H. If the mean annual temperature were significantly lower than at present we would find δD and $\delta^{18}O$ values significantly lower than present day meteoric water such as in the surface water samples (see Table 3: samples s1 – s5). The Wisconsinan glacial period, which deposited most or all of the unconsolidated sediments of the aquifer, was the most recent cold, glacial period (Dreimanis and Goldthwait, 1973). Ground water that is isotopically "light" in ^{18}O may represent Wisconsinan-age ice meltwater and recharge that occurred beneath or in front of those ice sheets (Eberts and George, 2000). The $\delta^{18}O$ value for Wisconsinan-age ice sheets has an estimated range from about -20 to -12 parts per mil (Yapp and Epstein, 1977; Desaulniers and others, 1981). The $\delta^{18}O$ value for all five groundwater samples fall in this range (see Table 3).

The paleotemperature of a ground water sample (i.e. mean annual atmospheric temperature when the meteoric water infiltrated the ground surface as recharge) can be estimated using the formula:

$$\text{Temperature (Celsius)} = 1.4\,(\,\delta^{18}O + 13\permil\,) \quad \text{(Mazor, 1997)}$$

This formula yields paleotemperatures between -3.4 degrees Celsius and 2 degrees Celsius for study area groundwater (see Table 4). Paleotemperature estimates based on fossil pollen place a mean annual temperature of about -4 degrees Celsius about 15,000 BP for the study area (Bradley, 1999). This matches the data nicely and corresponds with the end of the Wisconsinan ice age. Wisconsinan ice sheets left northern Ohio about 15,000 BP and mean annual temperatures reached near their present level around 10,000 BP (Dreimanis and Goldthwait,

1973). In their study of groundwater in the Lake Plains/Maumee River Basin, Eberts and George (2000) also found $\delta^{18}O$ values between -14 to -17 parts per mil at depths of 21 to 30 meters, with $\delta^{18}O$ values decreasing with depth. They concluded that very little recharge of the aquifers is occurring and thus Pleistocene-age water is preserved in the deeper parts below the Maumee River Basin.

Samples g3 and g5 are the "oldest" of the five samples and come from wells that are developed several feet into the shale bedrock. Thus these wells are extracting water both from the shale and the outwash above and therefore water that was emplaced earlier and at a colder mean annual temperature. Sample g2 comes from the shallowest of the five wells, being developed in only the top few feet of the outwash layer, and accordingly has the "youngest" $\delta^{18}O$ value of all five samples (Table 3).

SUMMARY AND CONCLUSIONS

The ionic and isotopic data and the hydrogeologic characterization of the study area combine to show that the deeper portion of the unconsolidated glacial aquifer is receiving little, if any, significant recharge currently. The net precipitation-minus-evapotranspiration gain in the area is the lowest in the state at about 26 centimeters. Compounding the negative effect on recharge is the anomalously high rate of surface runoff in the Lake Plains/Maumee River Basin. In most streams the ratio of surface runoff/groundwater discharge decreases as you move downstream, however in the Maumee River Basin the opposite occurs (Eberts and George, 2000). The glaciolacustrine clays and clayey tills in the top 5 meters of the surface create a "parking lot" effect, causing nearly all of the available precipitation to run off into streams rather than infiltrating down into the aquifer.

Hydrogeologic characterization of the area shows that the negligible amount of precipitation that does infiltrate down past the surficial clays is then trapped in the equally clayey till below it and will not move significantly for a very long period of time. The very low

hydraulic conductivity of the glacial sediments and the lack of horizontal hydraulic gradient in the area combine to form a very slow, restrictive groundwater setting where very minimal recharge takes place. Chemical data from groundwater in the area resonate with this characterization. Sulfate and nitrate are completely absent from the groundwater, confirming that at least the lower portion of the aquifer is a stagnant, anoxic environment with little flushing and no interaction with surface water. Isotopic data from groundwater also confirm that the aquifer is very static hydrologically and that groundwater has a very long residence time in the aquifer. Isotopic data indicate that groundwater has been sitting virtually immobile in this aquifer since the late Pleistocene epoch.

RECOMMENDATIONS FOR FUTURE RESEARCH

In light of the apparently small amount of recharge that occurs in this aquifer, a quantitative estimate of recharge needs to be done for this area. Current demand for groundwater in the area is low due to the lack of livestock farming, lack of use for agricultural irrigation, and the small human population. However, it is not quite clear if supplies will continue under the present pumping rates and demands, nor is it clear whether current demand will remain static over the next several decades. The population in the nearby town of Delta (4 kilometers to the southwest) has grown dramatically in the last 5 years due to the arrival of the Norstar Aluminum and Worthington Steel plants. Subdivisions are now replacing farms closer and closer to the study area. Can the glacial aquifer support even greater demands for domestic supplies of water? The next reliable aquifer below the glacial sediments would be the Detroit River limestones and dolomites at about 80-85 meters below the surface (based on well logs), which would substantially increase drilling costs and likely increase the need for treatment of the ground water. Local officials will likely be seeking this kind of information soon if they haven't already.

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Table 1

Whittlesey Beach Ridge- Fulton Co./Fulton Twn.

phi size	description	tot. mass		% of total	cum %		phi size	
-1	pebbles	29.47	g	3.393871	3.393871		-1	3.394
	very coarse							
0	sand	30.62	g	3.526309	6.92018		0	6.92
	coarse							
1	sand	60.07	g	6.917877	13.83806		1	13.838
	medium							
2	sand	507.83	g	58.48353	72.32158		2	72.322
3	fine sand	220.3	g	25.37054	97.69212		3	97.692
	very fine							
4	sand	13.59	g	1.565073	99.25719		4	99.257
5	silt	6.45	g	0.742805	100		5	100

total mass   =   868.33 g

Table 2

Major Cations and Anions

Sample	analyzed	dilution	F mg/L	Cl mg/L	Br mg/L	N (NO3) m	SO4 mg/L	Sample	analyzed	Na mg/L	K mg/L	Mg mg/L	Ca mg/L
s1	082400a	10	0.36	114.2	0	20.211	75.8	S1	081800c	55.9	6.04	20.7	91.4
s2	082400a	10	0.53	115.7	0	31.053	59.6	S2	081800c	57.7	4.64	24.7	131
s3	082400a	5.5	0.3	17	0	0	92.7	S3	081800c	5.34	2.52	13.7	50.4
s4	082400a	10	0.42	39.9	0	26.239	51.1	S4	081800c	11.7	9.22	22.1	106
s5	082400a	10	0.42	72.9	0.12	30.838	44.8	S5	081800c	35.6	4.94	22.8	122
g1	082400a	10	1.86	180.4	0.16	0	0	G1	081800c	150	2.19	13.3	21.8
g2	082400a	10	2.19	70.8	0.12	0	0	G2	081800c	124	1.54	7.2	11.9
g3	082400a	10	1.13	366.6	0.28	0	0	G3	081800c	278	6.98	30.5	60.2
g4	082400a	10	1.63	171.5	0.18	0	0	G4	081800c	301	5.13	16.6	28.3
g5	082400a	10	1.24	253	0.2	0	0	G5	081800c	234	6.19	23.1	58.5

Sample	F mg/L	mMoles/L	Cl mg/L	mMoles/L	Br mg/L	mMoles/L	N (NO3) mg/l	mMoles/L	SO4 mg/L	mMoles/L	Na mg/L	mMoles/L
s1	0.36	0.018949	114.2	3.221193	0	0	20.211	1.442952	75.8	0.789061	55.9	2.431516
s2	0.53	0.027897	115.7	3.263503	0	0	31.053	2.21701	59.6	0.620422	57.7	2.509812
s3	0.3	0.015791	17	0.479512	0	0	0	0	92.7	0.964966	5.34	0.232277
s4	0.42	0.022107	39.9	1.125443	0	0	26.239	1.873318	51.1	0.531939	11.7	0.508922
s5	0.42	0.022107	72.9	2.056261	0.12	0.001502	30.838	2.201661	44.8	0.466358	35.6	1.548515
g1	1.86	0.097903	180.4	5.08847	0.16	0.002002	0	0	0	0	150	6.524641
g2	2.19	0.115273	70.8	1.997027	0.12	0.001502	0	0	0	0	124	5.393703
g3	1.13	0.059479	366.6	10.34054	0.28	0.003504	0	0	0	0	278	12.09233
g4	1.63	0.085797	171.5	4.837431	0.18	0.002253	0	0	0	0	301	13.09278
g5	1.24	0.065269	253	7.136269	0.2	0.002503	0	0	0	0	234	10.17844

Sample	K mg/L	mMoles/L	Mg mg/L	mMoles/L	Ca mg/L	mMoles/L		Sample	Ion Balance /Bicarbonate (mMol/L)	HCO3(mg/L)
s1	6.04	0.154482	20.7	0.851677	91.4	2.280553		s1	2.589242	157.9881
s2	4.64	0.118675	24.7	1.016252	131	3.268626		s2	4.448988	271.4645
s3	2.52	0.064453	13.7	0.56367	50.4	1.257548		s3	1.513891	92.37333
s4	9.22	0.235816	22.1	0.909278	106	2.644843		s4	3.768232	229.9268
s5	4.94	0.126348	22.8	0.938079	122	3.044064		s5	4.424903	269.9949
g1	2.19	0.056013	13.3	0.547213	21.8	0.543939		g1	3.574582	218.1108
g2	1.54	0.039388	7.2	0.296235	11.9	0.296921		g2	4.505602	274.919
g3	6.98	0.178524	30.5	1.254886	60.2	1.502071		g3	7.381252	450.3829
g4	5.13	0.131208	16.6	0.682987	28.3	0.706123		g4	11.07673	675.8702
g5	6.19	0.158319	23.1	0.950422	58.5	1.459654		g5	7.952869	485.2613

Sample	TDS (Total Dislvd Solids (mg/L))		Sample	F (meq)	Cl (meq)	Br (meq)	K(NO3) (meq	SO4 (meq)	Na (meq)	K (meq)	Mg (meq)	Ca (meq)	HCO3(mg/L)
s1	542.5991		g1	0.097903	5.08847	0.002002	0	0	6.524641	0.056013	0.273606	0.27197	218.1108
s2	696.3875		g2	0.115273	1.997027	0.001502	0	0	5.393703	0.039388	0.148118	0.148461	274.919
s3	274.3333		g3	0.059479	10.34054	0.003504	0	0	12.09233	0.178524	0.627443	0.751035	450.3829
s4	496.6058		g4	0.085797	4.837431	0.002253	0	0	13.09278	0.131208	0.341494	0.353062	675.8702
s5	604.4129		g5	0.065269	7.136269	0.002503	0	0	10.17844	0.158319	0.475211	0.729827	485.2613
g1	587.8208		s1	0.018949	3.221193	0	0.721476	0.39453	2.431516	0.154482	0.425838	1.140276	157.9881
g2	492.669		s2	0.027897	3.263503	0	1.108505	0.310211	2.509812	0.118675	0.508126	1.634313	271.4645
g3	1194.073		s3	0.015791	0.479512	0	0	0.482493	0.232277	0.064453	0.281835	0.628774	92.37333
g4	1200.21		s4	0.022107	1.125443	0	0.936659	0.26597	0.508922	0.235816	0.454639	1.322421	229.9268
g5	1061.491		s5	0.022107	2.056261	0.001502	1.10093	0.233179	1.548515	0.126348	0.469039	1.522032	269.9949

Table 3
Isotopic Data

Meteoric Water Line			Water Sample Data		
^{18}O ($^0/_{00}$)	D ($^0/_{00}$)		sample	^{18}O ($^0/_{00}$)	D ($^0/_{00}$)
-20	-150		s1	-5.2	-38.1
-19	-142		s2	-7.6	-51.1
-18	-134		s3	-1.1	-21.8
-17	-126		s4	-7.4	-48.8
-16	-118		s5	-7.6	-49.7
-15	-110		g1	-13.9	-99.5
-14	-102		g2	-11.6	-82.8
-13	-94		g3	-15.2	-109.1
-12	-86		g4	-13.5	-95.5
-11	-78		g5	-15.4	-110.8
-10	-70				
-9	-62				
-8	-54				
-7	-46				
-6	-38				
-5	-30				
-4	-22				
-3	-14				
-2	-6				
-1	2				
0	10				
1	18				
2	26				
3	34				

Table 4

Paleotemperature $= 1.4 (\delta^{18}O + 13^0/_{oo})$ (in Celcius)

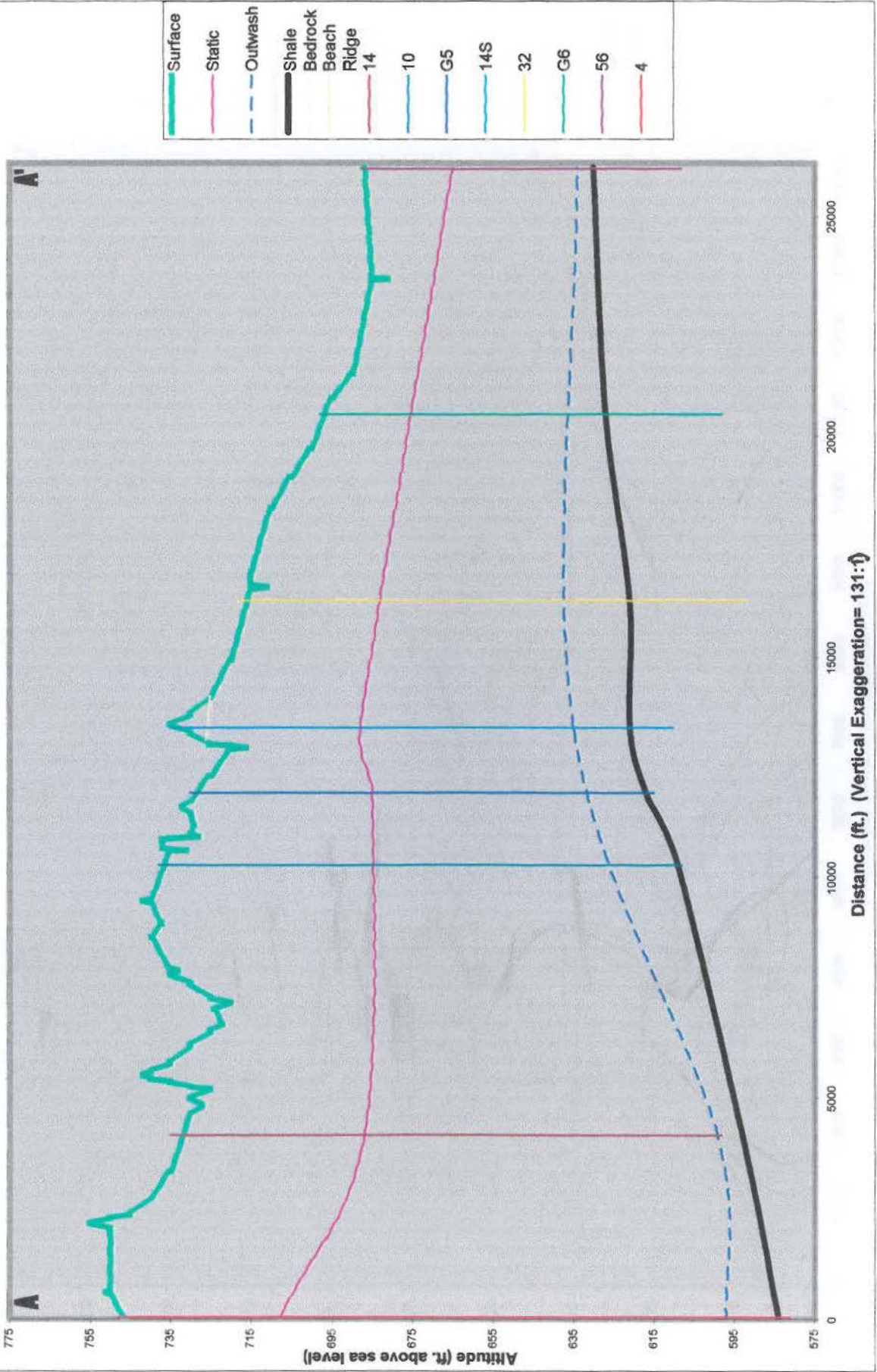| sample	^{18}O ($^0/_{00}$)	T_p
s1	-5.2	11.154
s2	-7.6	7.722
s3	-1.1	17.017
s4	-7.4	8.008
s5	-7.6	7.722
g1	-13.9	-1.287
g2	-11.6	2.002
g3	-15.2	-3.146
g4	-13.5	-0.715
g5	-15.4	-3.432

Figure 2

Figure 3

Figure 4

Figure 5