HYDROGEOLOGY OF THE FRED CREEK ALLUVIAL AQUIFER, ARKANSAS RIVER BASIN, TULSA, OKLAHOMA

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CHAPTER I

INTRODUCTION

The Oral Roberts University campus is situated on the east bank of the Arkansas River valley where floodplain and terrace deposits form groundwater aquifers (Kent, 1972). Fred Creek crosses these deposits after draining residential neighborhoods to the east and north of campus (Figure 1). If there are sources of water pollution in the area, the chemicals would move toward the river by way of the creek and the aquifers. Movement of chemicals through the groundwater depends upon 1) hydrogeologic parameters, 2) water solubility and the 3) the affinity of pollutants to adsorb to soil particles. Fate and transport studies are therefore very critical in assessing the risk to which a community is exposed when using a contaminated aquifer.

Although the primary water sources of the city are not from groundwater, a pilot study of the aquifer would have considerable value. City growth may eventually outpace the surface sources currently utilized and have to turn to groundwater as a supplement. Also, other midwestern cities that rely on groundwater from alluvial aquifers would benefit from knowledge gained from such a

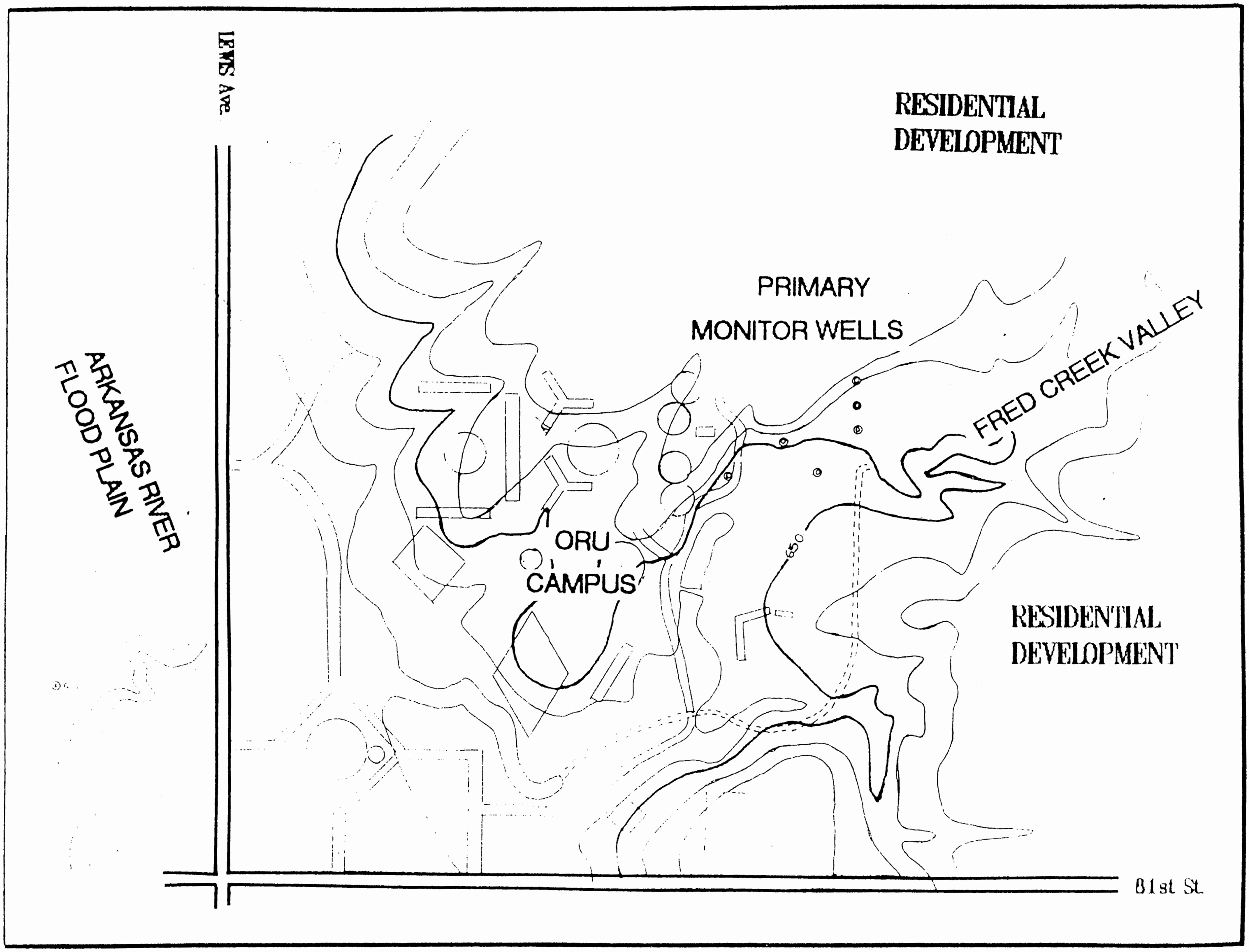


Figure 1. Map of Study Area

study. Data obtained from an evaluation of the hydrogeology and geochemistry of the deposits underneath the ORU campus will be used to model water and contaminant movement through a municipal aquifer.

Background

The non-point source effect of wastes disposed by homeowners in municipalities has the potential for introducing large volumes of hazardous chemicals to groundwater aquifers, yet these sources are very difficult to control. Solvents, motor oil, antifreeze, pesticides, and other household chemicals are commonly disposed of improperly. They may be poured onto the backyard soil or down household drains. Infiltrating rainwater will carry chemicals from the top soil down to the water table or leaks in sewer systems will provide other pathways to groundwater aquifers.

Whereas the Resource Conservation and Recovery Act of 1976 (RCRA) mandated restriction of burial of hazardous wastes with the ultimate goal of elimination of land disposal, regulations subsequently generated deal primarily with industries that generate large volumes of wastes (CFR 40,1988). Currently, no restrictions apply to residential sources of pollution. Most cities have looked to volunteer efforts to encourage homeowners to bring wastes to central sites on a periodic basis. Effective control of residential waste disposal, however, will be very difficult to enforce.

The hydrogeology of deposits in a tributary drainage basin affects the alluvial aquifer into which the tributary flows. Many cities are built on the banks of a large river which flows through a valley bearing an alluvial aquifer. Oftentimes, the river banks are not zoned for residential development because of flood threats or else industry is established there as a result of the river's benefits. Residential neighborhoods are on high ground but are linked to the primary river by tributary drainage systems.

Location

The study area in question is a tributary valley on the east bank of the Arkansas River in Tulsa County, Oklahoma. Fred Creek flows southwest from its headwaters where Pennsylvanian sedimentary rock lies within a few feet of the surface. These shallow bedrock layers generally yield, at most, a few gallons per minute of water and are only occasionally developed for rural domestic use. They are not classified as effective aquifers. Farther downstream, the Fred Creek valley widens and alluvium covers the valley floor. Finally, the creek flows onto the Arkansas River flood plain where it joins Joe Creek a mile upstream of its confluence with the Arkansas River. The total drainage of the Fred Creek basin is 1.87 square miles. The terrace deposits and creek alluvium are continuous with the flood plain alluvium of the Arkansas River valley All three sedimentary units contain groundwater.

The campus of Oral Roberts University is located on approximately 160 acres of the east bank of the Arkansas River, spanning the bedrock valley wall to the Quaternary terraces and also the flood plain proper. Additional university lands adjacent to the main campus are located entirely on the terrace deposits not drained by Fred Creek. Accessibility of the university property afforded the opportunity to establish a network of monitor wells for studying the hydrogeology and geochemistry of the ground water system. Because the university is a generator of hazardous waste, there is a potential for point-source contamination. Knowledge of the aquifer and of the background water quality are essential for any future assessment of the impact of the facility on the aquifer.

Purpose

The purpose of the study is to characterize the soil and aquifer material by physical and chemical tests, to analyze water samples from surface locations and ground water wells and to determine whether conditions favor or inhibit movement of contaminants from the residential areas to the main aquifer.

CHAPTER II

PREVIOUS STUDIES

Research pertinent to the present study has been conducted on three levels: 1) regional surveys of geology including Quaternary deposits and alluvial aquifers: 2) studies of individual aquifers analogous to the study area; and 3) reports on the geology of Tulsa County. All of these contribute to the understanding of the Fred Creek valley aquifer.

Regional Reports

Tulsa's water supply is taken from three man-made reservoirs on creeks in Delaware, Mayes, and Rogers counties. Groundwater has only been utilized as a water source in rural areas for isolated homes and farms.

The Water Atlas of Oklahoma (Pettyjohn, et.al., 1988), indicates the only major groundwater basin in Tulsa County to be floodplain alluvium and alluvial terrace deposits. In fact, in the surrounding counties, the only bedrock aquifer of note is the Upper Pennsylvanian Vamoosa Formation of western Creek and Osage Counties. In most of northeast Oklahoma, the

Paleozoic bedrock does not bear significant quantities of water until older carbonate formations bordering Missouri are reached. The outcropping Pennsylvanian clastics and carbonates in the Tulsa vicinity generally have insufficient permeability to provide adequate yields of groundwater. This conclusion is confirmed by Marcher and Bingham (1971) who surveyed the region for the state's Hydrologic Atlas project. Occasionally, outcropping sandstones are recharged with water, but discontinuous porosity precludes the development of high yields.

Early studies of the groundwater distribution and quality of the Oklahoma alluvial aquifers were part of the systematic description of the state's resources by the Oklahoma Geological Survey. These were mainly incorporated in county reports which were published as bulletins. Prior to that, water well data were tabulated as part of a project for the Works Progress Administration in 1936 (see Oakes, 1952 p. 140).

In 1952, the Geology and Mineral Resources of Tulsa County, Oklahoma by Malcolm Oakes was published by the Oklahoma Geological Survey. This report discussed the nature of terrace and alluvium deposits in the county and presented water level and water quality data. Chemical analyses of samples from zones including terrace, alluvium, and the bedrock units which outcrop in the study area were reported. Most samples were calcium bicarbonate type waters; however, some wells in the flood plain near the Arkansas River channel had high sodium and chlorine concentrations. He also referred to several fresh water springs emanating from alluvium and terraces in the Bixby and Broken Arrow areas that were once used as a source of drinking water.

Two papers treating the Arkansas River aquifer in the state of Arkansas were published by Bedinger in 1961 and 1963. In the first paper, grain size analyses were reported for various samples of sediment from the alluvium and terraces. Permeability determinations were made for the samples and the results were compared to hydraulic conductivities calculated from aquifer tests of pumping wells. From these data, Bedinger constructed a framework of hydraulic conductivity ranges to be expected for deposits of various median grain sizes. For example, very fine sand should have a hydraulic conductivity (K) between 10 and 30 gpd/ft^2 whereas very coarse sand could range from 1500 to 4000 gpd/ft^2. He concluded that the underlying relationship, $K = c\ d^2$ (where d is median grain size in mm., K is hydraulic condutivity in gpd/ft^2, and c is a constant) is valid for unconsolidated deposits of sorted and rounded sands and that K values thus derived are less than those calculated from aquifer tests.

In the second paper, Bedinger et.al. (1963), surveyed the terrace and alluvial aquifer in western

Arkansas between Fort Smith and Little Rock, the area called the Interior Highlands. They declared the alluvium to be "... the most important aquifer in the Interior Highlands." They describe the range of lithologies encountered with most sequences grading upward from basal gravels through sand to silts and clays. Bedinger concluded that, in Arkansas, older terraces at higher levels above the river are not in hydraulic continuity with the lower terrace-flood plain complex. Flood plain deposits of tributary streams are usually dominated silt and clay dominated, although, isolated gravel deposits do occur. Chemical analyses for one well from each of the counties bordering the Arkansas River from Ft. Smith to Little Rock are included in their report along with grain size determinations and well yields. Specific capacities of 30-75 gpm/ft are listed for wells completed in very coarse sand whereas fine-grained sand completions yield 0.5 to 1 gpm/ft. Bedinger et.al. (1963), classify the groundwater as a calcium magnesium bicarbonate type and suggest that localized high concentrations of other ions are due to mixing with water from bedrock sources.

Mention of alluvial aquifers in central and eastern Oklahoma is made in several of the county reports published by the Oklahoma Geologic Survey, (Shelton, et.al., 1979 - Noble County; Shelton, et.al., 1985 - Payne County; Greig, 1959 - Pawnee County). In addition to county reports, separate studies have been made on the major Paleozoic aquifers in the state. In local areas, bedrock aquifers subcrop the alluvium of one or more of the major rivers and the groundwaters are in communication. Tanaka and Davis (1963) report on the Rush Springs aquifer of west-central Oklahoma and describe the interrelationship of the Rush Springs with the Washita River alluvium. High sulfate concentrations in flood plain alluvium and in some of the Rush Springs wells is a function of solution of the gypsum beds outcropping in the region. They also describe several levels of terrace above the present day flood plain.

Both the Vamoosa Formation and Garber-Wellington aquifers are in contact with major river systems in their outcrop belts. D'Lugosz et.al., 1986, describe the Vamoosa from Osage to Seminole Counties. They propose that there is upward flow from the Vamoosa aquifer into the alluvium of rivers such as the Arkansas, North Canadian, and Canadian. These three rivers entrenched into the bedrock.

Havens (1989) undertook a project to apply a finite difference model to the alluvial-terrace complex of the North Canadian River from Oklahoma City to Lake Eufala. He describes the hydrogeology of the aquifer and states that river alluvium is in hydraulic continuity with the Garber-Wellington at some locations in central Oklahoma.

As shown by these reports, alluvial aquifers in entrenched channels are commonly in contact with bedrock aquifers. Bedinger et.al. (1963) state that variations in the chemistry of the alluvial and terrace waters of Arkansas are most likely due to mixing with water from bedrock zones.

Tulsa Area

In 1972 a compendium of papers dealing with Tulsa county was published by the Tulsa Geological Society under the title, <u>Tulsa's Physical Environment</u>. The purpose of the volume was to provide background information pertinent to Tulsa's environmental concerns. Many of the papers dealt with water and land use problems. As such, descriptions of the surface water resources, groundwater aquifers, and surface geology are included. A. P. Bennison (1972a-c) described each formation that outcrops in the study area in separate papers. He also edited the comprehensive geologic map that was included with the volume. Lithologic descriptions, formation thicknesses, and stratigraphic relationships were covered in detail in Bennison's collective work.

Also in the <u>Tulsa's Physical Environment</u> publication, three papers focused on the groundwater and two papers considered geological aspects of the alluvium and terraces. Stone, et.al. (1972) reviewed the Quaternary geology, relating deposits of Tulsa County to the broader framework of events in the midcontinent. They described erosional features of the river valleys as well as an assortment of ancient river related deposits. Thomas (1972) concentrated his work on aeolian deposits of Quaternary age in describing isolated loess exposures in the county.

Kent (1972) presented an overview of the hydrology of the Arkansas River aquifer system. He tabulated a water budget for the aquifer, considering discharge to the river and water loss by evapotranspiration. Using average values for saturated thickness, hydraulic conductivity, and hydraulic head, Kent calculated the contribution of the aquifer to base flow in the river. He reported an average thickness of 33 feet for the river flood plain and defined a median grain size for both sand (.3 mm.) and silt (.04 mm.). Gradients of 2.8 feet per mile along the channel axis and 35 feet per mile from the perimeter of the alluvium perpendicular to the channel were also calculated.

Schmidt (1972a) focused on the corrosive nature of groundwater drawn from a terrace aquifer in south Tulsa. He cited examples of corrosion of copper plumbing fixtures due to the slightly acidic nature of groundwater. Schmidt traces the acidity to dissolved carbon dioxide in depsoits not buffered by calcium carbonate. He compared water samples from residential wells in the terrace to others in river alluvium and listed the results of several chemical analyses. Gould (1972) described water resources in Tulsa County including both surface water and groundwater. By this time, outlying communities in the county were switching to surface supplies as growth spawned higher demands for potable water. He stated that Tulsa has adequate rainfall to maintain recharge of groundwater but that water quality is the limiting factor which keeps the groundwater from being widely developed. Chemical analyses of water from flood plain alluvium and some bedrock zones show high total dissolved solids to be a common condition.

Since the early 1970's the publication of hydrogeologic studies for the Tulsa area has been limited to regular reports of water quality and groundwater levels by the Oklahoma Water Resources Board and United States Geological Survey. Examples of these are the technical reports by Thomas and Glover, (1989) and Fabian and Myers (1990). The Tulsa City-County Health Department and the Indian Nations Council of Governments, and the City of Tulsa continue to monitor water quality as shown by the periodic articles in the local newspapers (eg. Hoffman, 1989). Most effort has been spent dealing with concerns of surface water pollution and storm water runoff.

CHAPTER III

MONITOR WELLS

Well Location Plan

Fred Creek crosses the campus from northeast to southwest, providing access to the valley bottom as well as the valley slopes and the river flood plain beyond the mouth of the valley. The topography implies a gradient in a downstream direction and also into the valley from both sides. This pattern is complicated by the man-made channel excavated through the river terrace on the east wall because discharge occurs here.

Sampling was designed to provide a degree of randomness throughout the valley while monitoring both upgradient and downgradient regions. The USEPA recommends upgradient wells to determine background water quality and downgradient wells to assess whether composition changes under the property in question (USEPA, 1986). Both upstream and lateral, valley slope locations were considered to be upgradient with flow funneling groundwater downgradient into the narrow valley center. Initially, three phases of wells were planned to achieve coverage of the hydrologic system.

Phase I wells were to be located in updradient and downgradient positions along the natural valley on the northeast edge of campus. Phase II wells were to be placed in comparable positions along the man-made channel on the east boundary. Phase III wells were to sample the downstream positions of the valley mouth and adjacent river flood plain (Fig. 2). (Phase III was postponed because the wells were to be in a high use area where underground utilities were vulnerable.)

The first wells drilled were located near the point where the man-made channel turns abruptly south from the natural valley. The I-1 well was successfully drilled north of the channel to a depth of 15.4 feet (4.7 m), 4.1 feet below the water table. A second well (I-2) was attempted south of well I-1 on the east bank of the excavated channel. At this location a coarse gravel deposit was encountered at 12 feet (3.7 m) so that further drilling with the hand auger was not possible. This well was abandoned without hitting groundwater. After the third well (I-3) was completed 500 feet (152m) downstream from I-1, in the old valley, a fourth well was attempted approximately 1000 feet (305 m) downstream from I-2 along the new channel. This well (I-5) encountered a gravel layer below 10 feet (3m) that halted drilling. Communication with local residents confirmed that a persistent gravel layer exists east of the excavated channel. Because of the difficulty in

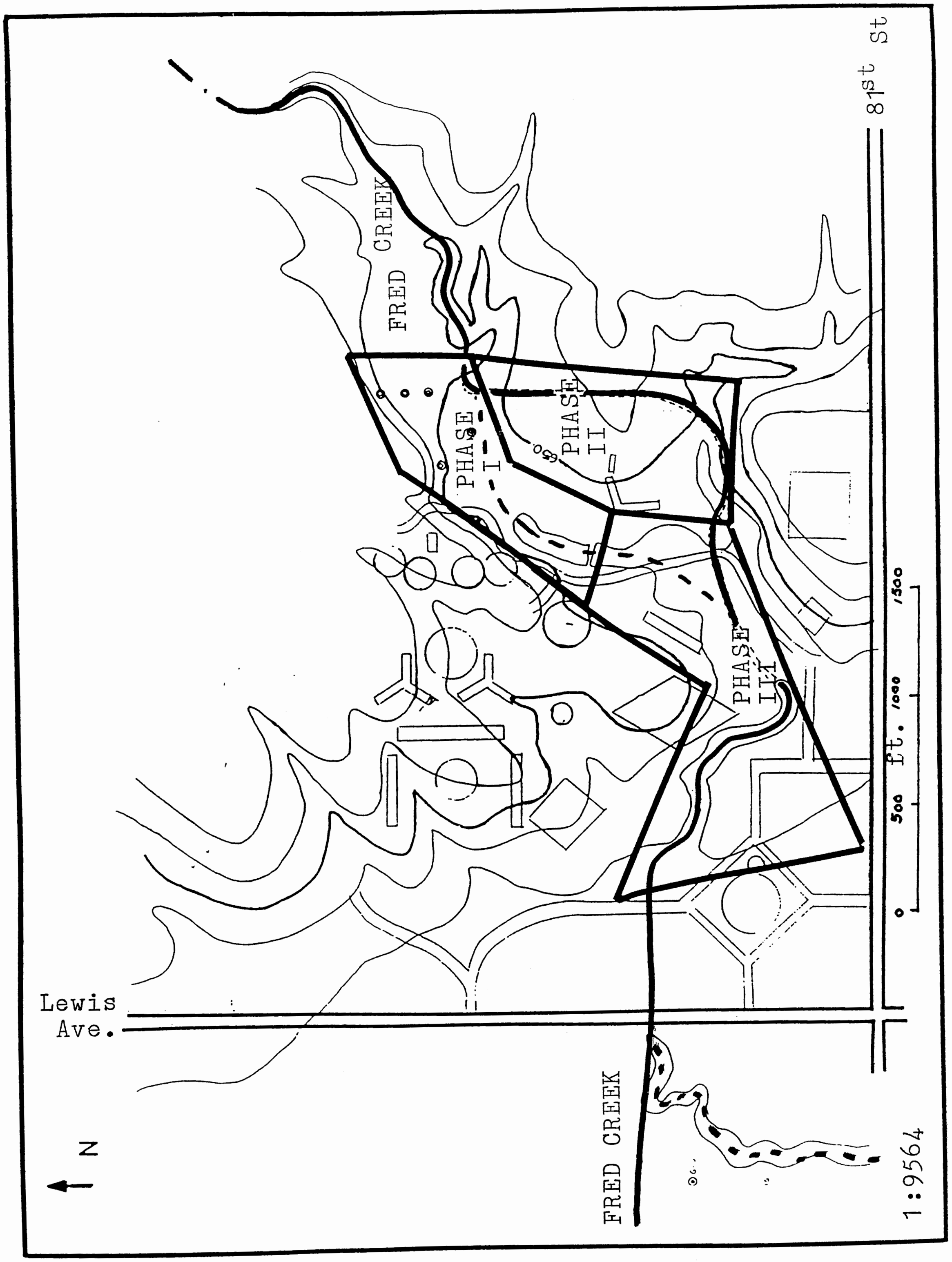


Figure 2. Well Location Plan

drilling along this bank, the plan to locate wells in the Phase II area was abandoned and Phase I was emphasized.

Seepage zones were recognized in the new channel up to a foot above the low water level. In lieu of monitor wells in the Phase II area, low flow water samples were taken from the creek as representative of discharging groundwater. Locations NEB, north of the I-2 well and TRIB, south of the I-5 attempt were monitored.

Well Construction

Wells were drilled an average of 4.5 feet (1.4 m) below the water table. Drilling in the saturated zone was hampered by caving and the common occurrence of a very sticky clay. As a result, none of the wells were drilled sufficiently deep to fully penetrate the saturated zone.

Drilling was accomplished using a 3 3/4 inch (9.5 cm) diameter stainless steel hand-auger. The lower 6 inches (15.2 cm) of the core barrel is closed and there is an additional 6 inches of partially open barrel that can accept more sample. As the assembly is turned, unconsolidated soil is pushed past the blades into the barrel so that nearly a foot of sample can be collected before the auger must be withdrawn and emptied.

The advantages of this method are the low cost and the capability for nearly continuous sampling.

Incorporation of cavings into the drill sample necessitates discarding the top few inches of core so that effectively samples less than a foot are taken.

Disadvantages of the method include slow drilling time and limitation to fine-grained, unconsolidated aquifers. Whenever coarser sediments are encountered, the possibility of hole caving exists. This occurred in wells that had clean sand beneath the water table. Indurated bedrock and gravel beds cannot be penetrated by the auger.

Holes to a depth of 21 feet (6.4 m) were drilled in the study area. Once a depth of 18 feet (5.5 m) was reached, the drill extensions had to be separated into two sections every time the barrel was withdrawn from the hole. The leverage of the extended length of drill extensions causes the string to bend under its own weight at too great a length.

Wells were completed following the guidelines of the U.S. EPA's Ground-Water Monitoring Technical Enforcement Guidance Document (EPA, 1986). Ten foot sections of two-inch ID PVC pipe (schedule 40) were joined together to be used as casing. The bottom two feet of the pipe was slotted with a saw at one inch (2.5 cm) intervals. The slots were 1/16 inch (1.5 mm) wide and were offset from slots on the opposite face of the pipe. Because a limited amount of saturated zone was penetrated, the screened portion of the pipe was located at the bottom to guard against the water table dropping below the screen. The base end of the casing was then capped with PVC and the slotted interval was wrapped with fiberglass window screen (mesh size, 1 mm). Approximately two inches (5 cm) of the base of the pipe was unslotted to act as a sediment trap.

After inserting the pipe into the well, the lower annulus was filled with coarse sand or fine gravel to a level above the slotted screen. Granular sodium bentonite was then poured on top of the gravel to fill the bulk of the annulus. The upper foot of the annulus was filled with cement, thus connecting it to the cement well apron.

Well Development

Wells were pumped using an inertial lift technique with a polyethylene tube. A check valve at the base of the tube allows water to enter as the tube is lowered into the well. When the tube is raised, the valve closes, preventing water from escaping. If the tube is lowered again, more water enters the tube. By rapidly raising and lowering the tube, a continuous column of water is established to the surface. Once water reaches the surface, the tube is quickly withdrawn about one half its length and the water is siphoned into a measuring container.

New wells were pumped vigorously to develop them.

Theoretically, wells should be pumped until the water becomes clear. All wells in the sampling network produced turbid water, even after developing. The fine grain nature of the aquifer should have required a fine grain filter pack and small screen size. Budget constraints necessitated hand slotting and so, the screen size was too large for a fine grained filter pack. Use of sand packing was abandoned in favor of gravel because the coarse screen allowed significant sand entry to the casing and inhibited pumping operations.

Elevations of the well pads were surveyed with a transit using a nearby sewer manhole as a base station. The manhole elevation was obtained from the City of Tulsa, Department of Public Works.

Altogether, nine wells were drilled into the saturated zone of the aquifer. These wells were all cased in the manner described above. Table 1 lists the wells along with pertinent data.

TABLE 1

MONITOR WELL LOCATIONS AND DEPTHS

WELL	LOC	TD.	STD WTR	ELEV
	sec 8-T18N,R13E			
I-1	NW NW SE	15.4'(4.8 m)	11.5'(3.5 m)	651.5
I-2	NW NW SE	12.3'(3.8 m)	dry	651
I-3	NW NW SE	17.3'(5.3 m)	11.9'(3.6 m)	649
I-4	NW NW SE	19.0'(5.8 m)	13.7'(4.2 m)	652
I-6	NW NW SE	14.4'(4.4 m)	10.2'(3.1 m)	656
I-7	NW NW SE	19.0'(5.8 m)	11.1'(3.4 m)	653
I-8	NW NW SE	15.4'(4.7 m)	12.0'(3.7 m)	648.5
I-9	NE NE SW	15.8'(4.8 m)	13.6'(4.1 m)	649
I-10	NW NW SE	15.0'(4.6 m)	11.8'(3.6 m)	649
I-11	NW NW SE	15.1'(4.6 m)	11.6'(3.5 m)	649
II-1	SW SW SE	17.3'(5.3 m)	13.4'(4.1 m)	632
	sec 7-T18N,R13E			
G-1	NW SE SE	19.5'(5.9 m)	18.5'(5.6 m)	623
G-2	SW NE SE	21.1'(6.4 m)	19.5'(5.9 m)	625

All wells cased with 2", schedule 40 PVC pipe, slotted over bottom 2 feet.

CHAPTER IV

HYDROGEOLOGY

Introduction

Both the matrix and the fluids in the pore space must be considered when investigating the hydrogeology of an aquifer. Discussion of the matrix includes the topics of texture, mineralogy, porosity, permeability, and aquifer dimensions, as well as the lateral and underlying boundaries. In the present study, the boundaries are sedimentary rocks which affect the aquifer and must therefore be examined. The initial discussion will focus on geology and will include a treatment of both bedrock and alluvium.

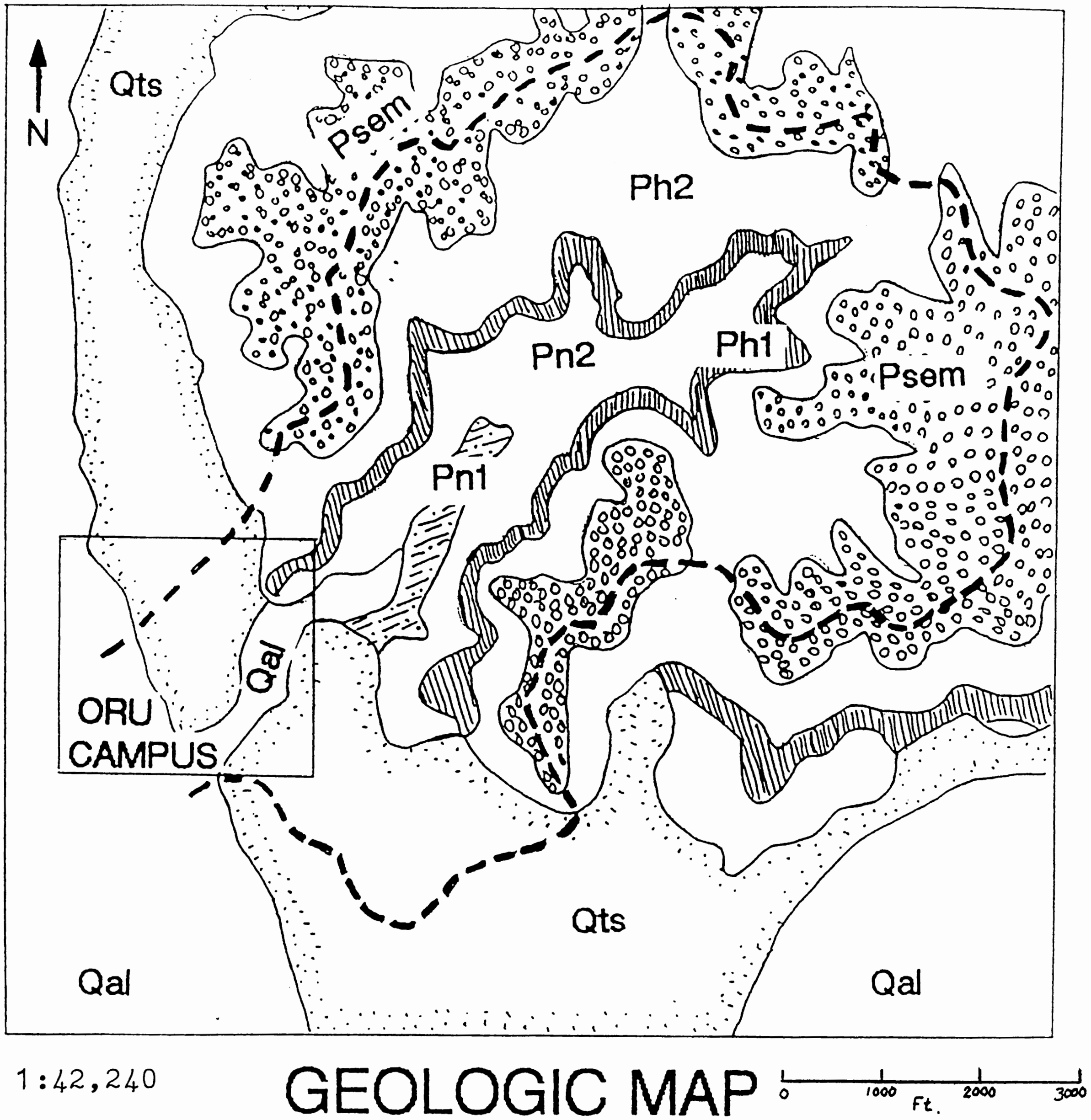
Facies Relationships

In 1972 the Tulsa Geological Society published Tulsa's Physical Environment. Along with articles describing the bedrock geology, a very detailed geologic map of Tulsa County was produced. The articles and map have proven invaluable for gathering background information on both outcropping formations and alluvial deposits.

Outcrops

Field work focused on the drainage basin which covers 1.87 square miles (4.8 km²) from a point nearly one half mile (0.8 km) north of 71st St. and Yale Ave. to the valley mouth east of 81st street and Lewis avenue. Figure 3 is an enlargement of a portion of the geologic map assembled by Bennison et.al., 1972. The basin limits are determined from a topographic map (U.S.G.S, Jenks Quadrangle) and superimposed onto the geologic map. This map shows the divides to coincide with outcrops of the Seminole Formation. The Seminole is dominated by quartz sandstones which support the prominent ridges throughout south Tulsa. Much of the outcrop belt is covered by residential development but in places, bedrock is exposed, such as on 71st St., halfway between Lewis and Harvard Avenues (outcrop and creek bank locations are noted on figure 4). At this locality (#H71), medium to thick bedded sandstone ledges are interbedded with siltstone and silty shales. The sandstones are composed of fine to medium-grained, subangular quartz grains loosely cemented by iron oxides. Many grains exhibit planar faces which may be the result of pressure solution at grain contacts. Auxiliary amounts of mica are present.

Siltstones are non-calcareous, comprised of very fine quartz sand and coarse quartz silt. Mica flakes



LIMIT of FRED CREEK - - - - - -

Psem - Seminole Fm.
Ph2 - Upper Holdenville Fm.
Ph1 - Lower Holdenville Fm.
Pn2 - Middle Nowata Shale
Pn1 - Lower Nowata Shale
Qal - Alluvium
Qts - Terrace

Figure 3. Geologic Map of South Tulsa (after Bennison, 1972)

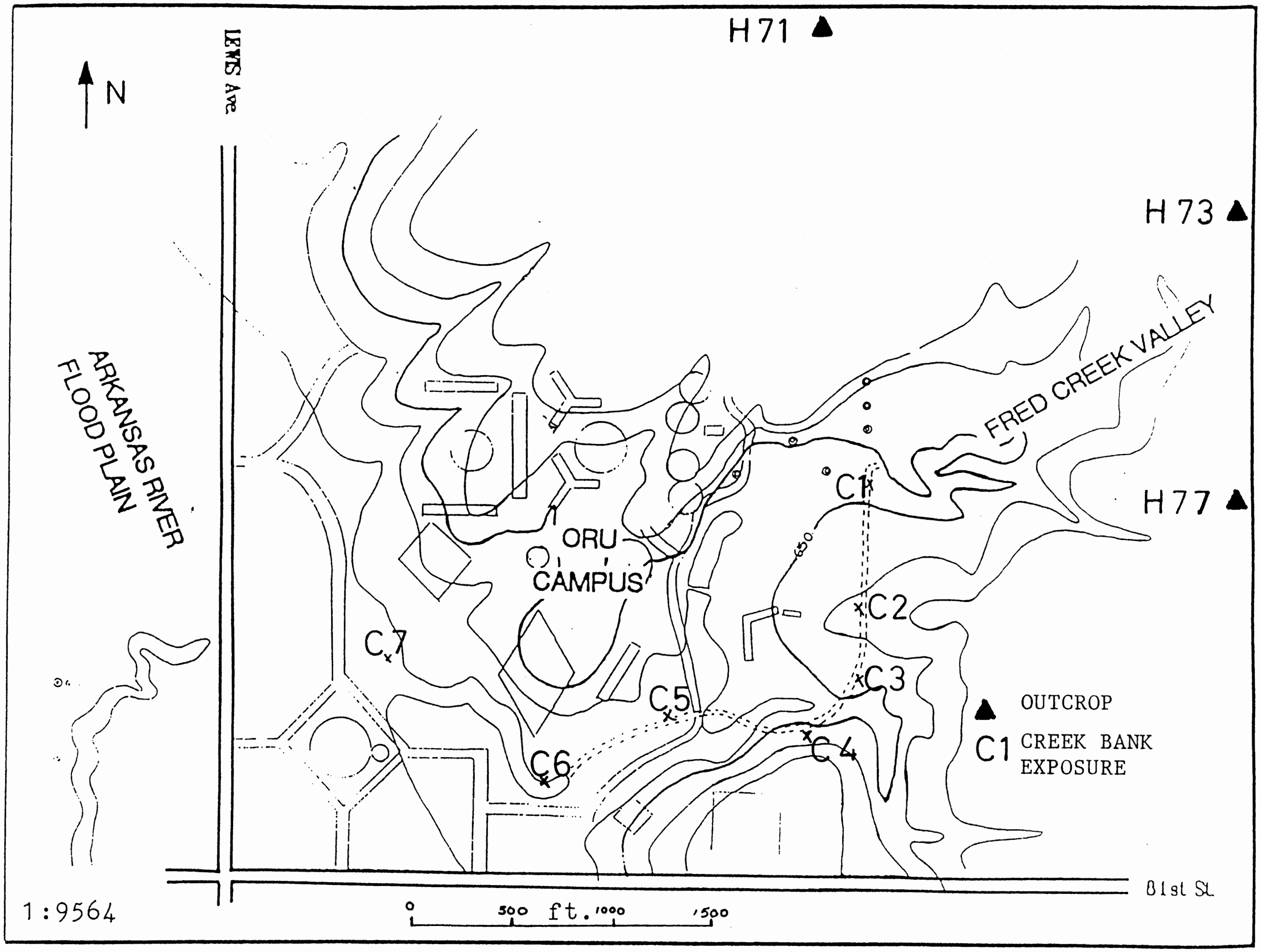


Figure 4. Outcrop Location Map

appear to be more common in siltstones than in sandstones. In outcrop, the silty layers weather more deeply than the sandstones.

Stratigraphically below the Seminole Formation are the Holdenville Formation and the Nowata Shale. All that can be seen of the Holdenville are occasional outcrops of crinoidal limestone on the middle slopes of the valley divide along Harvard Ave. south of 77th St. This may be the layer termed the 11th St. limestone by Bennison (1972b). Similar blocks occur as loose blocks (float) on the hill at the northeast edge of the ORU campus (Fig. 5). They are not in place, but nearby, probe holes encountered bedrock at a depth of three feet (0.9m). Most of the Holdenville outcrop is covered by soil in the study area.

The Nowata Shale is present in the bed and banks of Fred Creek where it flows under Harvard Ave. near 73th St. (Locality H73). Ledges of hard silty limestone and calcareous siltstone stand out in the creek in 1 to 2 inch (3-5 cm) layers. These appear to be the flagstone facies described by Bennison (1972a). A similar bed was uncovered in the pit dug for underground gasoline tanks on the slope north of the campus pond (Fig. 6). The flaggy layer occurred at a depth of three feet (0.9m) and laid upon a weathered siltstone section. The Nowata is partially exposed in the man-made channel dug for the rerouting of Fred Creek. The channel, which runs north-

Figure 5. Well I-1 with Inertial Pump Tube

90 2 10

Figure 6. Bedrock Hill at Edge of Valley

Figure 7. NE Bridge Locality with Rain Gauge

Figure 8. Man-made Channel Looking South

south along the eastern edge of campus (Fig.7), was apparently dug down to bedrock at a depth of 10-15 feet (3-4m)below the creek floodplain. Two facies are exposed in the creek bed. Approximately four feet of dark gray calcareous shale forms a small bench where the creek has not been able to cut down through it. Laterally, the shale changes to mottled gray and tan, highly weathered silt and claystone. The transition is so abrupt that a small relief fault is indicated. Just above the low water level, this weathered clayey siltstone appears at various spots down stream as well. At one point, just south of the physical plant building (Locality CB-5) the typical mottled clayey siltstone has a thin crust of iron oxide on top of it. Bennison (1972a) describes a thin persistent iron oxide layer at the top of the Nowata Shale, marking a local unconformity. The Nowata, as mentioned earlier, is truncated from south to north across Tulsa County at a loss of about 20 feet (6m) of section per mile (1972a).

No other outcrops were detected in the study area; however, float of Seminole sandstone is common on the divide slopes. An isolated knob on campus, west of the man-made channel, contains float of medium-grained iron-stained, sandstone. It is probably a local sand in the Holdenville Formation because it is at an elevation much lower than the main Seminole outcrops. Cobbles of sandstone in the bed of Fred Creek appear to be from the

Seminole Formation.

Alluvium and Terrace Deposits

Bank Exposures. Wherever Fred Creek makes a major bend, there is an abrupt cut bank which exposes deposits of terrace or alluvium. Due to the rerouting of the channel to the east side of campus, several of these cut banks reveal sections of the terrace deposits. Beyond the mouth of the creek valley, on the west side of campus, the present day channel cuts into the flood plain of the Arkansas River (Fig. 9). These sheer banks reveal 6 to 12 foot (1.8-3.7m) sections of different zones of the alluvial complex which can be correlated to the sediments encountered in well core samples.

The cut bank (CB-1) closest to the majority of the wells is located at the north end of the man-made channel (Fig. 8). This is just downstream from the U.S.G.S. rainfall and storm flow gauge. The most prominent feature of this bank is a group of lenticular gravel beds located in the lower three feet (Fig. 10). These lenses have a sigmoidal shape and appear to be gravel bars developed in an ancient channel. Because they are quite distant from the central valley of the Arkansas River, they are more likely related to the erosion of Fred Creek valley than to the terrace of the Arkansas. The bars are composed of medium to coarse gravel of iron-cemented sandstone. The sand grains are

Figure 9. Cut Bank #7 Where Fred Creek Channel Exposes Mollic Soil of Flood Plain

Figure 10. View of Gravel Lens at CB #1

fine-grained, subangular, and well-sorted. Quartz grains commonly exhibit crystal faces which appear to be the result of pressure solution at grain contacts. These are also common to the specimens of Seminole sandstone from outcrop H-71). Lateral to the gravel bars, additional gravel is concentrated in three inch horizontal beds at the same level. This gravel is finer grained (1/2 inch [1.3cm] diam.) but is the same iron oxide-cemented sandstone.

The gravel bearing sequence sits on top of highly weathered, mottled, tan and gray clayey siltstone. This silt is bedded and compact, yet it is very soft and nonindurated and is interpreted to be weathered residuum of the Nowata Shale. Above the gravel beds there is up to ten feet of sandy silt of the terrace-alluvium deposit. This deposit is poorly sorted quartz silt and sand composed of subangular grains in an iron oxide matrix. Half way up the bank, there are striking features that are oriented vertically and are nine inches (23 cm) long by two inches (5 cm) wide. They are pockets of light gray colored silty sand which contrast with the tan and brown colors of the rest of the exposure. Under a microscope, the sand and silt grains are seen to be quartz mixed with a moderate concentration of black organic debris. There is very little iron staining on the grains. These "pockets" are interpreted to be root casts which were maintained in a reduced chemical environment due to the concentration of organic matter.

At least seven cut banks along Fred Creek expose portions of the terrace, alluvium, and flood plain on the campus (Figure 4). Several of these reveal the top of the weathered residuum of the Nowata Shale near the low water level. The block diagram of Figure 11 shows the local stratigraphic relationships.

The last major bank on the west side of campus (CB-7), provides a glimpse of the upper flood plain of the Arkansas River. Approximately 10 feet (3m) of fine-grained sediments are in this section. The upper six feet (1.8m) of the bank exhibit a very well developed A-zone in the soil. This thick, dark, topsoil is typical of the Mollisol soils of the prairies. The B-zone beneath is at least four feet (1.2m) thick and is reddish orange to tan clayey silt. The Nowata residuum does not appear to be present here and it is likely that the river valley has been cut much deeper than the creek valley.

Well Cores

As mentioned in the previous chapter, the aquifer was drilled several feet into the saturated zone at 12 locations on university lands. Nine of these were completed as monitoring wells below the water table and the remaining three met impenetrable barriers at

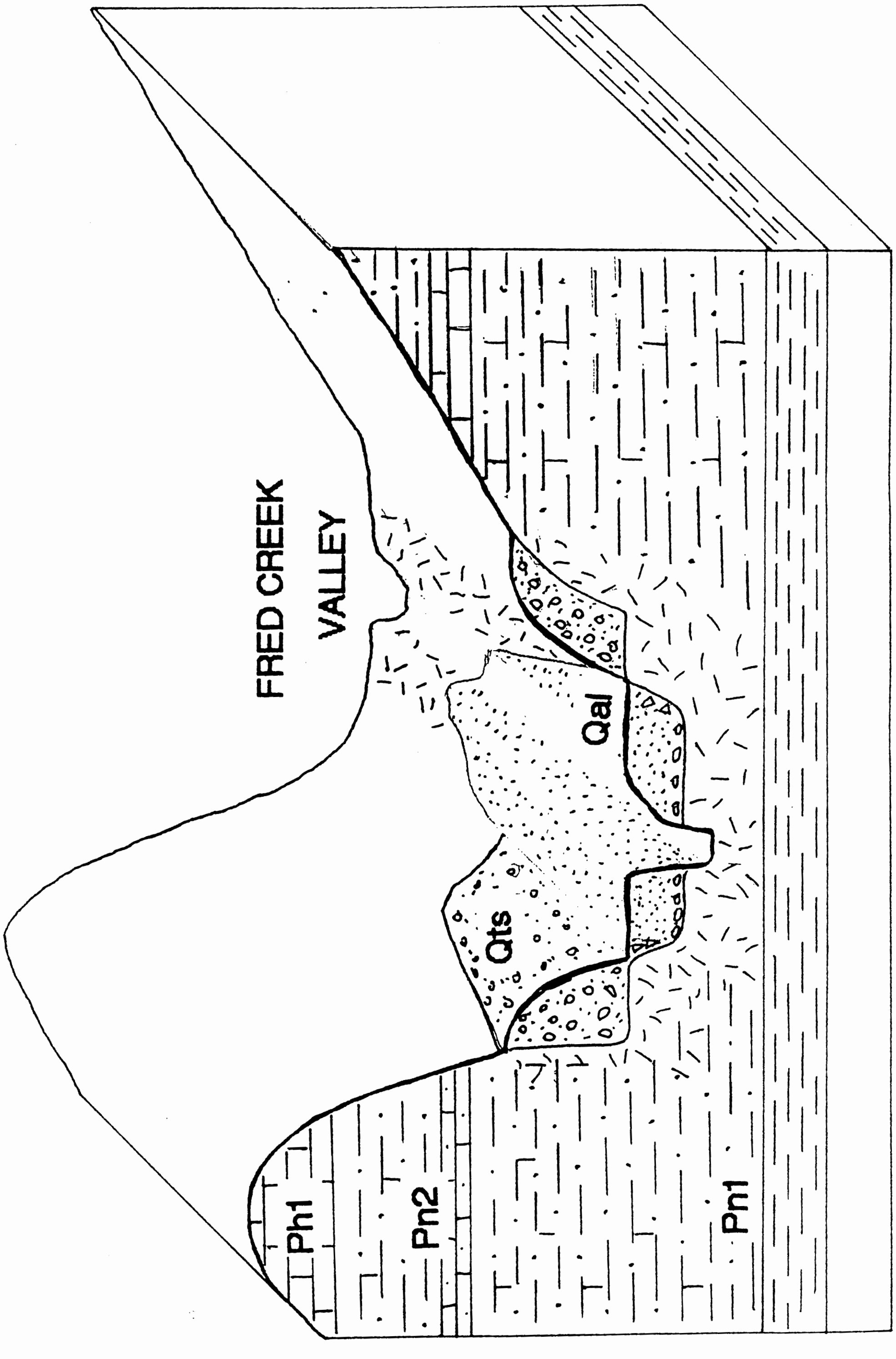


Figure 11. Block Diagram Showing Stratigraphic Relationships

shallower horizons. The drill samples from each of these wells were recovered in a core barrel which permitted continuous examination of the matrix from surface to total depth. Every well was described and logged at successive depths and samples were collected whenever lithology changed. Grain-size analysis using wet sieving and moisture content determinations were made on selected samples.

Lithologies of Core Samples. Most wells found the uppermost 1 (.3m) to 3 feet (.9m) to be recent fill material, spread across the area when the campus was being landscaped. This is particularly true of the wells at the northeast corner of campus where Fred Creek was rerouted. Much of the previous stream channel was filled in when the new channel was dug. The entire northeast corner (~20 acres [8 hectares]) is a low-use area and has been the site for considerable dumping of excavated earth from campus construction projects.

Beneath the fill is an organic-rich zone of loamy top soil. This dark brown horizon is the mollic A-zone which is typical of prairie soils. The extent of the A-zone varies from a foot to four feet in thickness in the valley fill of Fred Creek. In contrast, locality CB-7, on the Arkansas River flood plain, shows six feet of top soil development. The A-zone is dominated by silt and the organic content gives the deposit a dark brown color (Figure 9).

The section below the A-zone is quite variable from well to well and individual layers are not widely correlatable. Nevertheless, gross similarities do exist among nearby wells. The wells along the eastern fence (I-1, -6, & -7) are characterized by silt and fine sand (Figure 12) that is pervaded by iron staining. At various levels, concentrations of gravel occur, with cobble stones ranging from 1/2 inch (1.2 cm) to three inches (7.6 cm) in diameter. In several wells, large cobbles were recovered only after considerable effort was expended. The stones were elongated and only fit into the core barrel in one direction. As mentioned before, wells I-2 and -5 were abandoned due to dense concentrations of gravel. Lithologically, the gravel is iron oxide-cemented quartz sandstone, much like the gravel in the creek bank (CB-1). In general, the section beneath the A-zone is iron oxide rich with yellow brown to reddish brown stains common in the matrix and on sand grains.

Well I-7 deviates from the norm in having a more extensive section of coarse sand and fine gravel near the water table. The matrix for the sand is very dark brown silty clay (Spl 144-150) which is intermixed with a coal-black, subvitreous material. The black substance appears to be amorphous manganese oxide.

Wells I-9 and I-4 are located farther northwest

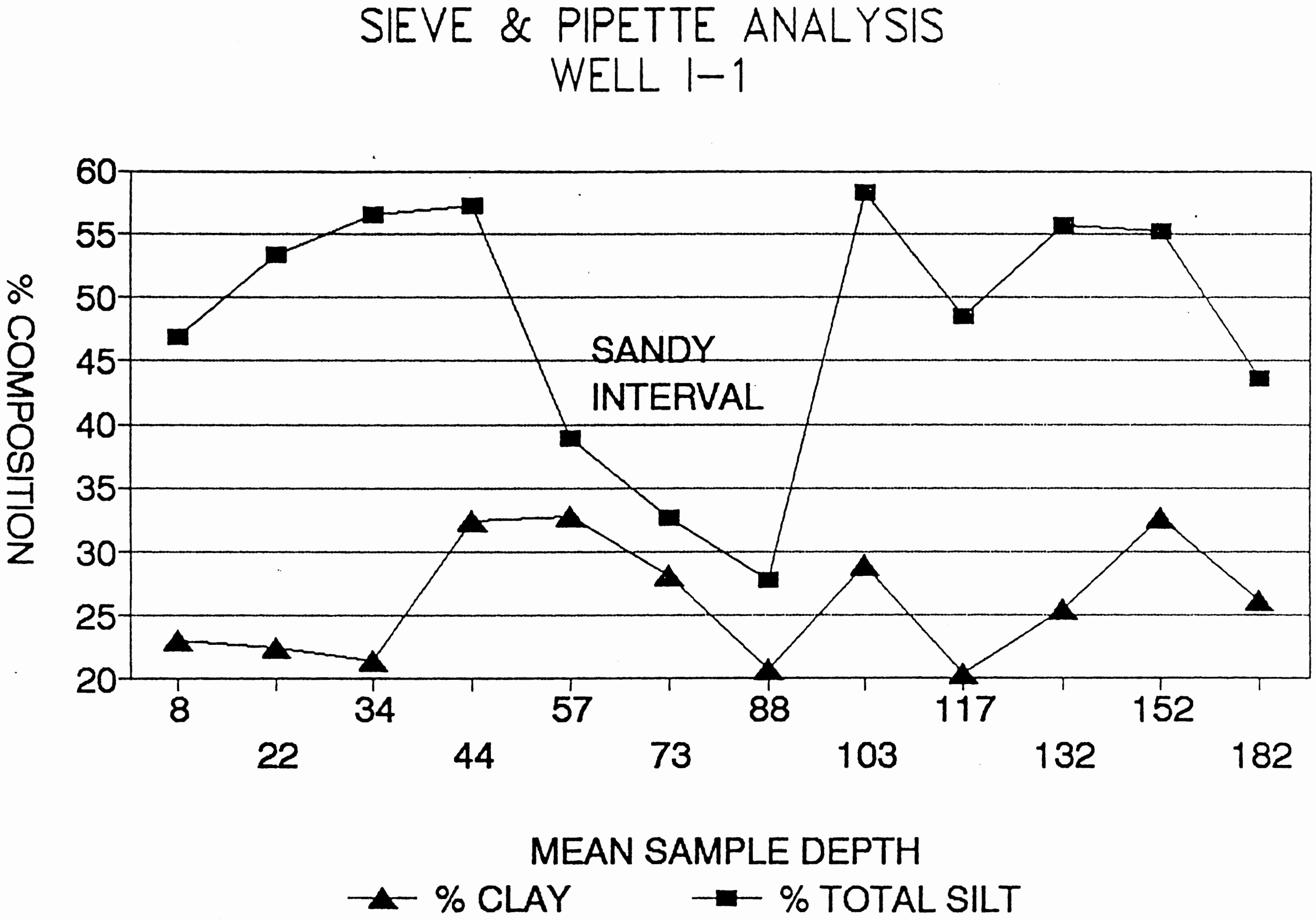


Figure 12. Grain Size Analysis - Well I1

than the aforementioned wells. At both of these locations, a section of black, organic-rich clay and clayey silt was drilled which resembled a swampy backwater deposit. In well I-4, the black clay and loam zone was four feet thick and the section beneath it was void of any oxidized iron stain. The sands and silts were light to dark gray in color. This sequence continued to a depth of 15 feet where highly weathered colluvium of Nowata Shale was encountered. Pieces of silty limestone were recovered along with tan and gray mottled silty clay.

In well I-9, the section below the black clay was unlike any of the other wells in the vicinity. Medium to coarse-grained unconsolidated clean sand was found from a depth of 12 feet to the total depth of 15 feet 10 inches. The well could not be drilled any farther because this sand caved in below the water table. This well is closest to the course of the creek channel prior to rerouting. The sand is most likely from a point bar that was formed in the ancient channel.

Well I-3 was also drilled along the original drainage as indicated by the mature walnut and oak trees on trend with the campus pond (Fig. 13). The sediments here are sandier as indicated by the grain size graph (Fig. 14). Also striking in the samples were beds of gray-green, plastic clay and a dried, rotten limb of wood (8 feet [2.4m] below the surface). This well did not have the black clay of the wells farther west, nor the dominant iron stained silt of the wells to the east.

Well I-8 is located 160 feet south of I-3, on the east side of the valley. The sequence of lithologies in this well was very much like that in I-7 which is more than 500 feet (52m) away on the other side of the valley. At depth, the cores exhibited pronounced lamination marked by iron oxide and manganese layers alternating with tan and gray clayey silt. This may be a facies in the residuum of the Nowata Shale. Well I-8 was drilled two days after a soaking rain and ponded water was still visible nearby. Nevertheless, soil moisture was quite low, resulting in slow difficult drilling from near surface to a depth of seven feet (2.1m). Moisture content gradually increased beginning five feet (1.5m) above the present water table. The lithology at total depth was fine-grained sand even though silt and clay dominated the remainder of the well.

Figure 13. Location of Well I-3
Among Trees Which
Mark Course of Old
Creek Bed

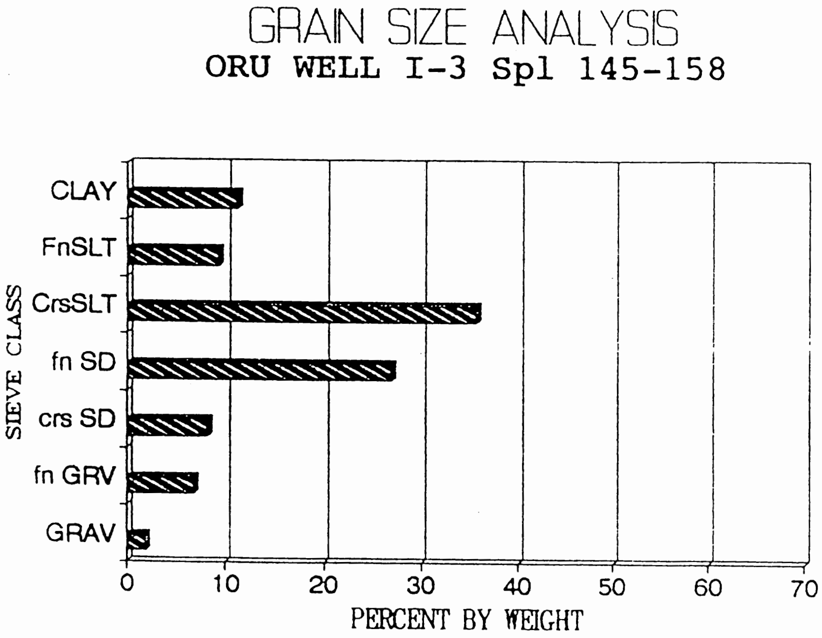


Figure 14. Grain Size Distribution of Well I-3

Wells Farther Downstream. Approximately 1800 feet (550m) southeast of the I-3 well, a solitary well was drilled near the mouth of the eroded creek valley. From this point west, Fred Creek continues, but its channel is cut into the Arkansas River flood plain. This well, II-1, was drilled to 17 feet (5m) in fine sand, silt and clay. It found greenish clays that were very plastic, much like the clays of well I-3. At a depth of five feet (1.5m), the drilling became difficult for an interval of four feet (1.2m). The samples of this zone turned out to be extremely dry silt.

Two additional wells were drilled one half mile (0.8m) west of well II-1. These wells were located along an abandoned stretch of the Fred Creek channel that was the victim of a second rerouting project. A straight channel has been dug due west to connect Fred Creek to Joe Creek instead of allowing it to meander through its original course to join Joe Creek farther south. Wells G-1 and G-2 were drilled 370 feet (113m) apart into the Arkansas River flood plain. Both wells found an upper section marked by a foot (0.3m) of black silty clay overlying more than ten feet (3m) of medium brown to reddish silty clay and fine sandy silt. A portion of this zone was dry and caused difficult drilling. At a depth of 13 feet (4m) in G-1 and 15 feet (4.6m) in G-2, the samples changed abruptly to dry, loose, medium-grained orange sand. The sand was extremely dry and did not hold together when handled. Three to four feet farther down, the sand became moist and then saturated. The wet, loose sand caved in and prohibited penetrating more than a foot below the standing water levels.

Mineralogy of Clay Fraction. Samples of the first four monitor wells (I-1, -3, -4, and -6) were analyzed for the mineralogy of the clay-size fraction using x-ray diffraction. This was done as a favor to the university by Garwin Powers at the Amoco Research Laboratory in Tulsa. Samples were chosen from the depth where water was first encountered in each well and from intervals 3 feet (1m) above and below that. Samples were mixed with water and then centrifuged for a specified time and speed until the suspension contained less than 2 micron size particles. The liquid was then transfered to a glass slide and allowed to air dry. Initially, a pattern was run from 2-36° 2 theta with a 0.01 step and a 1 second count time. Next, the sample was glycolated for 24 hours and run again to detect expandable clays (Garwin Powers, personal communication).

Summaries of the results are shown graphically in figures 15, 16, and 17. Sample numbers refer to the depth range of the samples in inches. Very little difference is seen in the overall distribution of mineral types from the three levels of sampling.

In all samples, quartz is the dominant mineral in the < 2 micron fraction. The optical identification of quartz sand and silt throughout all wells parallels this finding. Of the clays identified, mixed illite-smectite clays are most common (20-35% of total concentration) with illite and kaolinite equally represented at 10%. The near absence of calcite confirms the observations of core samples. Seldom is any calcareous matrix detected in the aquifer, even though the bedrock contains some limestone members. Some core samples effervesced in hydrochloric acid after drying. It is possible that calcite precipitated when the interstitial water evaporated. On the whole, all samples had similar clay fraction mineralogy.

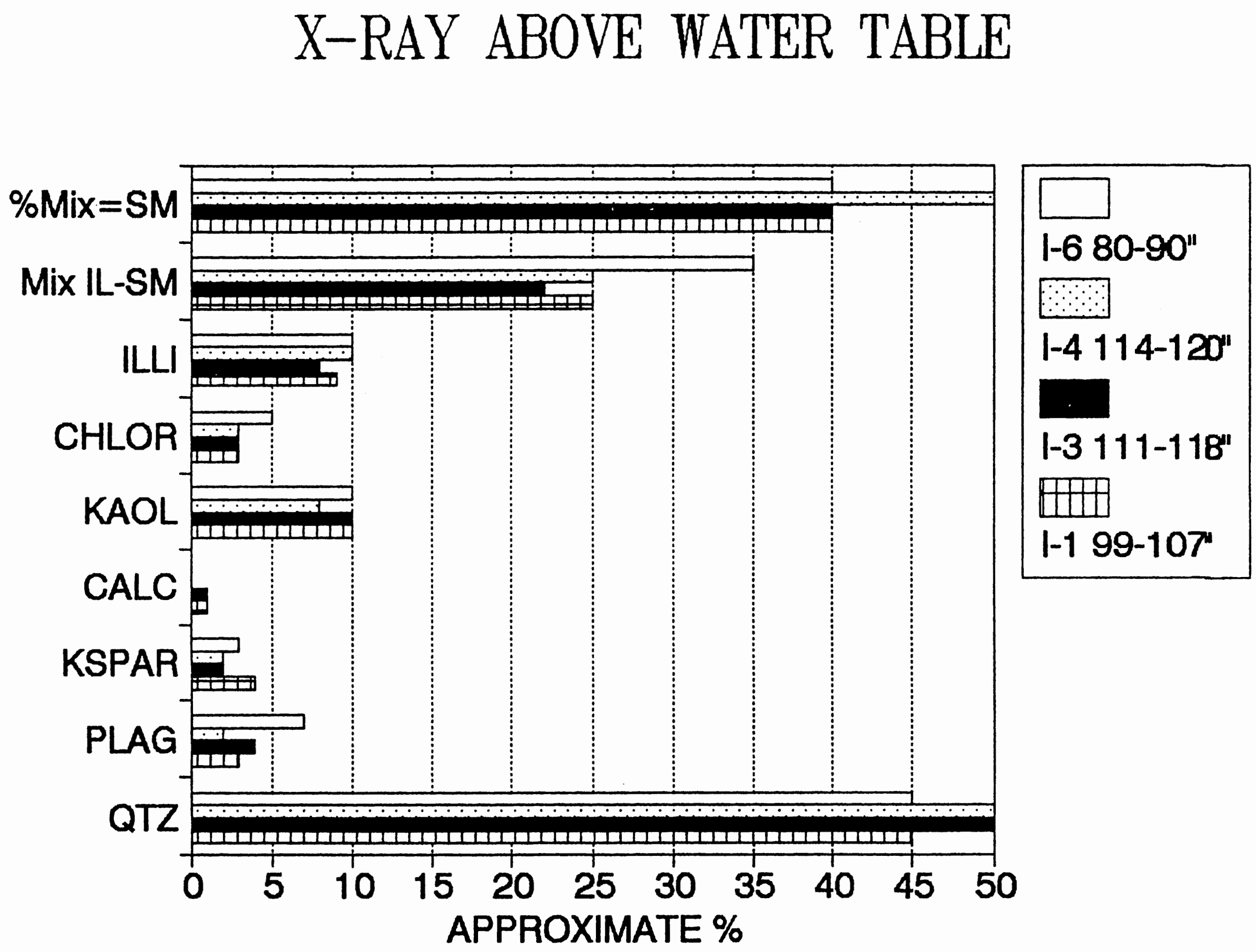


Figure 15. X-Ray Analysis, Samples Above Water Table

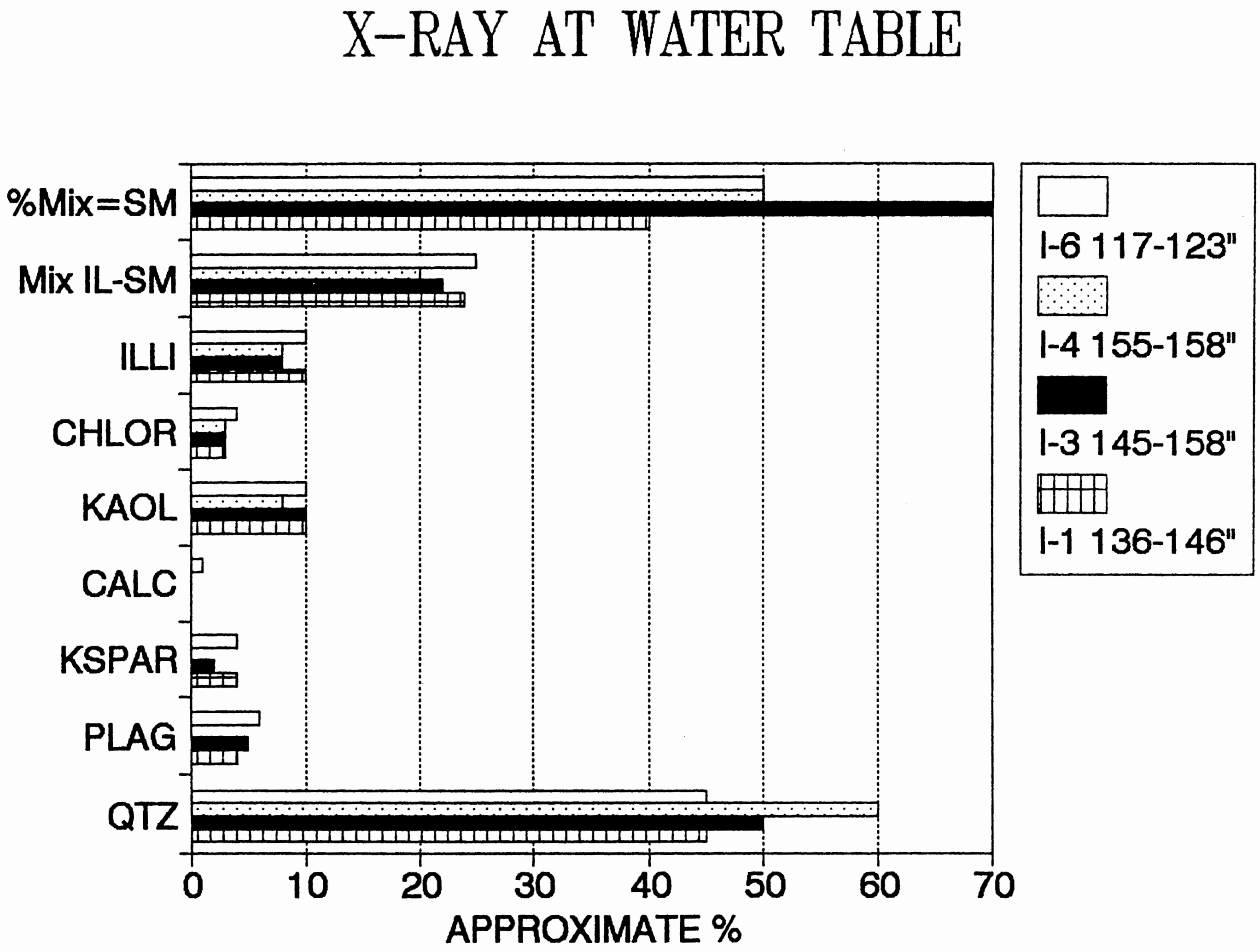


Figure 16. X-Ray Analysis of Samples At Water Table

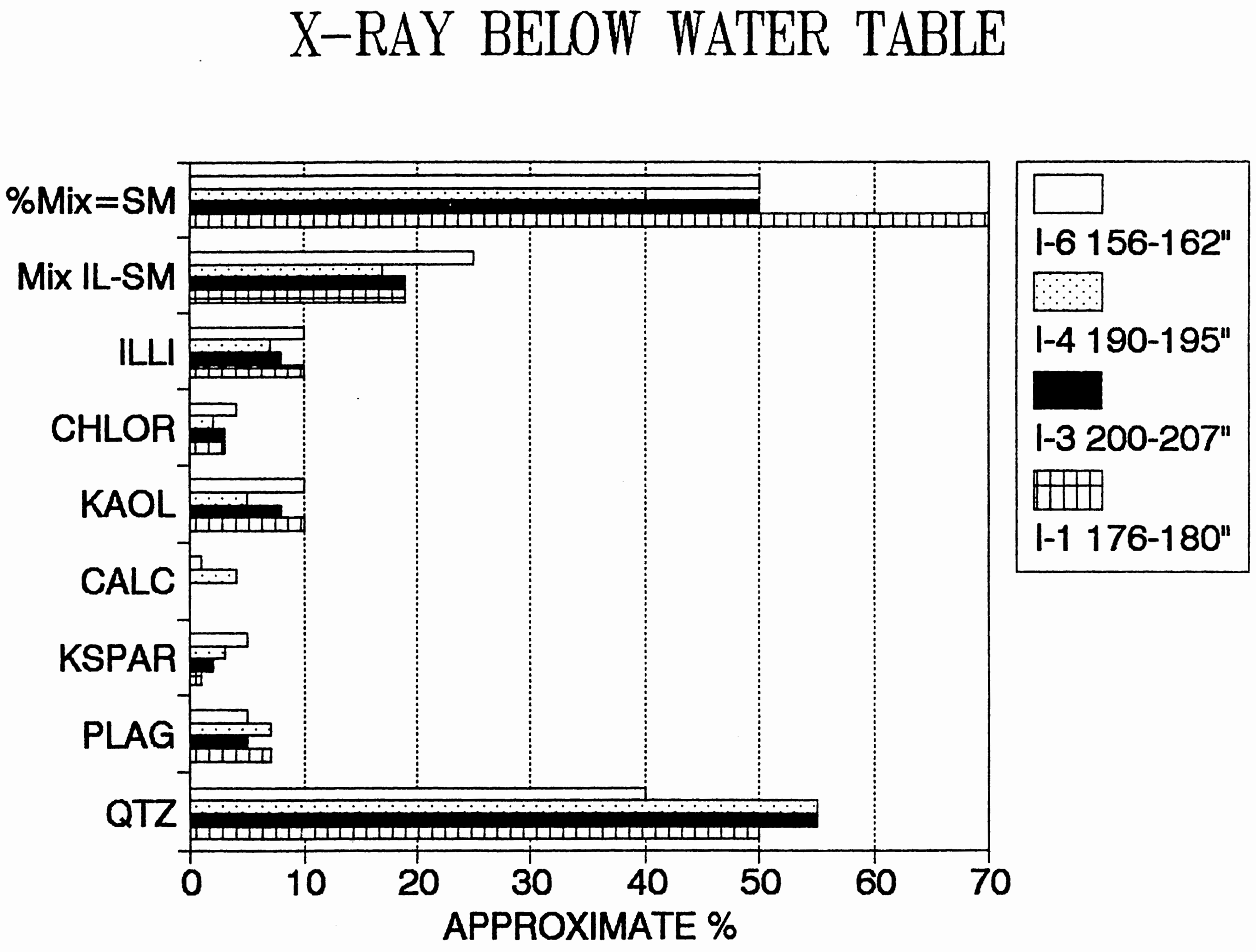


Figure 17. X-Ray Analysis of Samples Below Water Table

Summary of Significant Observations

Several prominent lithological relationships were recognized from the comparison of creek sections to well cores. They can be summarized as follows:

1.) The natural terrain on campus has been filled in with one to three feet of earth, thus modifying topography and the matrix properties of the upper soil profile.

2.) Silt, fine sand, and clay are the dominant grain sizes in the terrace/alluvium complex.

3.) Iron oxide content as grain coatings, cement, and matrix is high in the central and eastern portion of the valley.

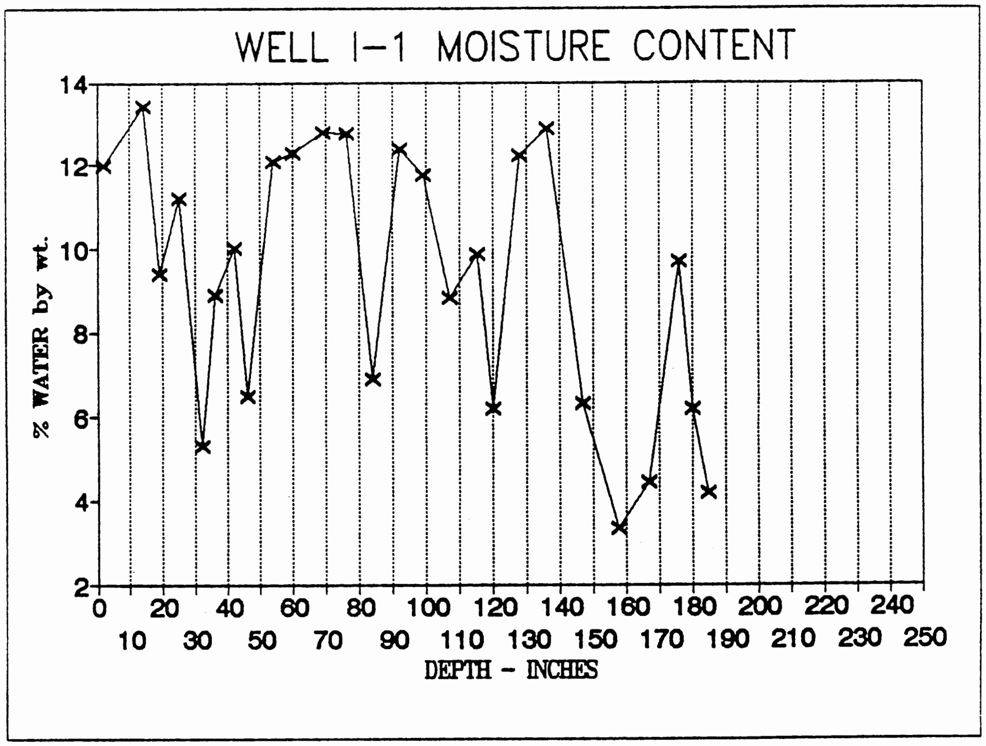
4.) Black clay loam deposits occur in wells on the northwest edge of the valley, in an area mapped as Quaternary terrace. These deposits appear to be organic rich back-water deposits.

5.) Sandstone gravel lenses and beds are common at about ten feet (3m) from the surface and appear to rest upon the Nowata Shale. They probably represent a lag deposit formed during the primary erosion of the valley.

6.) The Nowata Shale weathers deeply, especially where clayey silt members subcrop the alluvium. The residuum of this Pennsylvanian bedrock can be penetrated by hand auger and is not readily differentiated from the overlying terrace and alluvial silts. Although fine grained, the residuum bears groundwater and the water table is continuous with that in the alluvial deposits.

Moisture Content

The distribution of soil moisture was gauged by observing the ease of drilling, the relative moistness of fresh samples, and in selected wells by comparing the weight of fresh samples to that of air dried samples. The moisture content as a percentage of weight is portrayed for wells I-1, I-8, I-9, G-2, and II-1 in figures 18 and 19. Wells were drilled at various times of the year. Wells I-1 to I-6 were drilled in the late winter of 1990 when rainfall was above the average. Well I-7 was drilled on the 4th of July as rainfall was less frequent and well I-9 was drilled in late November after a dry autumn. Wells G-1, G-2, II-1, and I-9 were drilled during the winter of 1991 which was drier than average. Most wells experienced a noticeable section of very low matrix moisture which was manifested in difficult slow drilling. In some wells (eg. I-2 and II-1) the section was so dry that samples were arduously ground away from the packed sediment rather than being cut into by the auger blades. These dry zones varied in depth from a few feet down to a depth of six feet (1.8m). The dry sand zones of flood plain wells G-1 and G-2 were as deep as 13 and 15 feet respectively.



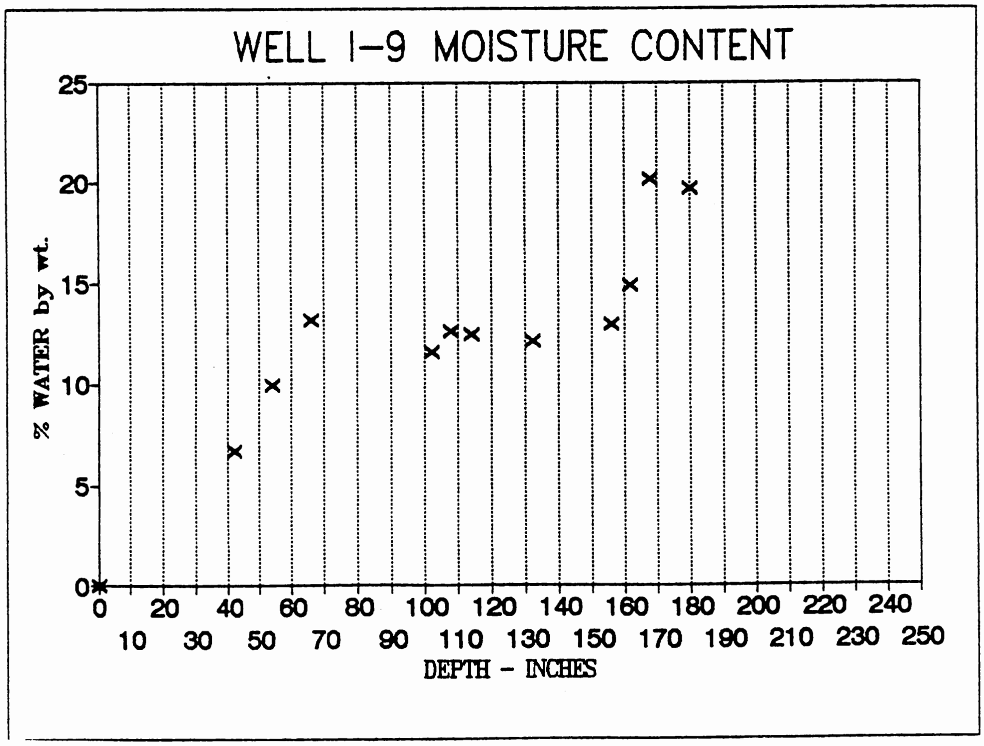
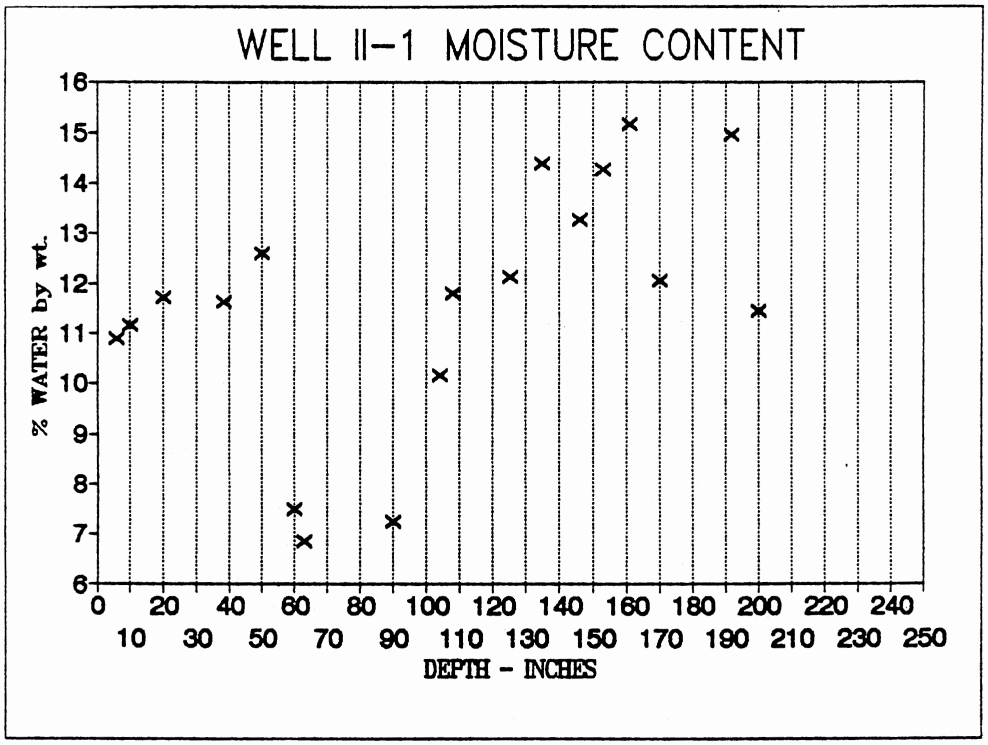


Figure 18. Moisture Content by Weight:
Wells I-1 and I-9



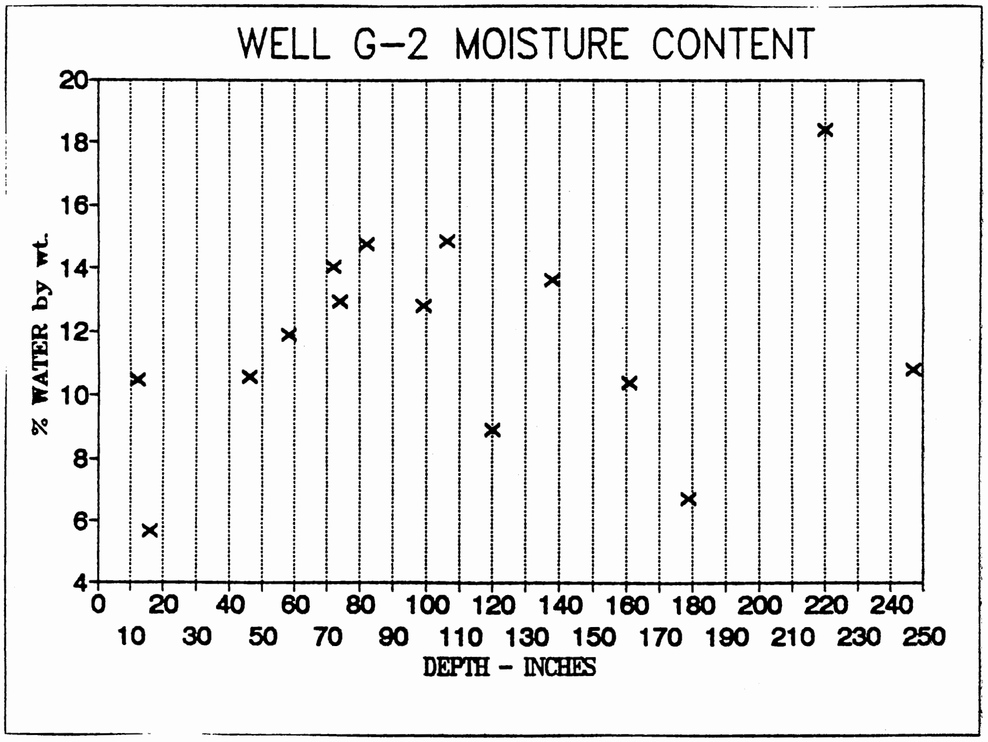


Figure 19. Moisture Content by Weight:
Wells II-1 and G-2

Shallow zones commonly had soil moisture averaging 12-14% by weight, but the dry zones were at least as low as 6% moisture. Grain size analysis of the I-1 well shows that moisture content was not merely a function of a texture - water retention relationship (Fig. 20). The persistent low moisture zone indicates that downward percolation of infiltrated water was not a major contributor to recharging the aquifer. Hydrographs show a short term response of the water table to major rainfall events (Fig. 22). Such recharge could not have moved down through the entire deposit leaving zones as dry as those encountered in drilling.

No tracer studies were conducted so it is not known whether water recharged through selective paths instead of a wetting front. Macropores such as burrows, root casts, and dessication fractures could allow vertical movement without wetting the entire section.

Alternatively, recharge could occur at the valley walls in colluvium deposits or directly into the weathered bedrock farther up the valley. Water reaching the saturated zone by these paths would circumvent most of the vadose zone of the alluvial complex. Excessive recharge would cause the water table to rise and successively saturate shallower sections of the alluvium.

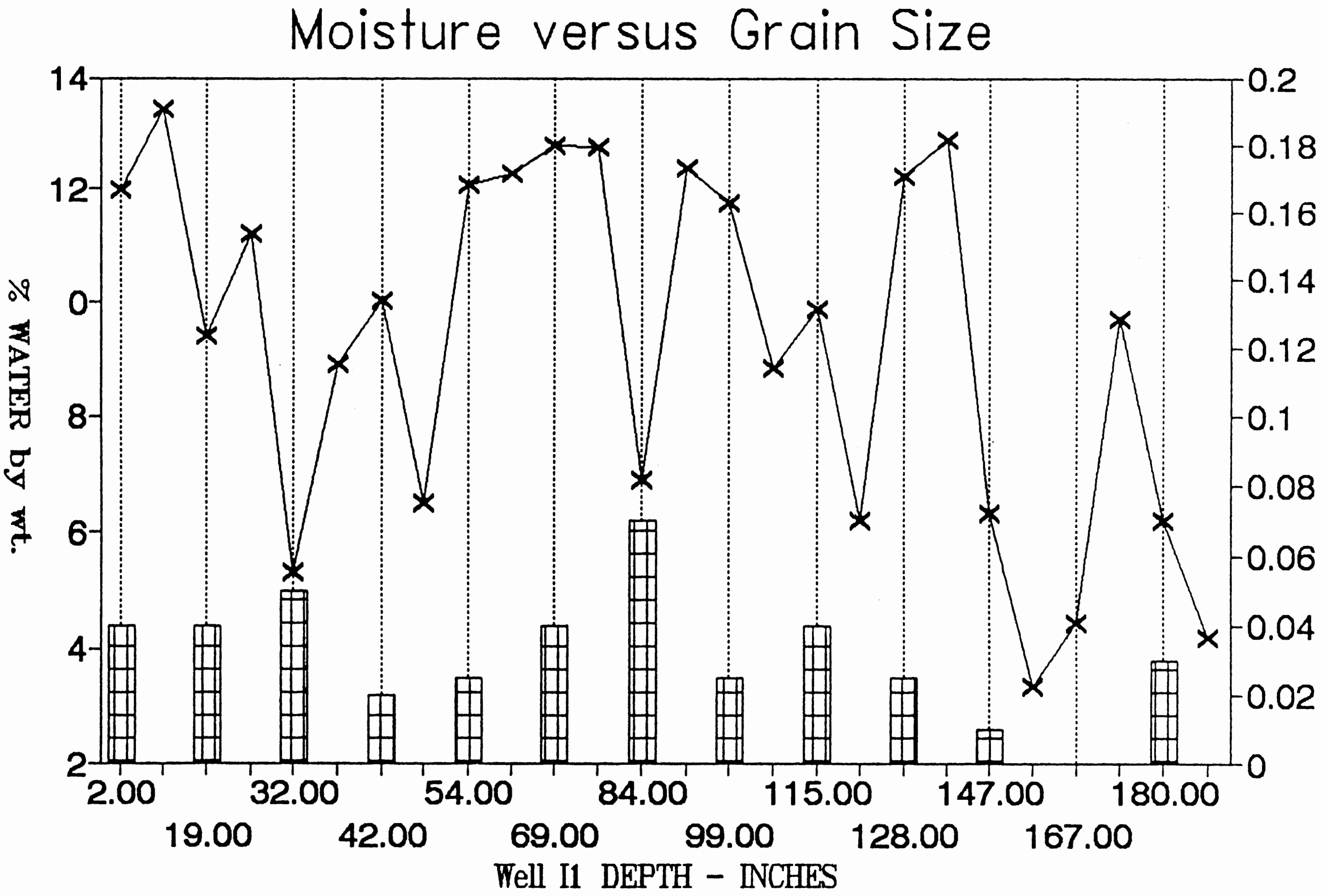


Figure 20. Well I-1, Grain Size and Moisture

CHAPTER V

HYDROGEOLOGY: GROUNDWATER

Water Table Fluctuations

Procedures

Thirteen wells have been completed as piezometers to monitor water table fluctuations and provide insight into hydraulic relationships in the aquifer. The initial four wells were drilled between the end of February and mid-March, 1990. Standing water levels in open hole were measured using a steel tape. Subsequently, the water level in casing was measured every week for a full year. Additional wells were added to this monitoring network in July, November, and as recently as March of 1991 providing less extensive records but adding to the spatial control. Three other wells were drilled much farther downstream to provide a more complete view of the valley fill - floodplain relationship.

All wells were slotted over the bottom two feet of casing so that a limited zone beneath the water table was sampled. The annulus of each well was sealed with granular bentonite to guard against seeping of surface runoff to the saturated zone.

In addition to water levels in the wells, daily rainfall totals were provided by the U.S.G.S from a gauging station adjacent to the monitoring site. There were checked against the official weather bureau records to verify that no anomalous data were present.

Well Hydrographs

Seasonal Fluctuations. The fluctuation in the water table throughout the year was related to the amount of rainfall-induced recharge and the loss of water through evapotranspiration and discharge to the creek. Differences in hydrographs from well to well were caused by varying distribution of permeability in the vicinity of the wells. Water levels were recorded both as elevation above sea level (Figure 21) and also as depth to water from ground level (Figure 22). As shown on Figure 21, the primary trends of water level change are: 1) the rise following extended periods of rainfall and snow- melt, and 2) the steady recession during the growing season. Two cycles of persistent rainfall occurred during the early stage of observation. Several inches of rain and snow had already fallen in January, 1990, with episodic soaking rains continuing into March. This winter cycle is marked by a corresponding rise in

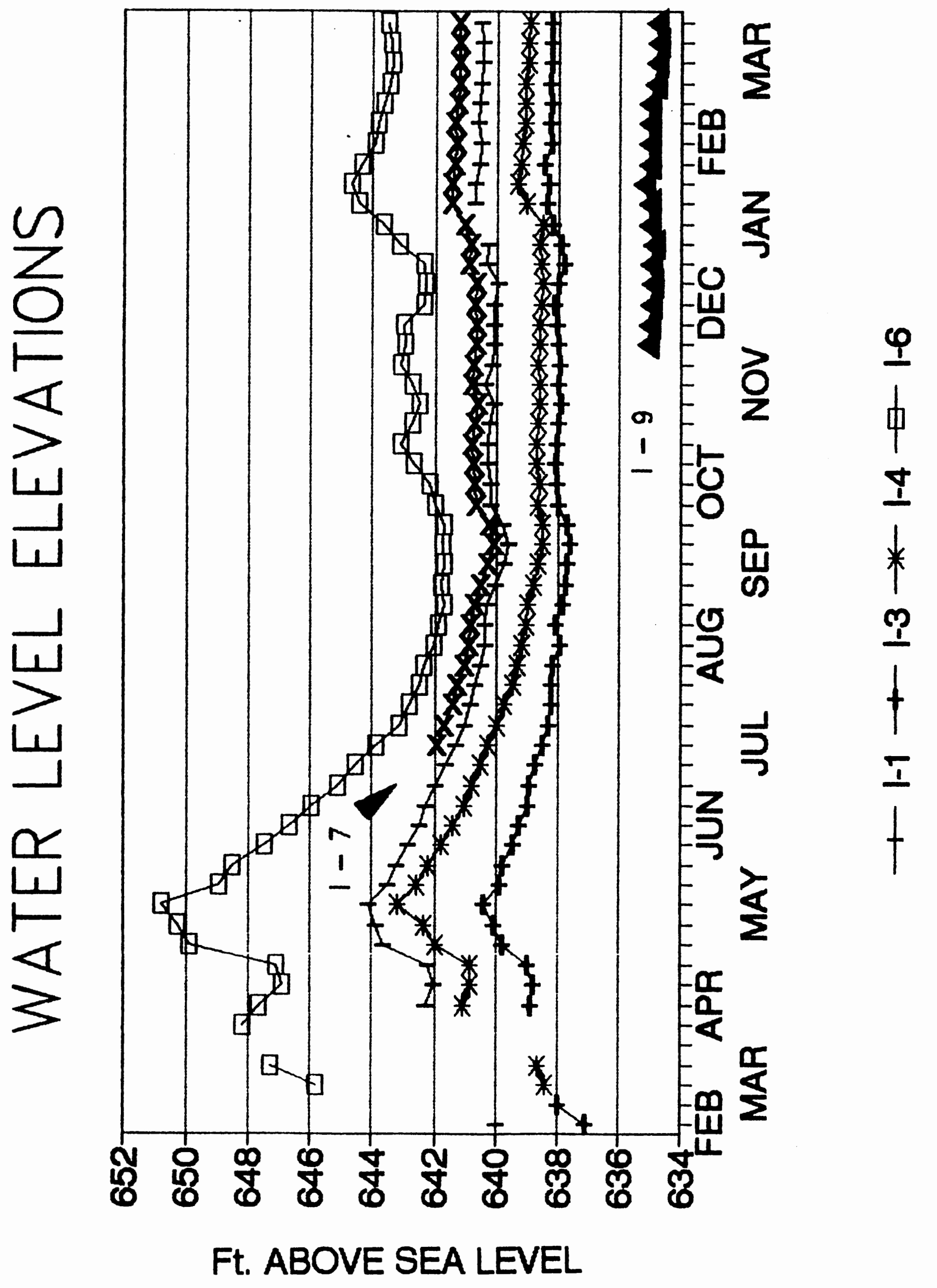


Figure 21. Combined Hydrograph of Series I Wells

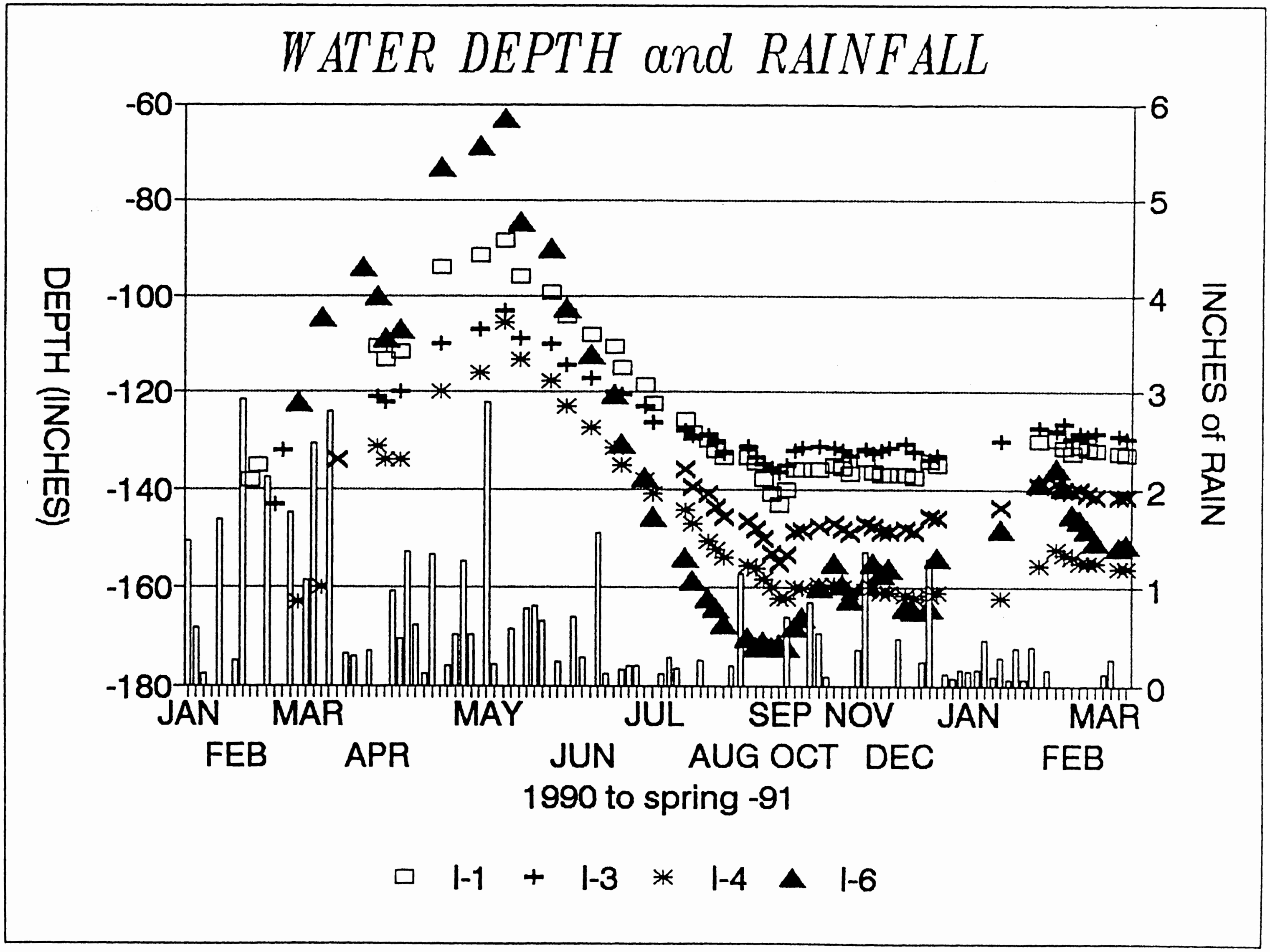


Figure 22. Hydrograph of Water Depths Plus Rainfall

water levels, peaking March 26, 1990. A second pulse of precipitation developed during April and May, the normal time for heavy convective storms in Oklahoma. Again, a marked rise in the water levels is recorded, reaching its peak May 7.

From mid-May through September, the water table steadily declined. This was in spite of more than 3 inches (7.5 cm.) of rain in late May and 2.5 inches (6.4 cm.) of rain in June. The rate of decline was very regular regardless of the amount of precipitation. In contrast, the water table rose in the winter and early spring and stabilized to a constant level during the fall (October through December).

Because the water level recession only occurred during the peak growing season, the most likely explanation for the steady drop is the loss of water to evapotranspiration, coupled with discharge to the creek. Meanwhile, rainfall was not effectively recharging the aquifer. This is apparent because the rainfall events had no effect on the water level during this time period.

Following the summer decline and the autumn stand still, the first evidence of recharge occurred in January of 1991. This was a response to a 2 inch (5 cm.) snow and ice storm on December 29 and 30. During the first week of January, temperatures rose above freezing on only two days. According to the National

Weather Service, (personal communication), snow cover remained until January 13. Water levels in all measured wells had risen by January 9 and continued rising till January 22. The maximum water level rise was 1.5 feet (46 cm.) in the I-6 well and a minimum of 5 inches (12.7 cm.) in I-1. No comparable response to a precipitation event had occurred since the spring of 1990. The immediate response to this event indicates recharge is more affective when moisture is released gradually than when concentrated rainfall occurs.

Well to Well Differences

Not all wells display the same rates of water level rise and fall. The wells most similar are those along the east fence (I-1 and -7) and the I-4 well on the northwest. The difference between high and low water levels in these wells was 4.5 to 4.7 feet (1.4 m) making an average drop of 3 inches (7.6 cm.) per week. These three wells fell steadily at their average declines during the spring and summer.

In contrast, the I-3 well hydrograph is more subdued, showing a 2 inch (5 cm.) per week decline with a high to low level difference of only 2.8 feet (0.9 m). The I-6 well is on the other end of the spectrum. The water level in this well rose and fell very rapidly. It responded very quickly to rainfall events and it receded rapidly as well. The difference between high and low levels was 9.1 feet (2.8 m) for an average drop of 7 inches (17.8 cm.) per week. The decline in this well was so drastic that the water table fell below the well screen in August and did not recover until October.

The comparable decline rates observed for wells I-1, -7, and -4 is most likely a function of the silty matrix which dominates the three and also the similarity in their elevation (within 1.5 feet [0.4 m] of each other). The three wells should have nearly the same hydrostatic head.

Well I-3 is in the valley floor at a lower elevation than the aforementioned wells. It follows the normal relation of water table to topography having a water level closer to the surface than most higher elevation wells. This well is in a location where the aquifer used to discharge to the natural stream and now sits in a low spot where flow lines converge from the water coming perpendicular to the stream and those flowing down the valley.

The vastly different response of the water level in well I-6 appears to be caused by a combination of factors. The location of the well is the highest elevation of the entire network (Figure 23) and it is the well closest to the eroded valley wall. Within fifty feet to the northwest, sizeable limestone blocks are exposed on the hillside. The rapid rise of water in I-6 is interpreted to be due to the proximity of the well to a high permeability recharge zone. Such a zone should be developed in colluvium deposits at the base of the eroded valley wall. Colluvium rubble has been recovered in wells I-4 and I-6 near total depth (Appendix A). Stone et.al. (1972) report common development of colluvium from shale outcrops in the county. The likely location for colluvium development in the Fred Creek area would be at the base of the eroded valley walls. Well I-6 is closest to this position. As infiltration from rainfall events reaches the colluvium, water would infiltrate and move quickly to the boundary of the colluvium and the silty alluvium. At this point, the water should back up because the permeability of the alluvium is too low to accommodate the rapid accumulation. This would explain why water rises so rapidly in well I-6.

After recharge tails off and the groundwater flow toward the creek drains the valley wall slopes, water levels at higher elevations should drop faster than those farther down into the valley. This is partly due to that fact that the increase in aquifer thickness downslope means there is less volume to drain in the valley perimeters and so it drains more quickly. Groundwater velocity should also be greater in the thinner portion of the aquifer. As shown below, the

$$Q = K I A \qquad \text{(Eq. 1)}$$

D'Arcy equation portrays gradient (I) to be inversely

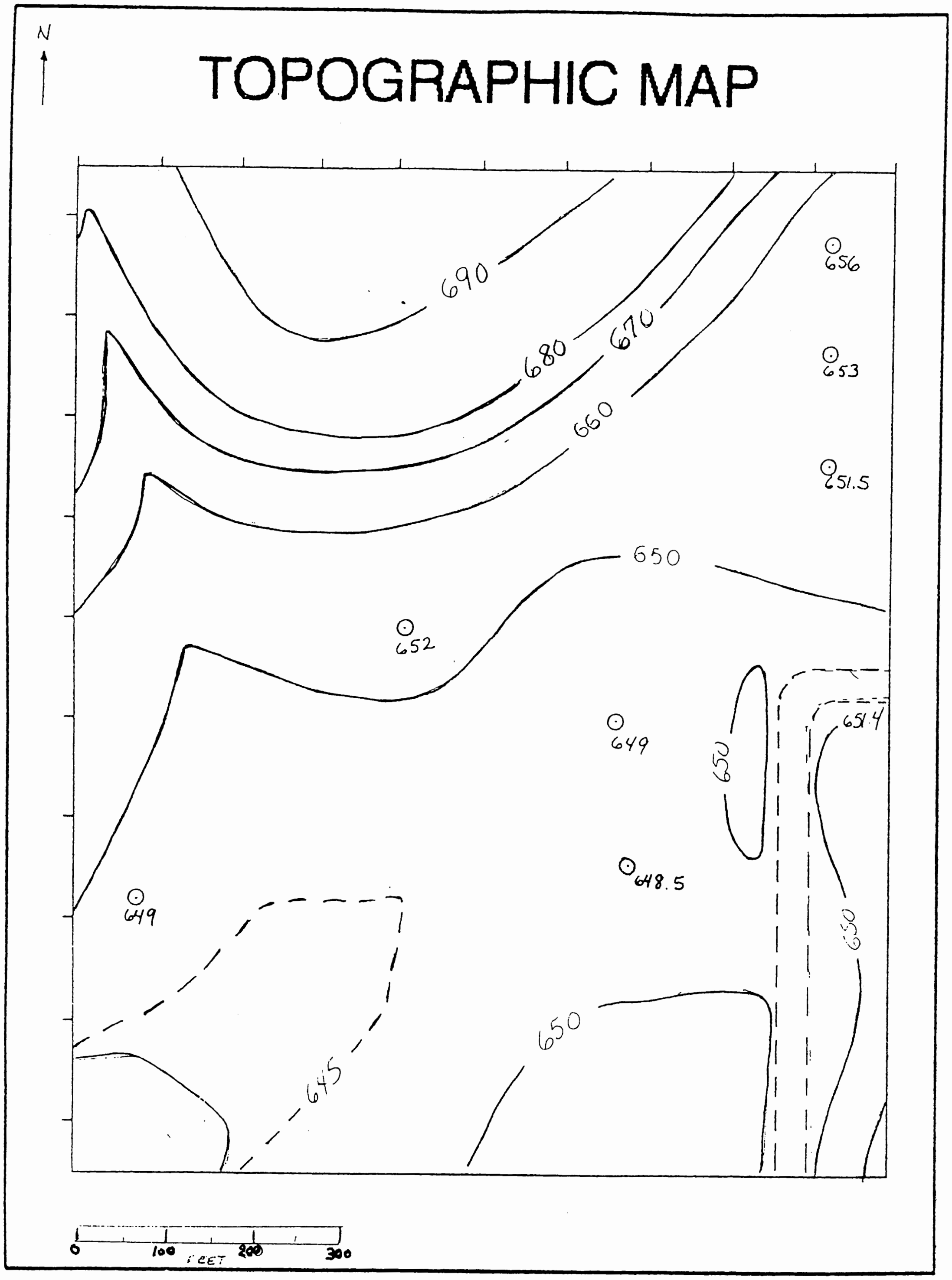


Figure 23. Topographic Map of Study Area (After USGS)

proportional to area (A), the dimension term. As long as there is no change in the hydraulic conductivity, gradient should increase when there is a decrease in the thickness of an aquifer. The equation for groundwater velocity (Eq.2) shows that gradient in

$$v = K I / a \qquad \text{(Eq. 2)}$$

turn is directly proportional to velocity. The gradient increase in the thin aquifer zone would generate a faster velocity causing it to drain rapidly. The net result is rapid water level declines upgradient.

Potentiometric Maps

In order to construct a potentiometric map of the area, the water levels in all the wells were compared to the topographic map. The topography is dominated by the slope of the valley wall on the north rising 50 feet (15 m) to the top of the divide and also by the broad flat valley floor. The valley floor has been highly modified by landscaping projects. Much of the valley has been leveled for athletic fields by filling in low spots and grading the higher points. Moreover, the previous creek channel has been filled and the rerouted channel has been cut along the eastern wall of the valley. Net flow should be down valley toward the southwest as a resultant of flow coming from the valley walls and flow down the axis of the valley. However, the central discharge point of the original creek has been disrupted with the filling of the channel so the discharge outlet is now farther east in the man-made channel. As a result, the potentiometric map is much more complex than would be expected from a normal stream valley.

The potentiometric maps are included as figures 24 through 26. One map was made for May at the high stand of the water table, one for September the lowest point of the year and one for March, an intermediate level following a long period of stability. These maps may be compared with the topographic map (Figure 23) for the same base area.

The May map shows a steep gradient from the valley wall toward the creek channel. Flow direction was to the south and southeast, perpendicular to the equipotential lines. The gradient from Well I-6 to I-1 was 0.0268 ft/ft whereas that from Well I-4 to I-3 was 0.0098 ft/ft. The elevation of the creek bed at this point is 640 feet, dropping to about 635 feet at the south border of the map. During most of the year, a zone of seepage extends a foot above the creek level. This can be seen as a dark band at the base of the creek bank in Figure 27.

By September, the water table had dropped and was much less steeply inclined (Figure 25). The gradient along the eastern line of wells was 0.0084 ft/ft to the south and the gradient in the vicinity of Well I-3 was

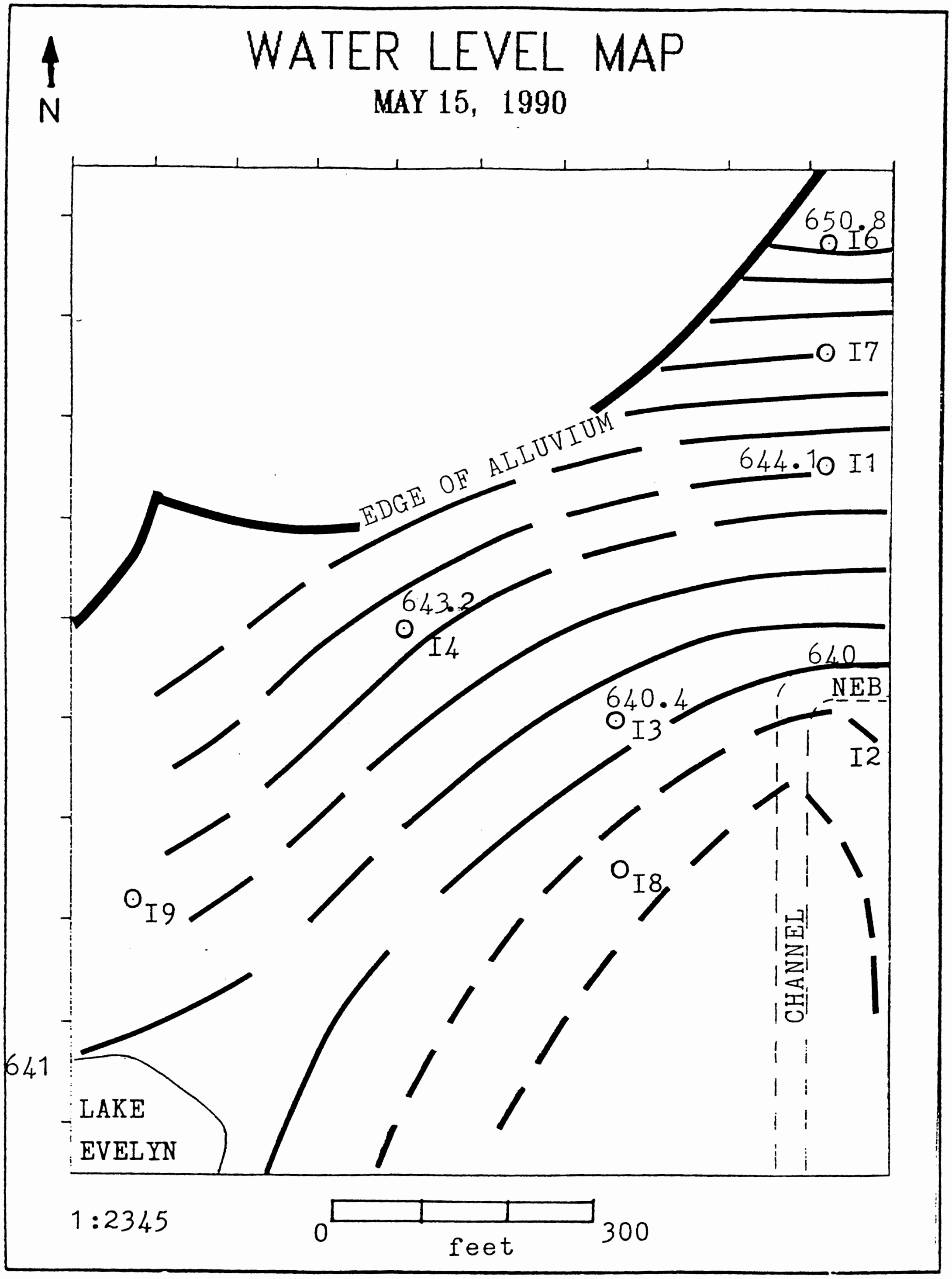


Figure 24. Water Elevation Map for May

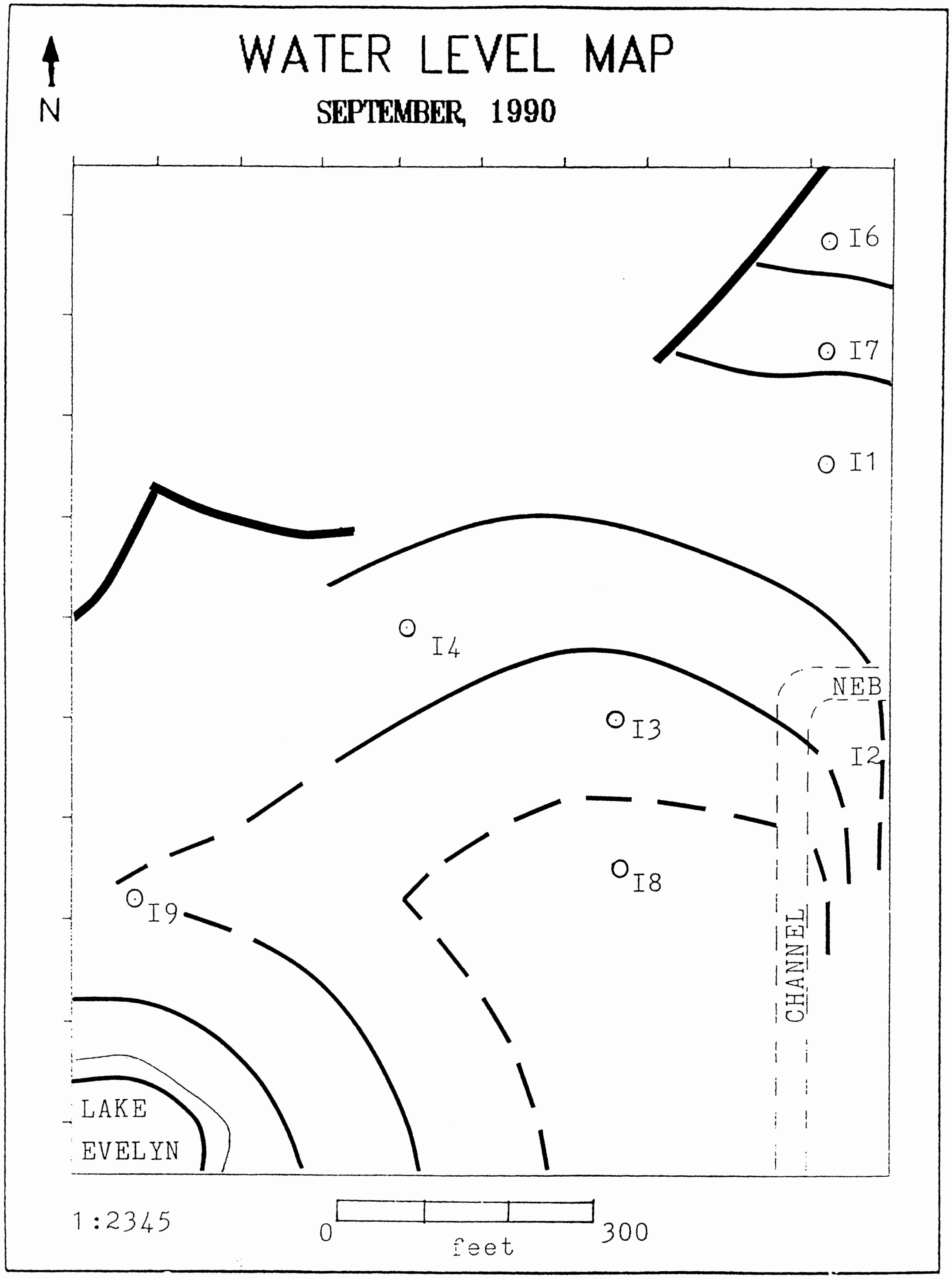


Figure 25. Water Elevation Map for September

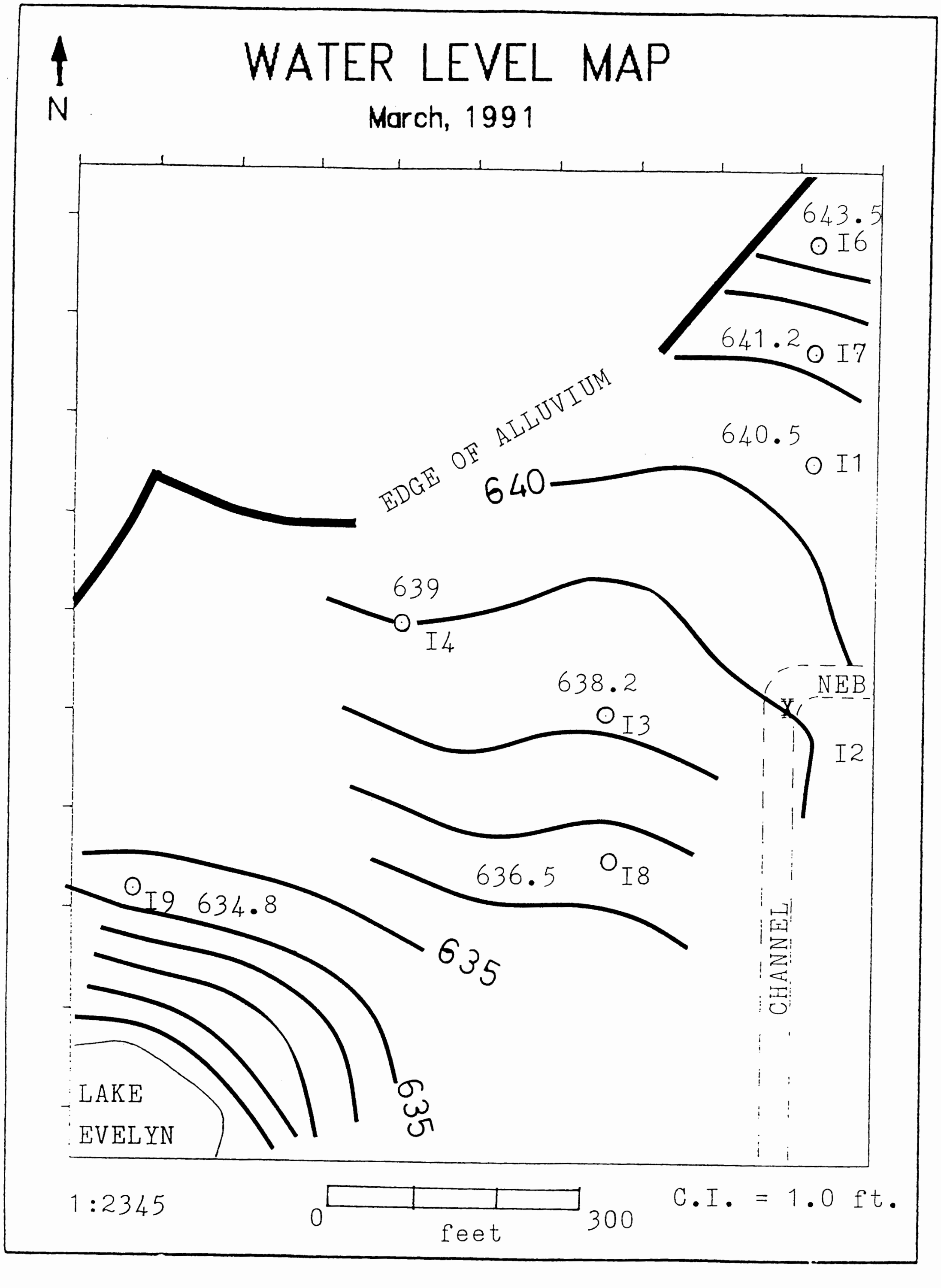


Figure 26. Water Elevation Map for March, 1991

0.0058 ft/ft. The surface elevation of the pond (640 ft.) was higher than the interpreted ground water elevation so that a counter gradient to the east is mapped. Discharge upstream from the northeast bridge was minimal during September. Standing water remained in the upstream channel but no water passed through the bridge culverts. Discharge continued below the bridge and the downstream portion of the creek continued to flow throughout the dry period.

Winter recharge initiated a rise in the water table and the gradient from I-6 to I-1 increased to 0.012 ft/ft on the March, 1991 map. The addition of the I-8 and I-9 wells expanded the spatial control across the filled channel area, showing a narrow trough in the map where the gradients converge (below 635 ft.).

Flow paths interpreted from the water level contours are dominantly south in the vicinity of the wells. The maps indicate that the I-6, I-7, and I-1 wells were in one flow path and the I-4, I-3, and I-8 wells were in a separate path. Within their respective paths, I-4 and I-6 were the most up-gradient wells, closest to the edge of the alluvium at the valley wall.

Lower Valley to Flood Plain Area

The average valley gradient of Fred Creek between Harvard and Lewis Avenues is 50 feet per mile or 0.009 ft/ft. This provides an estimate for the potentiometric

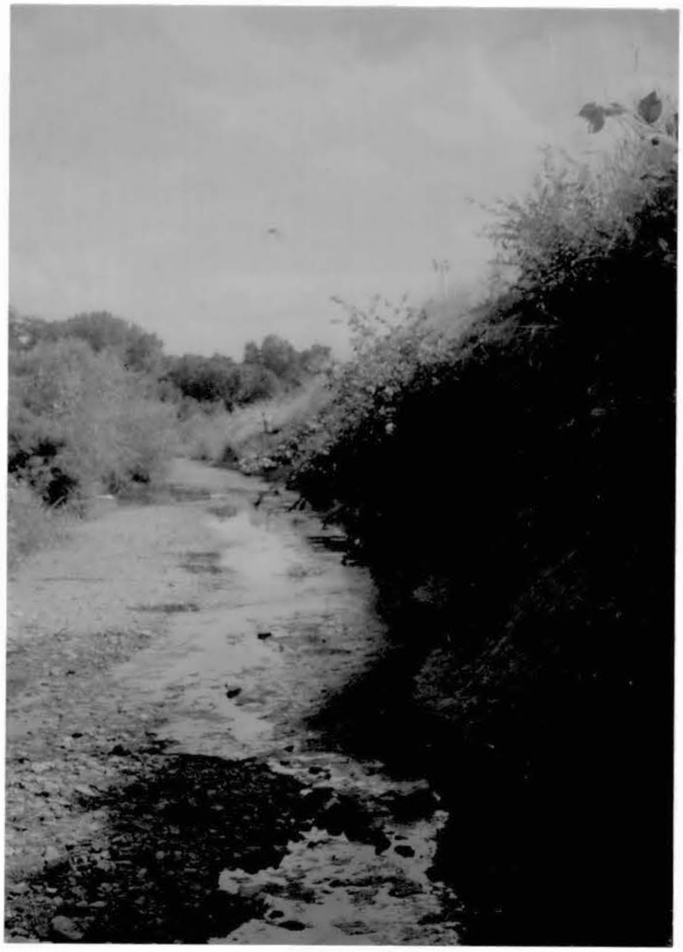


Figure 27. Man-made Channel
Showing Seepage
Zone Near Water
Level

gradient down the axis of the valley. The gradient from well I-9, north of the pond, to II-1, at the mouth of the valley is 0.01 ft/ft (over an 1800 foot distance) which confirms the estimate from the surface gradient. In contrast, the gradient across the flood plain is much less. Comparing well II-1 to the G-1 and -2 wells, a gradient of 0.004 ft/ft is calculated over a distance of nearly half a mile.

The water table at the G wells raises additional questions about the interrelationships between the zones in the aquifer system. If an aquifer is unconfined, the water table should mimic the topography except that the water table is deeper under the uplands than under the valley floors. The article by Kent (1972) reports this type of relationship for the Arkansas River complex. He states that the average depth to water in terrace deposits is 15 feet (4.6 m) and the depth in the flood plain is 3 to 5 feet (1.5 m). The Fred Creek monitoring network roughly fits the pattern when valley wall wells are compared to the valley axis but not when the tributary is compared to the river flood plain.

The II-1 well, at the valley mouth, is at the same approximate depth as the wells upstream. In February, 1991, the depth to standing water in II-1 was 12.5 feet (3.8 m) when water was from 11 to 14 feet (3 to 4.3 m) in the network wells. On the flood plain, the G-1 and G-2 wells found the water table at 18.5 and 19.5 feet

(5.6 to 6 m), respectively. This depth corresponds to an elevation of 605 feet which is the estimated level of the water in Joe Creek about 800 feet (244 m) farther west. This is 10 to 15 feet (3 to 4.5 m) lower than anticipated, based upon the report by Kent (1972).

Stream bank exposures in the tributary valley and out onto the flood plain show that porous deposits are continuous from the terraces and creek alluvium to the river flood plain. This precludes a permeability barrier between the creek valley and the flood plain so that a perched water table condition should not exist here.

To explain the abnormal drop in the water table into the lower elevations, it is necessary to recognize what is unique about the study area. The most obvious difference in the area is the extent to which man has modified the natural drainage. At several locations the course of Fred Creek has been altered and new channels have been dug deeper than before. On the southeast corner of the campus, this has resulted in an increased stream gradient for a secondary tributary causing extensive downcutting and channel widening. The spot where this tributary joins Fred Creek looks like badlands topography in miniature. The excellent bank exposures described in this report are the result of recent earth falls where the creek has undermined the banks. There are even locations where bank erosion is threatening a cooling unit and bridge supports. Such examples of erosion are not apparent upstream from the campus where the channel has not been deepened.

Wherever wells are drilled close to the creek, it is apparent that the water table is controlled by the creek depth. Because the creek has been deepened throughout campus, the water table reflects these depths rather than the natural topography.

On the river flood plain more changes were made to Fred Creek, deepening it and straightening it where construction dictated. Moreover, extensive changes were made to Joe Creek which once paralleled Fred Creek before they joined southwest of campus. Because of disastrous flooding in the 1970's and 80's, Joe Creek has been cut through directly to the Arkansas River. It was deepened, widened, and lined with concrete to better handle storm runoff. As a result, the old Joe Creek channel was robbed of its upstream discharge and now serves mainly as a discharge channel for flood plain groundwater. Meanwhile, the old Joe Creek channel was deepened to protect newly erected apartment complexes on its banks.

The result of all this rearranging has been that the bottom has dropped out of the water table. That is, the flood plain groundwater has drained to the level of the deepened Joe Creek as measured in the G-1 and G-2 wells. The lowest reach of Fred Creek, which crosses the flood plain, is a be a losing stream because the water table is about 8 feet (2.4 m) below the creek bed. At this point, the upper 15 feet (4.6 m) of the flood plain is composed of clayey silt, whereas the present day water table is in medium-grained, clean sand. If Fred Creek is recharging the underlying sediments as a losing stream, the seepage is not keeping pace with the discharge from the highly permeable sand into Joe Creek farther west.

These relationships are of broader significance than merely for understanding the water table distribution in the study area. Urban hydrogeological studies often encompass areas that have had major drainage alterations for construction and flood control projects. Drastic lowering of the water table by flood control channels may affect groundwater use in such an area.

Aquifer Characteristics

Hydraulic Conductivity from Grain Size

Kent (1972) surveyed the hydrogeology of the Arkansas River alluvial aquifer in Tulsa County. In his report he presented a regression between mean grain size and hydraulic conductivity which had been developed for the Arkansas River sediments by Bedinger (1961). Kent applied this regression to the grain sizes he recognized in Tulsa, which typically fell into the range of very fine sand or fine medium sand. The very fine sand range (30-60u) fits the coarse silt-fine sand size recognized in the Fred Creek alluvium. Based upon this suggested relationship, hydraulic conductivity for the study area could average around 6 gpd/ft^2.

Calculation of Hydrologic Parameters

Transmissivity is an expression of how well the aquifer can transmit water and is used as a basis for calculating hydraulic conductivity and storativity. Aquifer tests provide the primary means of determining transmissivity for equilibrium conditions (Jacob method) and non-equilibrium conditions (Theis method). Both time drawdown data using a single observation well and distance drawdown using more than one observation well can be used in the calculations (Fetter, 1980; Driscoll, 1986).

Aquifer parameters were calculated by performing an aquifer test in the field and also by collecting natural water table decline data over a long period of time.

Seasonal Hydrograph Decline Data. The recession curves of the monitor well hydrographs were analyzed to see what information could be retrieved. During the late spring and summer, the very steady decline of the water table resembled the progressive drawdown of observation wells in the cone of depression of a pumping well. Accordingly, calculations were made, applying both the Theis and Jacob time-drawdown equations (Fetter, 1980) to the hydrograph regression data (Figure 21). Well I-1 was selected as a well with a steady drawdown. The weekly water table declines are listed in Appendix B.

The discharge rate (Q) of water pumped during an aquifer test is required in both the Jacob and Theis calculations. In applying these methods to long term decline instead of a pumping well, Q represents discharge from the aquifer. During a period of low stream flow, the creek discharge was gauged at a constricted portion of the channel by filling a plastic container. This value was 1 gallon per minute.

In July and August, regular measurements of the pond level showed a steady drop of 1.5 inches (3.8 cm.) per week. This was interpreted to represent evaporation loss, a figure which was one half of the recession rate of the water table. Based on this value, the total loss of water from the aquifer was interpreted to be two times the discharge into the creek or 2 gallons per minute.

Calculation using the Jacob method gave a transmissivity of 110 gpd/ft. and storativity of .02. The Theis method yielded a transmissivity of 125 gpd/ft. and storativity of .015. These values are within reason for a fine grained unconfined aquifer (EPA, 1990).

In order to derive hydraulic conductivity (K) from transmissivity (T), the saturated thickness (b) must be known:

$$K = T / b \qquad \text{(Eq. 3)}$$

The aquifer thickens toward the center of the valley where wells have been drilled to nearly 20 feet. Solid bedrock was never reached; however, colluvium and low permeability clay layers at the bottom of wells I-3 and I-4 may be close to the bottom seal of the combined aquifer. This would be a thickness of around twenty feet, half of which is saturated at any one time. Therefore, an average of 10 feet of saturated thickness is used for the calculation. Hydraulic conductivity is then calculated from equation 3 to be 11 gpd/ft^2. This is comparable to the value listed earlier for a silty aquifer.

Aquifer Tests

More reliable determinations of aquifer parameters were made when aquifer tests were performed. When a well is pumped at a constant rate for a substantial period of time, the drawdown recorded in nearby observation wells forms the basis for calculating transmissivity and storage coefficient.

The Theis equations are commonly used for aquifers in which the cone of depression has not developed to a condition of equilibrium. Drawdown measured in observation wells is plotted on logarithmic grids versus elapsed pumping time. The curve that is derived from the plot is fitted to a type curve. When a best fit of curves is achieved, a match point which is a function of the ideal curve, is determined. The drawdown and time at the match point are used to calculate T and S based on the following equations:

$$T = 114.6\ Q\ W(u)\ /\ s \qquad \text{(Eq. 4)}$$

where Q is discharge rate of pump (gal/min), s is the drawdown at the match point, and W(u) is the chosen function of the match point. For these calculations $W(u) = 1.0$ and $u=0.1$.

$$S = T\ u\ t\ /\ 2693\ r^2 \qquad \text{(Eq. 5)}$$

where t is the time of the match point and r is the distance in feet to the observation well.

Water Table Aquifers

The Theis equation is limited to confined, non-leaky aquifers in which water is instantaneously removed from storage due to compaction of the matrix and expansion of confined water. Additionally, the transmissivity is assumed to be constant within the aquifer, the well is to be fully penetrating, and the aquifer is homogeneous, isotropic, and not constrained by flow boundaries. For water table aquifers, the assumption of constant transmissivity is violated because production occurs due to removal of water from the pores within the cone of depression in addition to the water produced by compaction and expansion. As the water table is lowered and the cone enlarges, the saturated thickness is diminished. As a consequence, transmissivity changes during the test.

Because of gravity drainage, the drawdown values must be adjusted by a factor which converts them to a range more like nonequilibrium, confined conditions (Prickett, 1964). For time drawdown data, the values are corrected by the following transform:

$$s' = s - (s^2/ 2m) \qquad \text{(Eq. 6)}$$

where s is the observed drawdown in feet, m is the saturated thickness prior to pumping, and s' is the corrected drawdown.

Secondly, the time drawdown curve takes on an atypical shape in the early stages of pumping. After an immediate drawdown response which approximates the ideal curve, the slope of the curve flattens drastically. The gravity drainage contributing to the water being produced is seen as a positive flow boundary in the drawdown curve. This portion of the curve cannot be utilized for calculations. Only when the water table drop in the cone of depression balances the water production due to gravity drainage, does the curve approach the ideal Theis curve. When this occurs, well into the testing period, the type curve can be fitted and calculations can be made for T and S (Prickett, 1964).

Aquifer Test Conditions

An initial test was attempted April 20, 1991 using an electric peristaltic pump. The I-3 well was chosen to be the pumping well because of its mid-valley location and because of the somewhat larger penetration depth (6.5 feet [2 m] of water column). The observation well, I-10, was located 63 feet (19 m) to the south and a second well, I-8 was 160 feet south of the pumping well. The peristaltic pump was required to lift water 17 feet (5.2 m) from the bottom of casing and the maximum pumping rate that could be achieved through 1/2 inch tubing was one gallon per eight minutes (.125 gpm). This rate was insufficient to produce any drawdown in the observation well after three hours.

A second attempt was made the following day using the downgradient well, I-8, as the pumping well. This placed the nearest observation well, I-10, 92 feet (28 m) away. The well was pumped as a maximum rate of 0.06 gpm for 8 hours, but no drawdown was detected.

On May 17, another aquifer test was undertaken. In the meantime, an additional observation well, I-11, was dug 21 feet south of well I-3 (Figure 28). This time, a 3 hp. gasoline powered centrifugal pump was used. The pump was choked down to 5/8 " from the original 2" intake so that a garden hose could be used for pumping. The I-3 well was pumped at a rate of 0.25 gpm for 9 hours during which time drawdown was recorded for both I-11 and I-10 wells.

Results of Aquifer Test

Time Drawdown Data from the aquifer test are presented in Appendix D. Although the maximum drawdown realized in the 9 hour period was less than 2.0 inches (5 cm.), the data permit calculation of transmissivity and storativity.

The plot of time drawdown values in log-log format produces a typical water table aquifer type curve. Drawdown is the I-11 observation well proceeded for 29 minutes before leveling out. For the following 78 minutes, the curve remained flattened due to negligible drawdown. At a point 107 minutes after pumping began, drawdown began to increase and continued at a regular rate until the 317 minutes mark. For the the remaining 4 hours of the test, no additional drawdown was detected.

The time drawdown curve can be subdivided into four separate stages. The first segment represents initial water production where horizontal flow dominates. Next, gravity drainage develops and the vertical flow into the cone of depression provides virtually all the produced water. This causes the water level decline to stall at

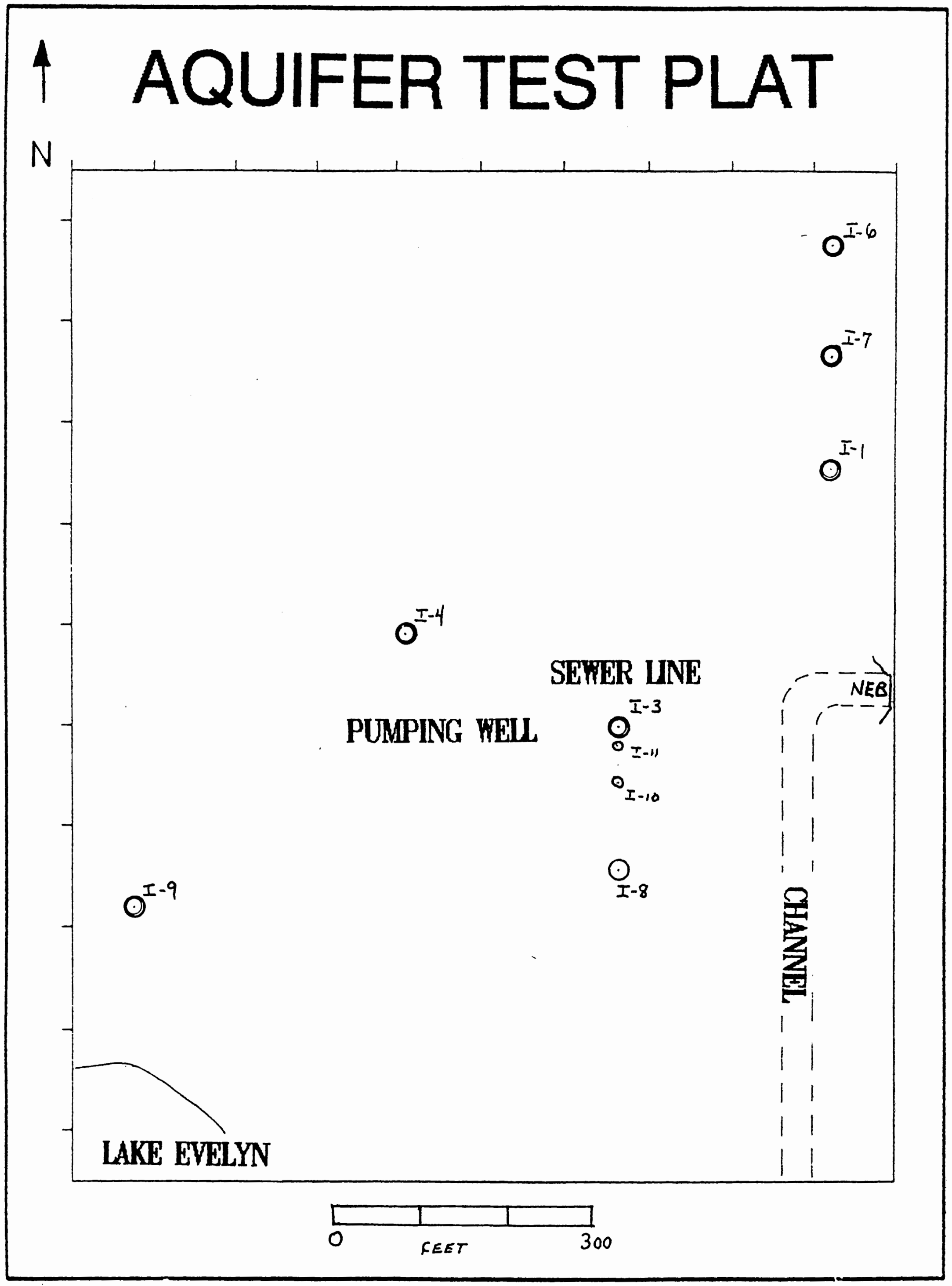


Figure 28. Area of Aquifer Test

greater distance and thus the curve flattens. As the cone enlarges, the vertical flow component diminishes and the water table begins to fall again. The stage of renewed drawdown began at 107 minutes and this portion of curve was used for making aquifer calculations with the non-equilibrium type curve.

A fourth segment of the curve developed later into the test. The last portion exhibits decreased drawdown and so falls below the type curve. This is likely due to the cone of depression intersecting a positive flow boundary. The man-made channel of Fred Creek is located 150 feet (46 m) east of the pumping well. Also a sanitary sewer line runs east-west, 41 feet (12.5 m) north of well I-3. High permeability zones in the fill around the line could cause increased flow into the cone of depression. It is also possible that the sewer is leaking, adding flow to the system.

Calculation of the distance from the pumping well to a boundary is possible using data from the time drawdown curve. The time when a particular drawdown was reached prior to the boundary effect is compared to a point after the boundary. This second point is where a divergence between the ideal curve and the actual drawdown is equal to the preboundary drawdown. The following formula is used for the calculation:

$$r_i = r_p\sqrt{t_i/t_p} \qquad \text{(Eq. 7)}$$

where r_p is the distance to the observation well, r_i is half the distance to the boundary, t_p is the time of the selected pre-boundary drawdown, and t_i is the time of an equal divergence after the boundary. Using this method, the last segment of the curve indicates a boundary could be 78.6 feet (24 m) from the pumping well. This distance is closer to the sewer line than to the creek.

Both time drawdown and distance drawdown curves were constructed for data in both wells. Limited recovery water level values provided additional data for the I-11 well. The Theis and the Jacob methods were used for making calculations of transmissivity and storativity. Table 2 summarizes the range of values calculated. The average value for transmissivity is 294.5 gpd/ft. and for storativity is 6.96×10^{-3}. Pumping time may have been inadequate for the Jacob method to be valid. Calculation of the time for straight line development on the Jacob plot was made using estimates of T and S. This number is 18 hours, twice the length of the actual test.

The average values for the Theis calculations alone were 177.8 gpd/ft. for transmissivity and 6.12×10^{-3} for storativity. Hydraulic conductivity for a 10 foot saturated thickness would be 17.8 gpd/ft^2. These values are consistent with a very fine-grained aquifer, dominated by silt and very fine sand.

Groundwater velocity was also calculated using the hydraulic conductivity and the average potentiometric head:

$$V = K I / 7.48 \qquad \text{(Eq. 8)}$$

Using the May gradient of 0.025 ft/ft and the September gradient of 0.006 ft/ft, the following velocities were derived:

Sept Velocity = 0.014 ft/day
May Velocity = 0.060 ft/day.

It can be concluded from the aquifer test that the very fine grained aquifer will yield water at low discharge rates and that flow velocities are extremely slow.

TABLE 2

CALCULATED AQUIFER PARAMETERS

Method / Well	T (gpd/ft)	S
AQUIFER TEST RESULTS (CORRECTED VALUES)		
THEIS - Time Drawdown		
Well I-11		
Later Curve	164	9.1×10^{-3}
Early Segment	130	3.0×10^{-3}
Recovery	118	3.9×10^{-3}
Well I-10	123	4.8×10^{-3}
THEIS - Distance Drawdown		
235 minutes	354	9.8×10^{-3}
Average Theis	178	6.1×10^{-3}
JACOB - Time Drawdown		
Well I-11	244	6.7×10^{-3}
Well I-10	333	1.7×10^{-2}
Jacob - Distance Drawdown		
235 minutes	890	1.4×10^{-3}
OVERALL AVERAGE	295	7.0×10^{-3}
HYDROGRAPH DECLINE		
Jacob - Time Drawdown		
Well I-1	110	2.0×10^{-2}
Theis - Time Drawdown		
Well I-1	125	1.5×10^{-2}

CHAPTER VI

GENERAL GEOCHEMISTRY

Procedures

Samples from all wells were analyzed chemically in order to: 1) type the groundwater and define the chemical environment of the aquifer, 2) study interactions of the groundwater and matrix, 3) use trends of chemical change within the aquifer to clarify flow paths, 4) look for the presence of contaminants, and 5) determine the aquifer's effect on the transport of potential contaminants.

Sampling and Analysis

Two approaches were followed in gathering chemical data. Some tests were made in the borehole or at the well site without taking samples. Dissolved oxygen and temperature were measured in place using a Yellow Springs International dissolved oxygen meter. The detector was a remote device that could be lowered into the casing and submerged. A potential difference was developed between the groundwater and a standard solution of KCl across a membrane in the detector.

Specific conductance was also measured in the wells using a conductivity meter that detected electrical resistance with a wheatstone bridge. The conductivity meter was temperature compensated because of the variation of conductivity with temperature. Both types of in-well readings were made before and after pumping to determine whether there were differences in standing water and fresh formation water.

Most of the chemical data was determined from samples which were withdrawn and analyzed in a laboratory. Samples were either pumped or bailed from the wells. The inertial pumping method described in Chapter 3 was used in sampling. To insure fresh samples and also to clean the pumping tube, the wells were always pumped before sampling. Approximately two casing volumes were evacuated prior to taking samples.

Samples to be analyzed for major ions were taken in polypropylene bottles that had been prewashed. They were rinsed out with fresh groundwater before the final samples were taken. Sample temperatures were taken at the well site. As soon as the samples were collected, they were refrigerated until delivered to the laboratory. Generally, they reached the lab within 48 hours.

The bulk of the analyses were done by the same laboratory, Watershed Lab of Claremore, Oklahoma. The tests performed and the methods used are listed in

Table 3. Most of these are standard EPA methods described in detail in Koop and McKee (1983). All tests listed were done by Watershed chemists except for the sodium determination. Because the lab does not have the capability for testing for sodium, they must send the sample to another lab for either atomic absorption (AA) or inductively coupled plasma (ICP) analysis. The first three suites of samples did not have sodium analyzed at all.

TABLE 3

LABORATORY METHODS FOR WATER ANALYSIS

Parameter	Ref.	Procedure	Method
pH	1	150.1	Electrode
Specific Conductance	1	120.1	Wheatstone Bridge
Tot. Dislved Solid	1	160.1	Glass Filter Fibr
Total Fe	2	8008	Phenanthroline
Total Mn	2	8034	Periodate
Sulfate	1	375.4	Turbidimetric
Acidity ($CaCO_3$)	1	305.1	Titrametric
Alkalinity ($CaCO_3$)	1	310.1	Titrametric
Chloride	2	HACH	Man. Ferricynanide
Hardness ($CaCO_3$)	3	314B	EDTA Titration
Calcium	3	311C	EDTA Titration
Magnesium	3	318C	By Calculation
Potassium	2	HACH	Spectrophotometric
Nitrate	2	HACH	Spectrophotometric
Sodium	1	200.7	ICP

REFERENCES:
1. Koop and McKee, 1983. Methods of Chemical Analysis of Water and Wastes, U.S. EPA
2. Hach Handbook of Water Analysis
3. Standard Methods for the Examination of Water and Wastewater, 16th Edition

Information Provided by Watershed Lab, Claremore, Ok.

Samples were analyzed by the laboratory on five separate occasions. The first three suites of samples were drawn at two week intervals from early March to mid-May. This was during the time of maximum rise of the water table during the spring rains. At this time, only four wells had been completed, but surface water from Fred Creek was also analyzed from two locations. Locality "NE Bridge" is at the tunnel where Evanston Avenue crosses Fred Creek. This is also the location of the U.S.G.S. rain gauge and is at the eastern boundary fence of campus (Fig. 7). The water at this point in the creek represents groundwater and surface water runoff from the upstream reach of Fred Creek. A second surface sample was taken from a small tributary of Fred Creek located a quarter mile south of the NE Bridge. This water represents surface water runoff as well as groundwater discharge from a terrace deposit on the south valley wall. In addition to the creek water, one sample of fresh snow was analyzed for major ions to see the content of water before recharging the aquifer (Table 6).

Two of the original wells and a new well were analyzed in November in the middle of the dry spell. At this time the I-6 well could not be sampled because the water level was too low. The final suite of samples was taken in February, 1991, a time of slight recovery of the water table from the melting of winter snow.

In July, samples were analyzed by a different laboratory for general organic chemical indicators. The purpose of these tests was to look for indications of organic contamination without undertaking the very expensive compound-specific tests required to detect the wide variety of possible organic pollutants. Tests for total organic carbon (TOC) and total organic halogen (TOX) were made. The TOC tests are used to detect presence of hydrocarbons whereas TOX is used for chlorinated organics such as solvents and pesticides. The laboratory doing the tests had atomic absorption spectrometry, so a few wells were analyzed for sodium at this time.

Trace metal contamination is a major concern in urban aquifers, so attempts were made to analyze the Fred Creek groundwater for trace metals which are on the priority pollutant list. Oral Roberts University has atomic absorption spectrometry equipment and an arrangement was made to undertake a senior research project to look for trace metals. This was done by an undergraduate senior chemistry student, supervised by Dr. William Collier, professor of chemical instrumentation. The initial atomic absorption project was done in the spring of 1990. Subsequently, a second project was completed in the spring of 1991 in which samples were being for a different group of trace elements.

Late in 1990, an agreement was reached with the Oklahoma Water Resources Board (OWRB) to include two of the ORU wells in the state's regional sampling program. Water samples are taken quarterly from wells I-1 and I-4 to be analyzed for major ions and annually for trace metals.

Limited analysis was done for the downstream wells. A sample from well II-1 was sent to Watershed Labs for the standard analysis, but the water level in wells G-1 and G-2 dropped below the well screen before arrangement could be made to sample them. (These wells could not be drilled much below the water table due to severe caving problems.) Shortly after drilling the two wells, conductivity measurements were made in these wells, but no samples were analyzed by a commercial laboratory.

Finally, samples were taken from the flow line of wells which are used for irrigating the grounds of Southern Hills Country Club. These wells are located about one and a half miles north of the ORU campus and have been drilled into the same terrace deposit which rims Fred Creek and also into the Arkansas River flood plain. These samples were analyzed for major ions (Table 6).

Interpretation Techniques

Quality control is critical for maintaining analytical integrity. To evaluate the reliability of commercial labs, samples of known concentration could be submitted to see how close the results come to the actual value. Also, duplicates could be sent to several different labs to compare results. Because of budget constraints, these procedures were not undertaken; however, on one occasion, samples from closely spaced dates were analyzed by two separate facilities so a limited comparison of results was made possible. Instead, all analyses were evaluated for reliability using ion balance and ion ratios. These tests are incorporated in the computer program, WATEVAL, which has been assembled by Dr. Arthur Hounslow of Oklahoma State University.

Comparison of the individual cations and anions on a percentage basis provides insight to the general water types and may also reveal geochemical trends within an aquifer. The data tabulated in this fashion can then be presented graphically in Stiff diagram, Piper diagrams or various other formats. Stiff diagrams were constructed for all samples in the study area and for published analyses of waters in the vicinity. These show similarities in waters from nearby portions of the aquifer. Piper diagrams were constructed for the same samples. Specific trends of change can be interpreted from the triangular plots. Mixing of water types along flow paths can be indicated by straight line trends on the anion and cation triangles. Loss of ions from the water due to precipitation, replacement, or ion exchange may also become evident on the plots.

Consideration of thermodynamics of the aqueous system provides information as to which mineral species are liable to dissolve or precipitate from solution. The U.S.G.S. program, WATEQ4F was used to characterize the thermodynamic regime of both the groundwater and creek samples. In addition, a mass balance program (BALANCE, by Parkhurst et.al., 1982) was used to compare the ion species to source phases from which the ions were dissolved. This program was made available for personal computer by Dr. Arthur Hounslow. Based upon concentrations and mineral phase components, the proportions of source minerals contributing most to the solution can be reconstructed through mass balance calculations.

Finally, many types of cross plots were assembled comparing single ions or chemical parameters to each other. This was done to investigate causative relationships in exploring the chemical evolution of water types.

Tests for Accuracy of Analysis

Cation-Anion Balance

Natural waters are balanced chemical solutions containing equivalent anions and cations. For common ions, equivalency is a function of the atomic mass of the element or radical and the valence state of the ion. The sum of all anions in milliequivalents/liter should equal the sum of the cations. Hem (1985) claims that if there is no more than a 2% difference between the total of cations and anions, then the laboratory analysis has been accurately done. Different analysts use varying cutoff values in the cation-anion balance, above which they do not accept the data. Commonly, a 10% variance is used as a limit. Of the thirty analyses performed by Watershed Lab, all but two had cation-anion balances under 10% and 18 of the analyses were under 5%. The highest percentage differences were in analyses from February 18 (Table 4). Of these, four out of six were significantly greater than 5% and two were greater than 15%. All these had excessive cation totals due to very large concentrations of calcium. Moreover, each of these had a suspect value for the ratio of specific conductance to the sum of cations which could have been caused by an erroneously high calcium value. Had a hardness determination been requested, the possibility of an erroneous calcium value could have been further evaluated.

In the analyses, bicarbonate concentration was reported as alkalinity in mg/L of $CaCO_3$ and had to be recalculated to an equivalent concentration of HCO_3^-. When this was done for the I-9 well in the November 21 sampling, the bicarbonate concentration was higher than the measured TDS value. The cation-anion balance was off by -6.63% which would be acceptable. It is very likely that the alkalinity titration was in error and that possibly the large calcium value is also in error. The ratio of conductivity to sum of cations indicates an excessive value in the cations. These two errors would have offset each other to keep the balance in a reasonable range. The conductivity and TDS by evaporation are in agreement with each other so they appear to be reasonable indicators of the true solution. With the exception of these four analyses, the remainder are considered acceptable.

Comparison of Results from Different Laboratories

As part of an undergraduate research project, Dzurik, 1991, analyzed water samples from the Fred Creek wells in March, 1991. In addition to these tests, the Oklahoma Water Resource Board analyzed samples from wells I-4 and I-1, taken February 14, 1991. Analyses from both of these parties resulted in values for sulfate that were significantly higher than those from Watershed Labs. Consequently, a request was made for Watershed to reanalyze the stored samples for both sulfate and calcium. When this was done, larger sulfate levels and slightly lower calcium levels were reported and the revised figures gave cation-anion balances for

TABLE 4

CATION-ANION BALANCES

WELL	I-1	I-3	I-4	I-6	NEB	TRIB	I-7	I-9
DATE				% Difference (1990)				
4/09	11.0	5.7	5.9	9.3	2.0	5.8		
4/23	7.4	3.1	-3.3	3.0	-2.5	3.5		
5/15	10.5	5.5	-0.8	6.3	2.8	8.6		
11/21	1.6		9.0					-6.6
				(1991)				
2/18		9.4	14.6	16.8	7.2		3.1	0.6
				RETEST				
2/18		-3.4	-0.9	2.1				

wells I-3, -4, and -6 that were less than 5%. The revised values were accepted as reasonable.

Statistical Variation

Samples which are not representative of the population generate misleading interpretations. If there are extreme data they must be identified as either resulting from experimental error or as natrually occurring variation.

Tests for the magnitude of dispersion can be made on sample populations which are normally distributed. Even when the distribution is "moderately anormal", dispersion statistics are thought to be meaningful (Snedecor and Cochran, 1967, p. 120). To appraise normality, frequency distribution histograms of conductivity were constructed (Figure 29). The

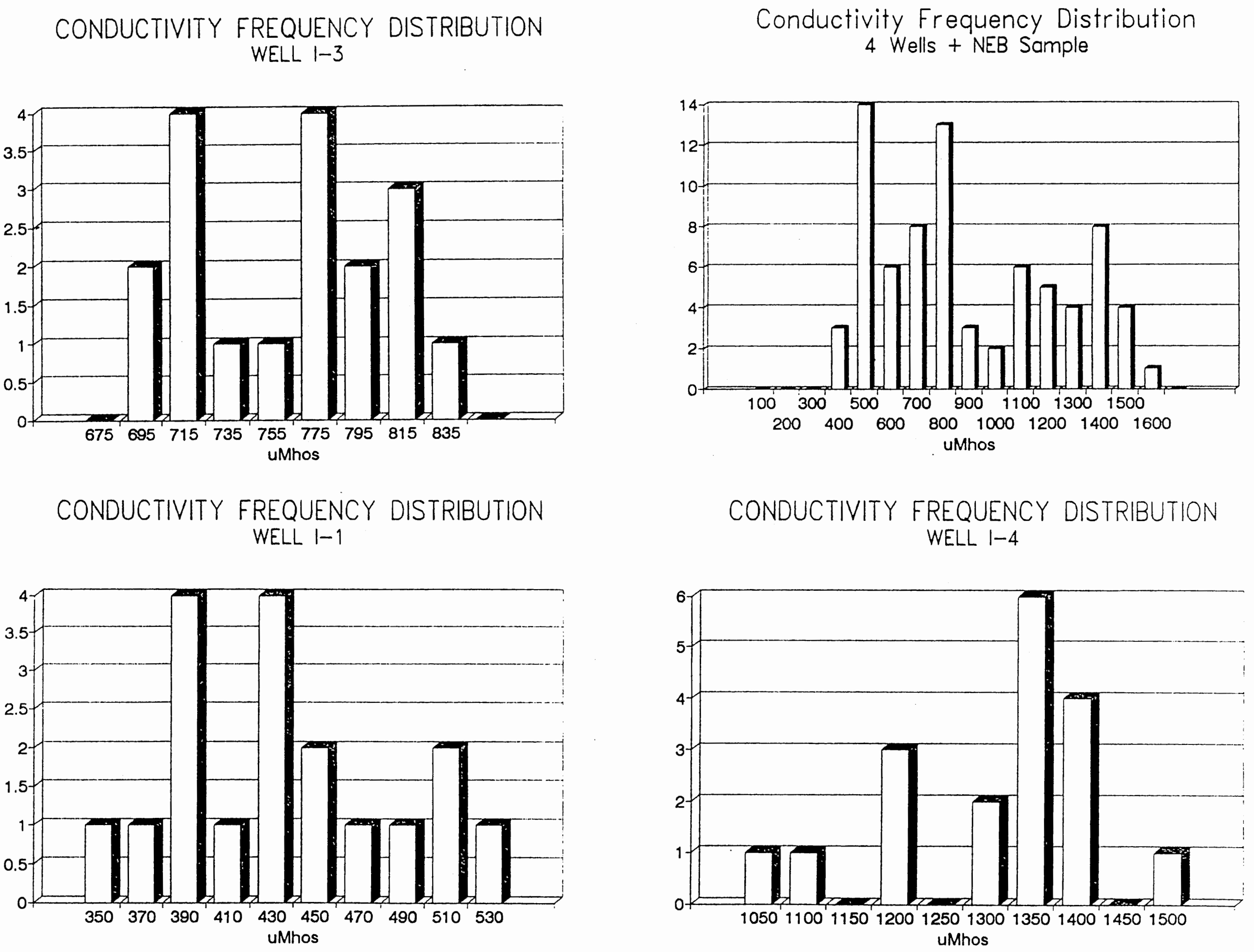


Figure 29. Frequency Distributions of Conductivity

conductivity values were used because they provide a much larger sample than do the ion concentrations. Visually, the data from Well I-1 is skewed to the right, Well I-4 is skewed to the left and both Well I-3 and the collective data have a degree of bimodality. The bimodal nature reinforces the interpretation that there are two sub-populations or end members to a mixing system. Because the frequency plots do not show strong symmetry, the sample populations cannot be considered normally distributed. Therefore, inferences made from sample statistics can only be indicators of population trends.

The coefficient of variation (C.V.) was chosen as a standardized statistic for dispersion so that data of differing ranges could be compared. In Table 5, lists of the statistics for both conductivity and ion concentration are presented. Coefficients were calculated for the data of wells I-1, -3, -4, -6, and the samples from creek location, NEB as well as for the collective data base. Dispersion within data of the same well was always much less than for data which included several wells. The C.V. for the overall conductivity data was .41 whereas the range of coefficients for single wells was .06 to .18. These results indicate that the statistical variation is greatest spatially and least on a temporal basis. The low dispersion values for individual wells is interpreted to mean there was generally no significant variation in concentrations during the sampling period. The exception to this were the sulfate values in the I-1 well samples (C.V. was 2 to 5 times greater than for other samples).

Conductivity Compared to Concentration

The complete data base of conductivity measurements for the main wells and NEB creek location has a coefficient of variation of 0.41. For comparison, the coefficients of the ion concentrations were also calculated. As seen from Table 5, calcium, bicarbonate, potassium, and sodium have comparable dispersion and chloride is much lower. From this comparison, it is concluded that these ion concentrations are analytically reliable because they compare in distribution to the conductivity data base.

The coefficients for sulfate are somewhat higher than the others. On a per well basis, the sulfate C.V. of the Well I-1 samples is approximately two times greater than for the above mentioned ions. Sulfate data from wells I-3, -4, & -6, however, have C.V.'s which correspond to the other ions. Table 6 shows that sulfate concentrations increased dramatically in well I-1 in the winter of 1991. The analyses made on 2/18/91 and 3/26/91 were both high, even though they are from different laboratories. For this reason, it is doubtful that the extreme values are a result of analytical error, but constitute natural variation.

Magnesium data exhibits the highest dispersion for the composite data base (C.V.= 0.81) and also for individual well calculations. The magnesium levels are very low in the spring, 1990 analyses (<10 mg/l) and so significant increases cause a dramatic inflation in dispersion statistics. The large C.V. values for magnesium suggest that the data could be unreliable.

In conclusion, the coefficients of variation for ion concentrations and conductivity compare well for overall data and for individual wells. The exception to this is the magnesium data. Statistical variance is greatest on a spatial framework due to the contrasting values of samples from wells I-4 and I-1. Variations within wells is much narrower, indicating that variation over time is much less than that between areas at the same time.

TABLE 5

STATISTICAL COMPARISON OF CHEMICAL DATA

COMPOSITE DATA

ION	MEAN	STD. DEV.	COEF. VAR.
Calcium	735.9	331.7	.48
Sulfate	151.4	94.1	.62
Chloride	30.3	6.8	.22
Bicarbonate	420.5	179.5	.47
Magnesium	10.7	8.7	.81
Potassium	1.8	0.9	.50
Sodium	26.9	13.6	.51
Conductivity	845.5	344.2	.41

COMPARISON BY WELL

COEFFICIENT OF VARIATION

ION	I-1	I-3	I-4	I-6	NEB
TDS	.18	.56	.07	.02	.12
Calcium	.13	.07	.11	.03	.12
Sulfate	.46	.07	.23	.18	.08
Chloride	.14	.06	.37	.11	.21
Bicarbonate	.06	.06	.12	.12	.09
Magnesium	.86	.36	.70	1.15	.26
Potassium	.07	.22	.10	.11	.11
Sodium	.26	.18	.60	---	---
Conductivity	.12	.06	.08	.07	.19

Interpretation

The results of the various chemical analyses are presented in Table 6. Perusal of the data quickly shows the high concentrations of calcium and bicarbonate ions in all samples. As such, the groundwater from the aquifer can be characterized as a calcium bicarbonate water. This would indicate a common mineral source for the waters regardless of the location in the aquifer.

TABLE 6

RESULTS OF CHEMICAL ANALYSIS

CONCENTRATIONS (in mg/l)

CALCIUM

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
4/09	101.6	162.4	367.2	236	136.8	132.8		
4/23	93.6	161.6	324	232	105.6	111.2		
5/15	99.2	168.8	327.2	225.6	124	120.8		
11/21	78.4		294.4				177.6	
2/18	78	143.3	274.4	244.8	108		225	106

Mean 177.15 STD 81.945 CV = .463 RANGE 78-367

SULFATE

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
4/09	50	120	375	140	105	60		
4/23	41	120	325	165	95	65		
5/15	40	105	300	170	85	65		
11/21	30		175				39	
2/18	84	120	280	215	102		35	25
3/26	94	128	310	211	103			

Mean 126.11 STD 94.869 CV = .753 RANGE 30-375

CHLORIDE

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
4/09	26	33	30.5	33	34	45		
4/23	22.5	29	27.5	31	24	35		
5/15	23	32.5	23.5	30	28	53		
11/21	31		54.4				6.5	
2/18	28	33	28.5	25.5	39		3.4	22.6

MEAN 29.729 STD 10.448 CV = .351 RANGE 3.4-54.4

BICARBONATE

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
4/09	202.4	339	546.2	436.5	336.5	348.7		
4/23	221.9	380.4	721.8	485.3	321.9	317		
5/15	214.6	390.2	738.9	512.1	341.4	314.6		
11/21	229.2		673				636.4	
2/18	197.5	378	731.5	577.9	275.5		668.1	356

MEAN 424.73 STD 170.66 CV = .402 RANGE 198-739

TABLE 6 (continued)

CONCENTRATIONS (in mg/l)

MAGNESIUM

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
4/09	1.9	6	1.9	0	7.8	7.8		
4/23	3.4	10.2	9.2	0.09	14.1	11.7		
5/15	2.4	9.2	16.5	23.3	14.1	14.1		
11/21	10.2		30.6				8.7	
2/18		15.1	20.4	24.8	14.6		3.9	15.6

MEAN 10.64 STD 7.7583 CV = .729 RANGE 0-30.6

POTASSIUM

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
4/09	1.5	1.4	1.7	1.9	3.3	2		
4/23	1.4	0.9	1.6	2	3.7	3		
5/15	1.4	1.2	1.5	1.6	3	2.2		
11/21	1.6		1.9				1.8	
2/18		0.4	1.5	2	3.1		1.4	1.5

MEAN 1.8036 STD 0.8069 CV = .447 RANGE 0.4-3.7

SODIUM (ORU)

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
3/05	0.8	6.9	21.6	14.5	20.5			
3/12	0.1	7.7	17.2	14.4	10.6	8.7		
3/19	0.3	10.5	25.6	20.2	21			
3/26	0.8	10.1	26	16.7	19.1	23.7		

SODIUM (COMMER. LAB)

DATE	I-1	I-3	I-4	I-6	N.E.B.	TRIB	I-9	I-7
7/19	10	16.9	19.6					
11/21	14.5		50				8.7	
2/18		21.8	38.5	31	40.1		7.7	18.9

MEAN 23.142 STD 13.725 CV = .593 RANGE 7.7-50

TABLE 6 (continued)

Well II-1 (Valley Mouth)
3/04/91 TDS: 558 COND: 675

Na^+	20.3	$SO_4^=$	49.0
K^+	4.6	HCO_3^-	421.9
Ca^{++}	47.2	Cl^-	21.5
Mg^{++}	38.9		

SNOWMELT (ORU Campus)

2/25/91 TDS: 55 COND: 58

Na^+	1.0	$SO_4^=$	0.1
K^+	0.3	HCO_3^-	26.8
Ca^{++}	3.5	Cl^-	3.1
Mg^{++}	0.8		

SOUTHERN HILLS: T-1

11/15/90 TDS: 280 COND: 448

Na^+	38.1	$SO_4^=$	41.0
K^+	8.3	HCO_3^-	185.3
Ca^{++}	60.8	Cl^-	28.0
Mg^{++}	8.3		

SOUTHERN HILLS: M-COMP

11/15/90 TDS: 407 COND: 647

Na^+	21.4	$SO_4^=$	55.0
K^+	1.8	HCO_3^-	341.4
Ca^{++}	119.2	Cl^-	18.0
Mg^{++}	3.4		

Individual wells vary significantly in the magnitude of concentration of calcium and bicarbonate as well as in the other major ions present. For this reason, the question of source must be investigated more thoroughly to determine whether all waters underwent the same history during their chemical evolution.

Stiff Diagrams

A convenient means of comparing water samples is to represent concentrations of 6 components in a Stiff diagram. This format permits the display of 3 anions (in milliequivalents) and 3 cations in a symmetrical arrangement on three successive axes. When the end points are connected, a polygon is formed.

Fred Creek Valley.

All water analyses have been represented by Stiff diagrams. These are shown collectively in figures 30 and 31. Because the calcium and bicarbonate values are large in most samples, the middle axis is longer than the other two giving the shape the look of a diamond. Higher calcium and bicarbonate values (especially I-4 and I-6) draw out the diamond into distorted points.

The spring analyses did not have determinations made for sodium by the Watershed Lab. To make up for this lack, sodium values were estimated by regressing

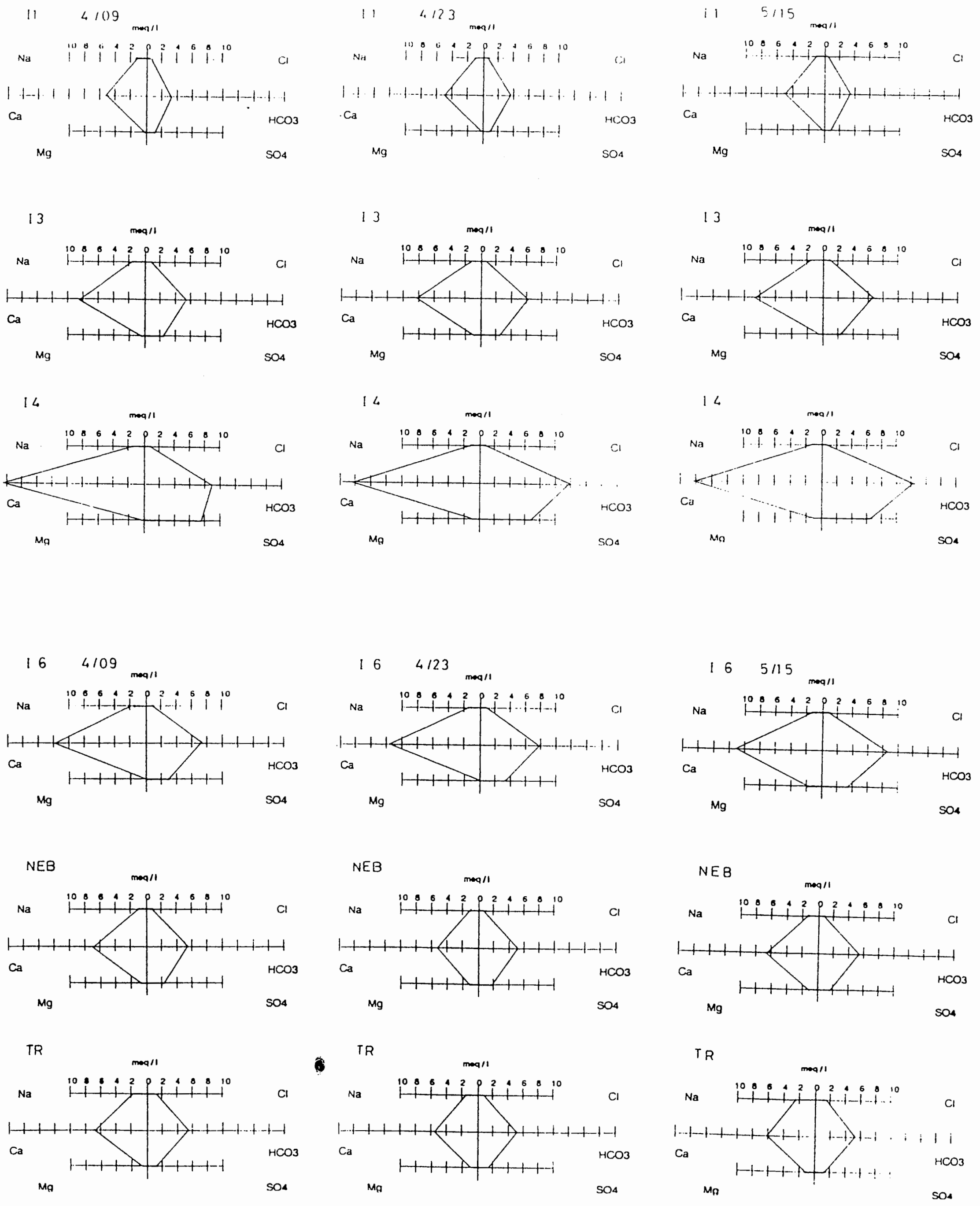


Figure 30. Stiff Diagrams of Fred Creek Valley Well Samples

sodium versus chloride for the analyses in which both were determined. The regression factor for the 11/21/90 and 2/18/91 analyses is 1.516 with a correlation value (r^2) of 0.92. Seldom were sodium or chloride detected in concentrations greater than 1.0 meq/L and they were generally balanced with each other.

Sulfate and magnesium are posted on the same axis; however, they are not related genetically. Sulfate is often assumed to be derived from solution of gypsum, although alternate sources shall be discussed later. Merely looking at the range of shapes, two types stand out based on the anion side of the diagram. One group (I-1 and "Tributary") have comparable magnitudes of chloride and sulfate, whereas the other group (I-4, I-6, I-3, and NE Bridge) have moderately to substantially greater sulfate. In particular, the I-4 figures show highest sulfate content.

Comparison of the shapes of the I series samples shows similarities, even though there are gradational changes from well to well. The shapes appear to indicate genetic relationship but there are spatial and seasonal differences within the aquifer. These variations will be treated in depth in the discussion of chemical trends.

Outlying Area

Stiff diagrams of other waters in the outlying area are presented in Figure 31. The greatest difference exists between the Fred Creek aquifer samples and water from the Arkansas River. The sample illustrated is an analysis of river water collected in August, 1988 at the 11th St. gauging station. Every year, analyses are published for river samples taken bimonthly (U.S.G.S. 1988). Stiff diagrams for all six analyses of 1988 are virtually identical. The river water is marked by high sodium and chloride concentrations due to the salts dissolved from the Permian halite deposits in northwest Oklahoma. (U.S. Army Corps of Engineers, 1972).

Other significantly different waters are the examples of groundwater produced from permeable zones in the Pennsylvanian bedrock. Although not from the immediate vicinity, the samples of Nowata and Seminole water are from the city of Tulsa. These two formations comprise most of the sedimentary rock units outcropping in the Fred Creek valley. Both water samples have high sodium and chloride values which may reflect the salty conate water preserved in marine sediments.

The waters most similar to those in the study area are from locations less than two miles away. Well T-1 and M-Comp are water samples from wells operated by Southern Hills Country Club near 61st St. and Lewis Ave.

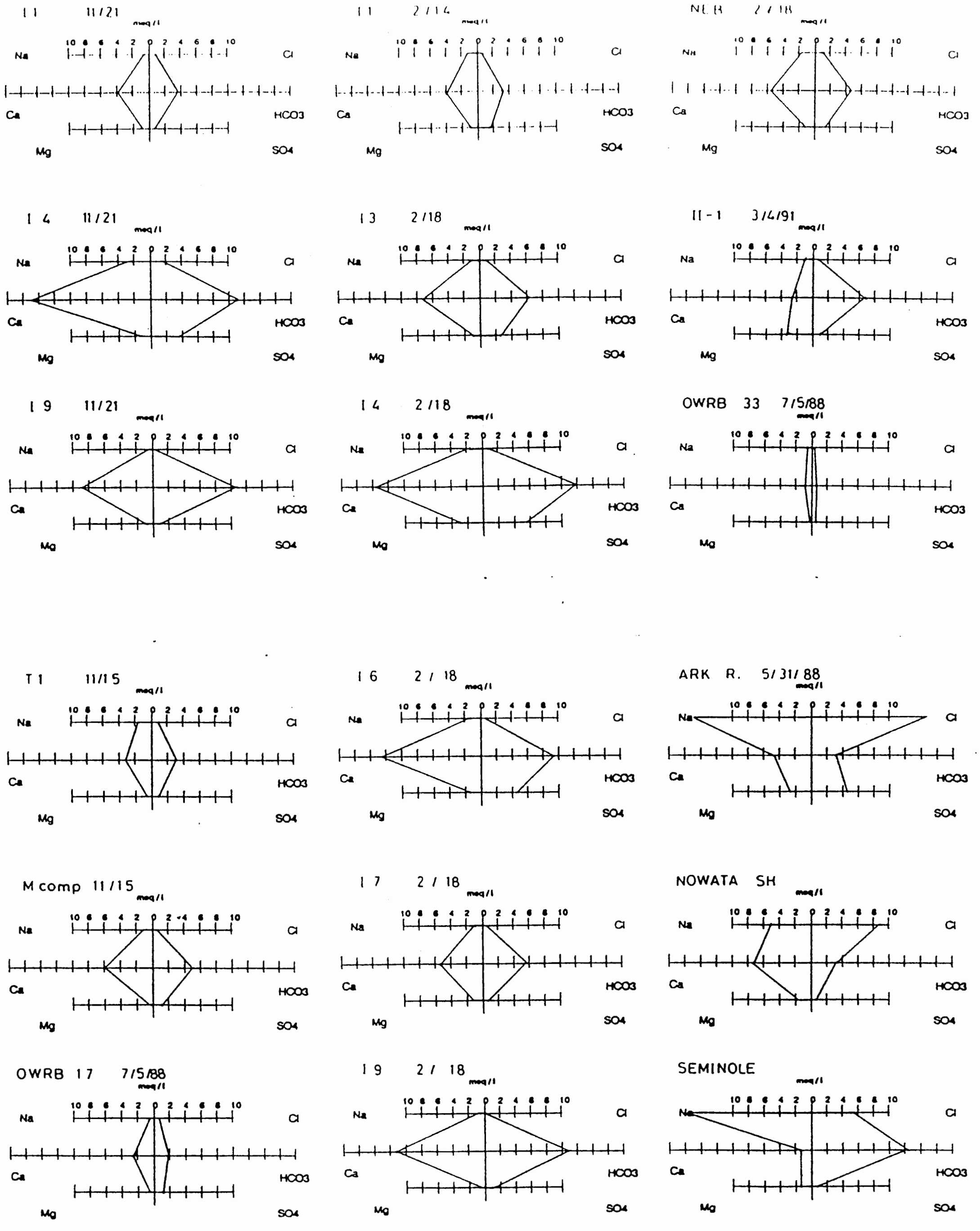


Figure 31. Stiff Diagrams: Fall and Winter Plus Outlying Areas

Although M-Comp is a collective sample from a feeder line serving several wells in the flood plain and T-1 is a solitary well at the edge of a Quaternary terrace, they both have a shape highly reminiscent of the Fred Creek wells. The other example, ORWB s. 17, is a well sampled and analyzed by the Oklahoma Water Resources Board. It is located one and a half miles south of ORU in a Quaternary terrace deposit. The analysis was published in the technical report by Thomas and Glover (1989).

One last group of samples is illustrated which has different shapes marked by especially low concentrations of ions. These are typified by the Schmidt terrace sample. Several analyses from wells in a terrace northwest of Bixby, Oklahoma, were published by Schmidt (1972) in the Tulsa's Physical Environment volume. Many of these show a similar shape. The ORWB s. 33 well (Figure 31) is from the same general area and is also from a terrace. This group is represented by a narrow Stiff figure due to the low concentration values.

Stiff diagrams show that there are similarities of samples whithin a local geographic area and that the greatest differences show up with waters farther apart. To explain the family resemblance within the major water types and also explore the range of variations, the sources of ions must be identified.

Piper Diagrams

Trilinear plots of ions as a percent of total cations or anions in milliequivalents per liter are the bases for the Piper Plot. The resultant diamond plot (Figure 32) incorporates all seven major ions and by varying the diameter of the circle around the plot marks, includes a representation of the total concentration of each sample. Comparison of different analyses is readily made, showing similarities and differences which may reflect genetic relationships. Trends of change in water types through time and space may also be observed.

Spatial Trends

Piper plots made for each date of analysis are presented in figures 33 to 36. The three spring samplings exhibit similar trends in the anions, cations, and combined plots. The anion plot for a given date aligns in a trend oriented perpendicular to the base of the triangle. This is due to the progressive increase in sulfate percentage from a minimum in the I-1 well to a maximum in the I-4 well.

The cation plot shows a trend less distinct than that of the anions. Most pronounced on the April 9 diagram, the plots form a line which is directed away from the calcium apex. The I-4 well has the highest

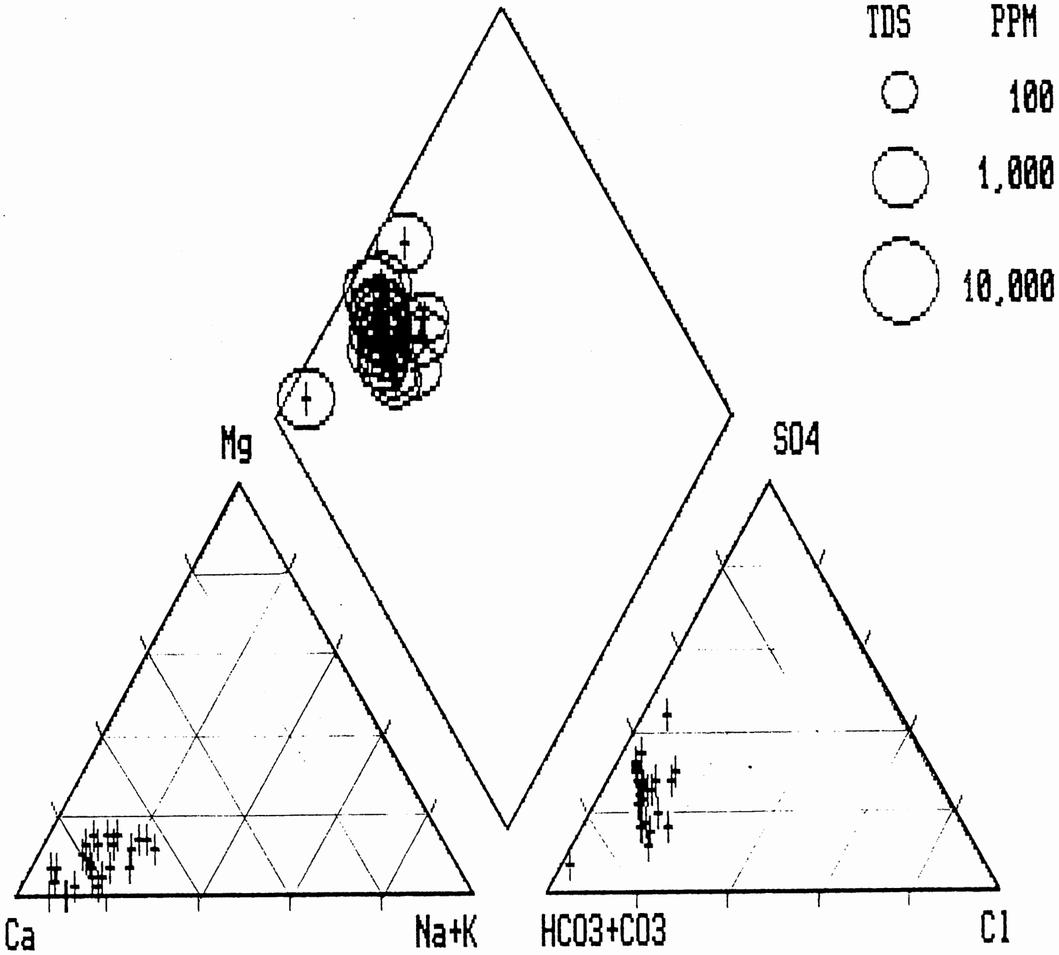


Figure 32. Piper Plot of All Well Water Samples

percent concentration but the other wells fall in a different order from those on the anion trend.

Straight line trends may indicate mixing of two water types to produce intermediates. Simple mixing, with no other mechanisms involved, should plot in comparable rends on both anion and cation plots. Because the two plots exhibit slightly different arrangement, other factors must be influencing the relationship of the waters.

The November plot does not contain enough data to evaluate trends and the February plot does not show the same linearity of the spring trends. There may be a seasonal control to the development of trends which must be investigated further.

Time Trends

Piper plots were also made for each well to show changes from one date to another. The I-4 and I-1 wells show a vague linearity which may constitute a trend. The anions of I-4 are more enriched in sulfate and calcium in the spring than in the winter. Those of I-1 have a similar arrangement of cations but the anion trend is disrupted by a high sulfate value in the February analysis. These seasonal changes must be evaluated by other means.

The I-3 and I-6 wells have plots which are very tightly clustered. Although a degree of linearity

APRIL 9 PIPER DIAGRAM

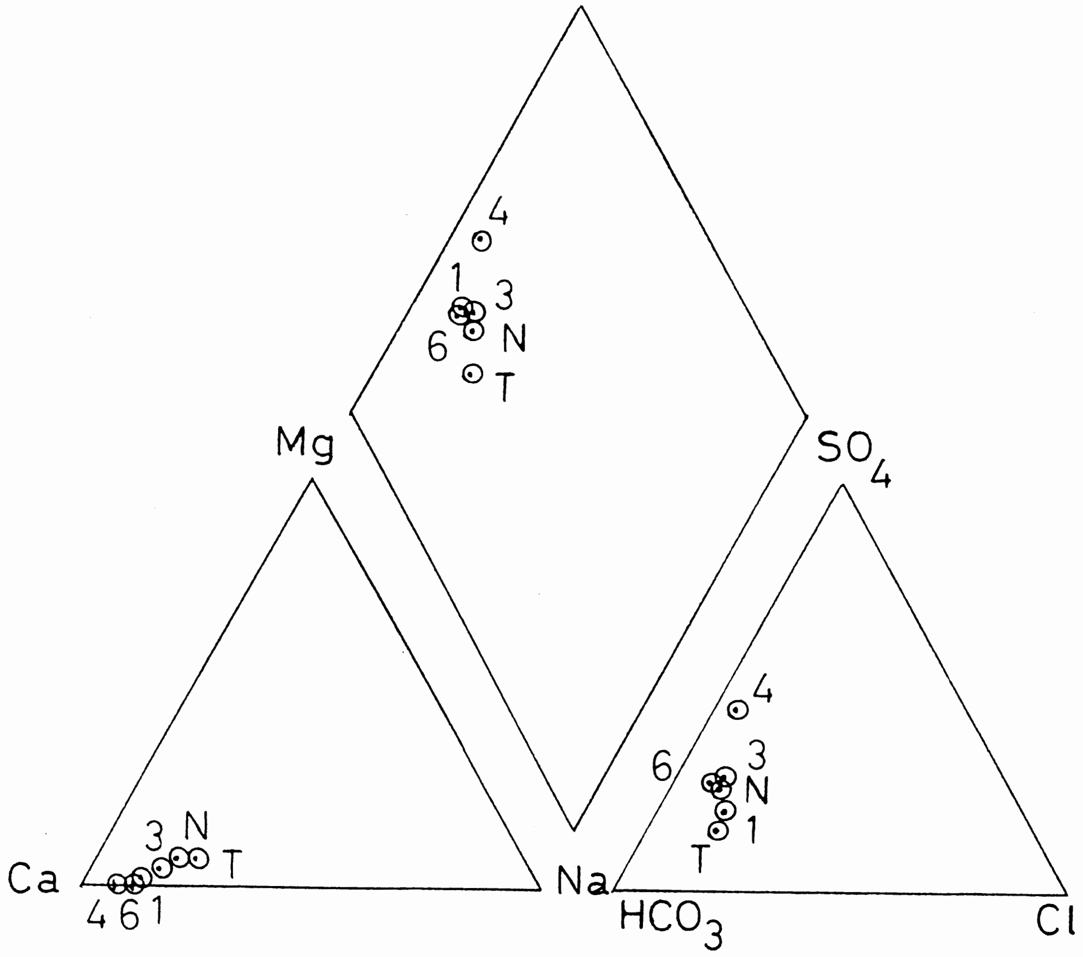


Figure 33. Piper Diagram: April 9 Analyses

APRIL 23 PIPER DIAGRAM

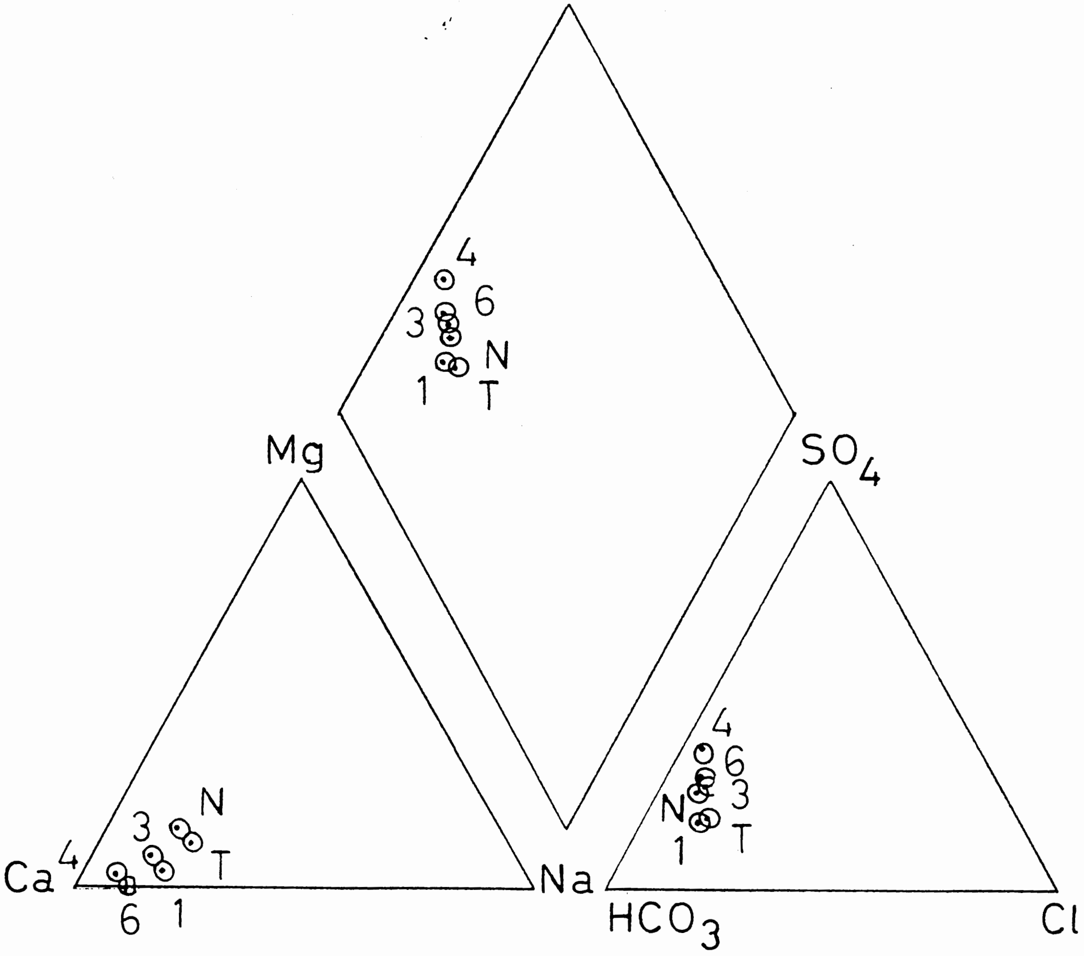


Figure 34. Piper Diagram: April 23 Analyses

MAY 15 PIPER DIAGRAM

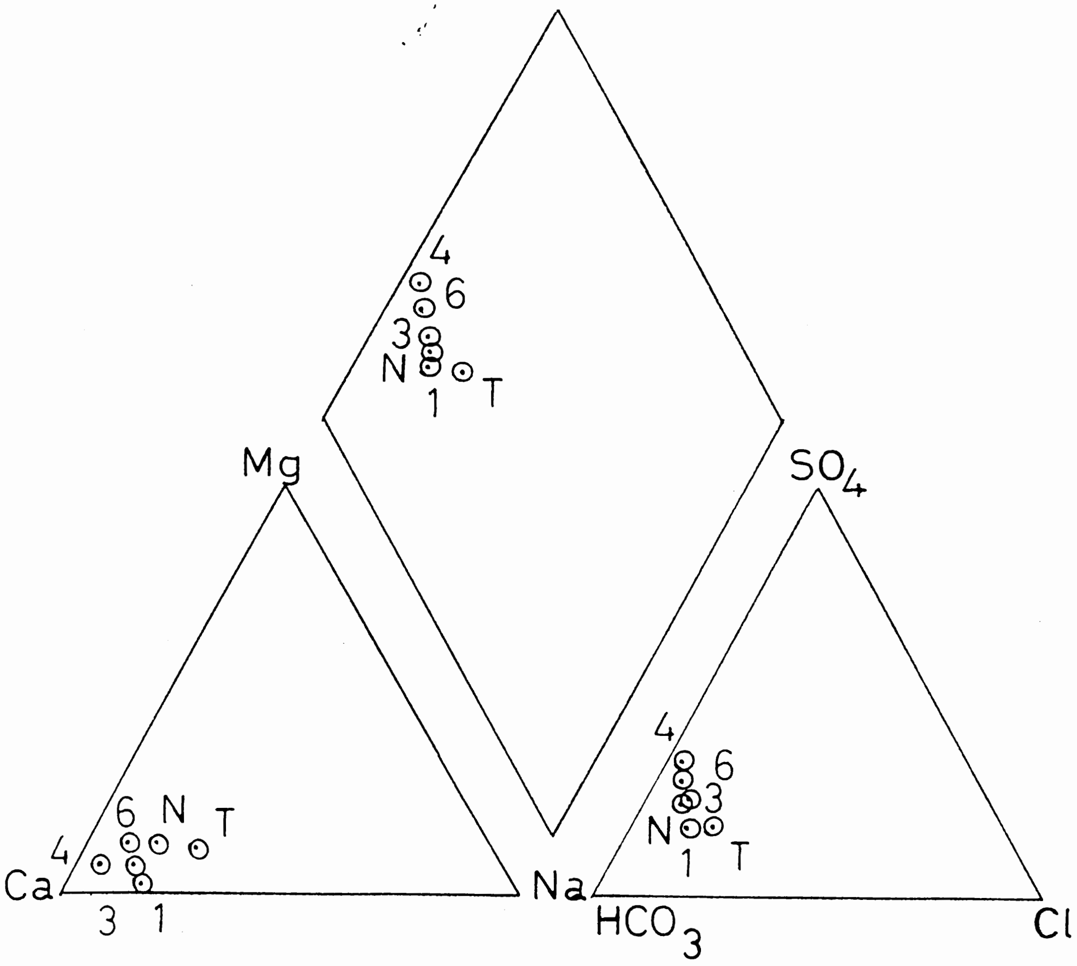


Figure 35. Piper Diagram: May 15 Analyses

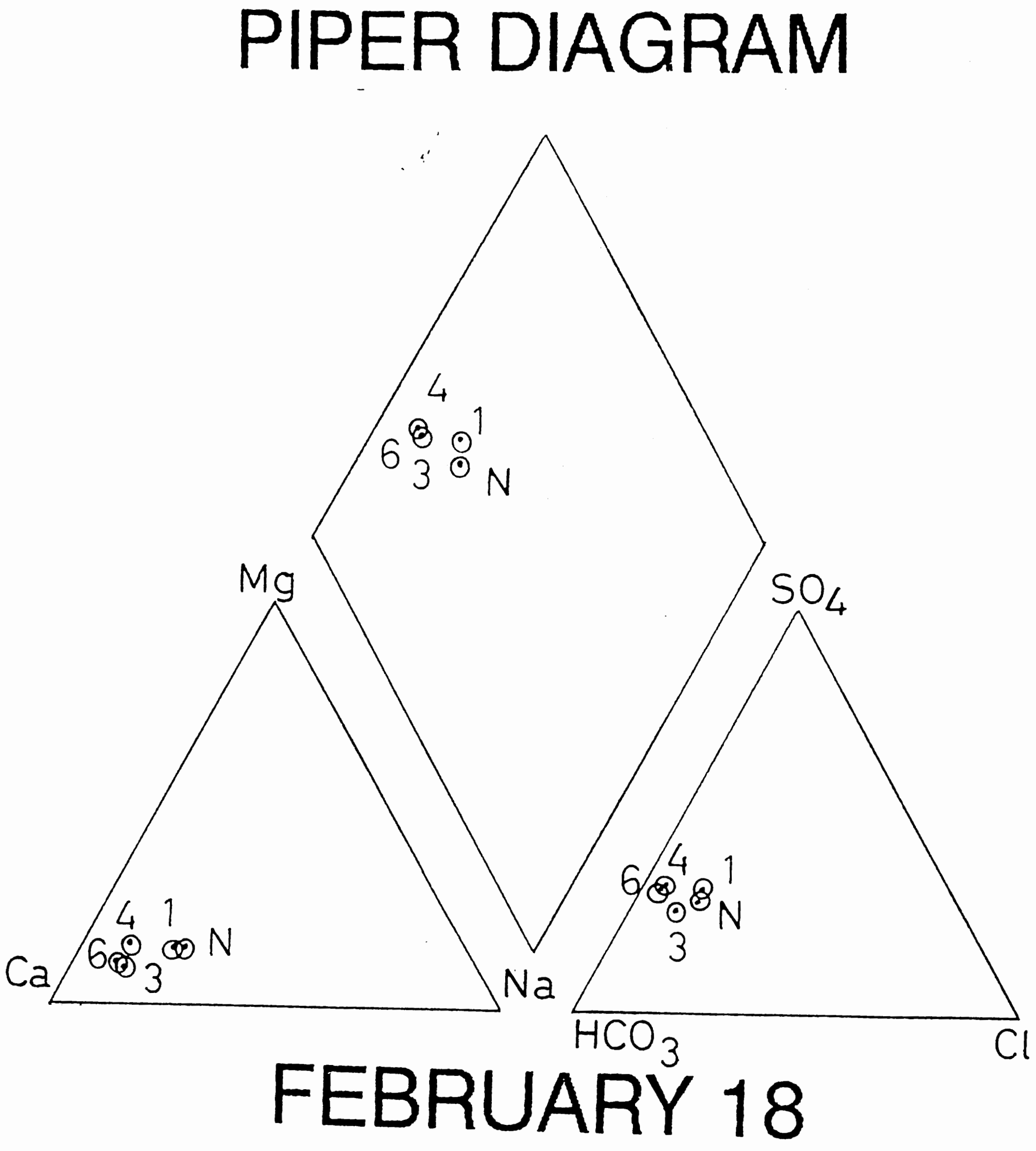


Figure 36. Piper Diagram of February 18 Samples.

exists, the amount of change over time is quite small. The plots for the surface location, NEB, do not show trends consistent with the wells. Surface runoff may mask the chemistry of the discharging groundwater and thus make the trends less meaningful.

Conclusions

Trends are distinct on certain dates and show a likely interrelationship of samples. There is a progressive change in the chemical composition away from the I-4 type. This may be due partially to mixing but other factors are clearly exerting influence on the system. By themselves, the Piper Plots are not adequate to define the geochemical regime of the aquifer.

Durov Plots

A more sophisticated trilinear type of plot was developed by Durov (see Lloyd and Heathcote, 1985). The Durov plot incorporates anion and cation triangles which are placed so that their bases are perpendicular to each other making two sides of a square. The cation and anion plot locations are projected into the square where the intersection is plotted. Locations within the square indicate generalized water types as defined by nine subordinate fields. The analyses from the Fred Creek Valley all project into the calcium-bicarbonate dominated field (Figure 37). Lloyd and Heathcote state

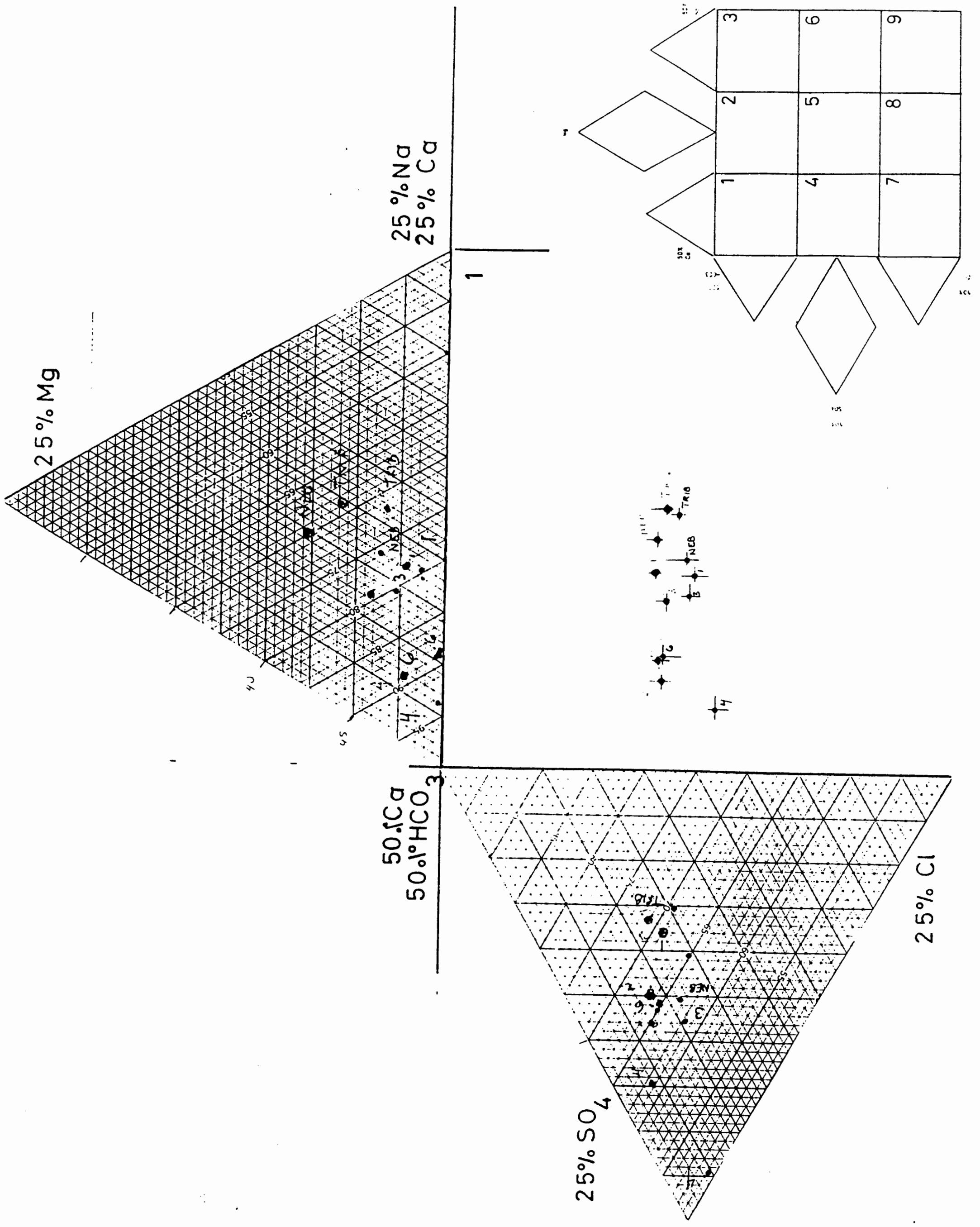


Figure 37. Expanded Durov Plot

that such waters may represent active recharge in an aquifer.

Ion Cross Plots

The previous techniques have provided a basis of typing the water and have hinted at interrelationships among the waters. Cross plotting chemical parameters further illuminates the factors which underlie relationships.

Individual ions were plotted over time for the five separate dates of analysis. Total dissolved solids (TDS) and conductivity were also viewed as a function of time. Conductivity was measured on 17 occasions as opposed to the 5 samplings for complete analysis. Changes in concentration for most ions were gradual with increases and decreases varying according to the individual wells. Overall, conductivity and TDS decreased slightly over time but the differences through the year were far less than the differences between the wells. Moreover, for all parameters except chloride and magnesium, the highest values were found in the I-4 well and the lowest in the I-1 well. Wells I-3 and I-6 generally had intermediate levels, between the two extremes.

Ion concentrations were also plotted against TDS, pH, and temperature. There is a general increase in calcium, sulfate, and bicarbonate as TDS increases, whereas chloride, magnesium, and sodium show no significant relationships. This association could be interpreted to indicate that dissolution of calcite and gypsum comprise the primary source of ions. Plots of ion concentration versus pH show no dominant trends except that calcium and sulfate concentrations are low when pH is high. The various temperature plots showed no trends.

When water table elevations are plotted against ion concentrations for the collective data no clear trends stand out; however, individual wells show significant relationships. In the I-1 and I-4 wells there is a marked decrease in chlorides as the water level rises (Figure 38). Because chloride is a conservative ion, not chemically active in solution, its level of concentration indicates further dissolution with increased residence time or dilution by recharging waters. The plots for wells I-1 and I-4 exhibit a marked decrease in chloride concentration as the water level rises, thus indicating dilution of the water during the spring recharge episode. Wells I-3 and I-6 do not show this same phenomenon.

For the spring analyses, the sulfate content decreases with increasing water level in the I-4 and to a lesser extent, the I-1 wells. This trend does not bear out, however, in the fall and winter. There appears to be some evidence for dilution of sulfate but biologic

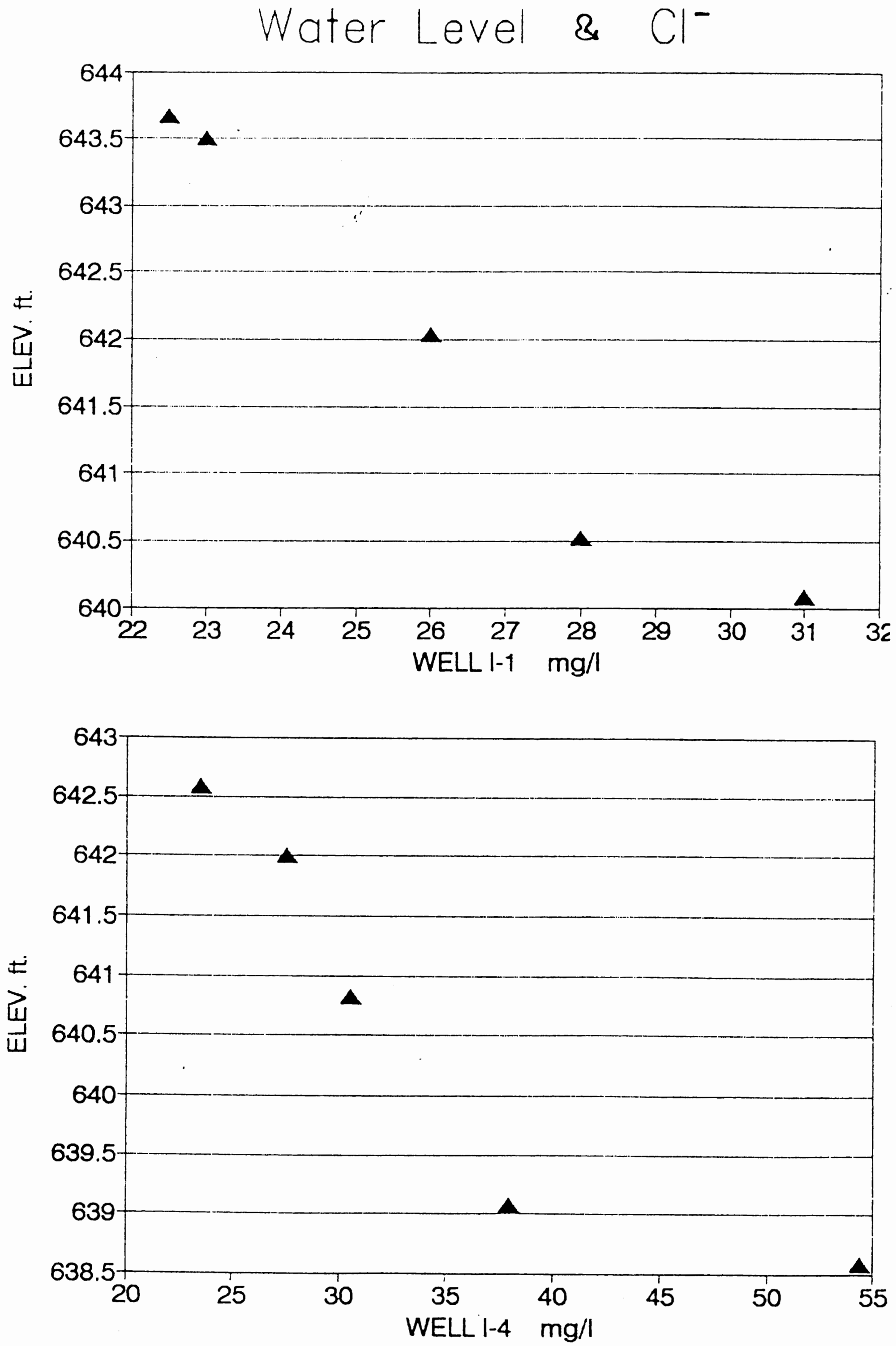


Figure 38. Crossplot of Chloride with Depth

and chemical controls to sulfate distribution most likely complicate the relationship.

Conclusions from Cross Plots

Cross plotting shows a definite difference between the extremes of the I-4 and I-1 wells. The I-3 and I-6 wells and also the surface localities generally fall in intermediate position to the end members. Calcium, sulfate, and bicarbonate vary directly with levels of total dissolved solids. This would appear to be caused by the dissolution of calcite and gypsum by the recharging waters. Decrease in the concentration of chloride ion as water levels rise indicates that dilution occurs during the spring recharge.

Sources of Ions

Rain water has minor amounts of dissolved ions depending on the proximity to the ocean where sea spray contributes sodium chloride to the atmosphere and also depending upon the particulates and chemicals introduced by industrial processes. Moreover, carbon dioxide is present as a dissolved species. Table 6 lists an analysis of fresh snow gathered from the ORU campus in February of 1991. This is the starting point to which the soluble ions are added when recharging water moves to and through the aquifer.

In a water table aquifer, bicarbonate ion is derived from the solution of carbon dioxide entrapped in the soil and also by dissolution of limestone. The fact that calcium and bicarbonate are balanced in most samples suggests that limestone could be the primary source. There is limestone in the Pennsylvanian outcrops in both the Holdenville Fm. and the Nowata Shale, but it is not the primary lithology of these formations. Neither is there more than trace amounts of limestone or calcite mineralization in the alluvium and terrace deposits encountered in well cores and creek banks.

According to Hem (1985) and other authors, sulfate is generally derived from solution of gypsum. Gypsum is quite soluble and is fairly common in evaporative sequences of sedimentary rocks. Unfortunately, very little gypsum is recognized in the rock or sediment which are in contact with the groundwater. Either the gypsum present is masked by the overwhelming dominance of quartz, clay and iron oxides or there are additional sources of sulfate in the area. When iron pyrite is exposed to an oxidizing environment it becomes altered to sulfate and the pH of the water goes down with the liberation of H^+ ions. Pyrite was not recognized in the visual inspection of core samples; however, much of the section penetrated by I-4 contained dark gray to black, unoxidized sediments. There may have been finely disseminated pyrite present. Sulfur is also liberated from plant material when it decays. Several articles have been written in agricultural and soil journals regarding the amount of sulfur load contributed to the soil. Papers by Johnson and Henderson (1979), Chao et.al. (1964), and Johnson et.al. (1981) deal with the sulfate which is adsorbed by iron oxides in soil and document that sulfate in the topsoil can be leached by infiltrating water. Froneberger (1990), has provided the author with data that show that sulfate concentrations are very high in water drawn by suction lysimeters from very shallow depths. In any case, there may be multiple sources for the sulfate in the Fred Creek aquifer.

The sodium and chloride ions are fairly minor constituents to the waters in question. They may easily have come from conate water in the marine sedimentary rocks. Also, some sodium and chloride should be in the meteoric water.

Finally, the magnesium most likely is derived from dolomite. Although minor beds of limestone are recognized in the valley, no dolomite has been documented from field work. That does not rule out the presence of dolomite associated with the limestones.

Balance Calculations

It is possible to calculate likely source combinations using a mass balance approach. Parkhurst et.al. (1982), designed a program called "BALANCE" which permits calculation of the mass of source being introduced to a water system based upon the mass of the components already in solution. They term the balance a "mass transfer" and also use the relationship to calculate the mixing product of two different waters. Assumed in the process are the common mineral types available, based upon knowledge of local geology. Several potential mineral sources are specified along with the number of units of each ion which would be present in a molecule of the mineral. The solution to the mass balance calculation is written as the number of millimoles of each source which, "..react with the initial solution to produce the final solution (positive for dissolution, negative for precipitation)." (Parkhurst, et.al. 1982, p.6). Instead of a mixing problem, the initial solution can be considered to be rainwater and the final solution is the water analysis in question. In this way, the proportion of each mineral dissolved to produce the specific solution can be estimated.

Table 7 lists the "BALANCE" results for significant phases which could have contributed to the final solution. The most striking result of the theoretical mass transfers is that the phases which should be contributing most to the final solution are calcite and carbon dioxide. Carbon dioxide in the soil is dissolved by infiltrating rainwater. Hem (1985) states that CO_2 in soil voids has been reported to attain concentrations many orders of magnitude greater than in the atmosphere. Rabenhorst et.al. (1984) discuss the conditions of chemical equilibrium for carbon dioxide, bicarbonate and calcium carbonate in the subsurface. The process of calcite solution involves solution of CO_2 in water to form carbonic acid and the subsequent dissociation of the $CaCO_3$ when the hydrogen ion combines with the carbonate ion. The combined reaction is written:

$$CO_2 + H_2O + CaCO_3 <===> Ca^{+2} + 2HCO_3 \quad \text{(Chem Eq. 1)}$$

Rabenhorst, et.al. remark that if the water bearing dissolved CO_2 moves out of contact with the source of gaseous CO_2, then half of the concentration of bicarbonate in the groundwater should be due to dissolved CO_2 and half due to dissolved $CaCO_3$. The above equation shows that the two moles of $CaCO_3$ produced come equally from one mole of CO_2 and one mole of $CaCO_3$. It is therefore reasonable to expect equal magnitudes of calcite and carbon dioxide phases in the mass balance results.

TABLE 7

RESULTS OF MASS BALANCE CALCULATIONS

APRIL 9	I-1	I-3	I-4	I-6	NE BR
Cal Bal	2.263	2.772	5.044	4.506	2.005
Gyp Bal	0.519	1.249	3.903	1.456	1.09
Dol Bal	0.078	0.259	0.078	0	0.321
Ion Exc	-0.33	-0.23	0.136	-0.072	-0.003
CO2	0.898	2.27	3.753	2.649	2.869
Ion Str	0.00839	0.01464	0.03184	0.01926	0.01343
TDS	430	680	1359	981	687
APRIL 23	I-1	I-3	I-4	I-6	NE BR
Cal Bal	2.069	2.761	4.692	4.446	1.358
Gyp Bal	0.426	1.249	3.382	1.717	0.988
Dol Bal	0.14	0.42	0.378	0.037	0.58
Ion Exc	-0.3	-0.398	-0.368	-0.412	-0.291
CO2	1.289	2.635	6.383	3.434	2.757
Ion Str	0.00803	0.015	0.0301	0.01964	0.01149
TDS	439	715	1333	983	602
MAY 15	I-1	I-3	I-4	I-6	NE BR
Cal Bal	2.268	3.182	4.676	3.305	1.987
Gyp Bal	0.415	1.095	3.122	1.77	0.884
Dol Bal	0.099	0.378	0.679	0.958	0.58
Ion Exc	-0.307	-0.443	-0.313	-0.403	-0.357
CO2	1.052	2.456	6.058	3.173	2.449
Ion Str	0.00814	0.015	0.03028	0.02126	0.01241
TDS	427	738	1316	1001	649
NOV 21	I-1	I-3	I-4	I-9	(FEB I-7)
Cal Bal	1.342		3.929	3.556	1.632
Gyp Bal	0.295		1.812	0.395	0.26
Dol Bal	0.42		1.259	0.36	0.642
Ion Exc	-0.101		0.345	0.12	0.111
CO2	1.575		4.583	6.153	2.919
Ion Str	0.00818		0.02832	0.01596	0.0108
TDS	306		1126	592	491
FEB 18	I-3	I-4	I-6	NE BR	I-9
Cal Bal	2.645	5.906	4.237	0.9	4.953
Gyp Bal	0.364	0.885	0.416	0.833	0.364
Dol Bal	0.621	0.839	1.02	0.601	0.16
Ion Exc	0.014	0.455	0.34	0.362	0.137
CO2	2.309	4.406	3.195	2.415	5.677
Ion Str	0.01335	0.02694	0.0208	0.01201	0.01806
TDS	647	1262	1025	521	871

Not all wells show comparable phases of CO_2 and calcite in the results. The creek water samples show a greater percentage of bicarbonate coming from CO_2 in every analysis. This is also true for the I-4 well on three separate occasions and the I-9 well in both of its analyses. In contrast, the I-1, -3, and -6 wells generally show a greater calcite phase than CO_2. These relationships will be considered further in the chemical evolution discussion.

The gypsum balance indicates a likelihood that gypsum is present in the source area, even though it was not commonly identified in field work. The part gypsum plays as a source does vary from well to well, however. Because calcium is derived from solution of both calcite and gypsum, comparison of the two balance values is of interest. Well I-1 shows a five-fold magnitude difference with calcite contributing more than gypsum, whereas well I-4 shows a closer agreement between the two values (Calcite is 1.3 to 1.5 times greater than gypsum).

Finally, the dolomite balance indicates very little source and the negative ion exchange values mean that calcium-sodium ion exchange is not operating. The sodium values are much too low to show calcium being removed from solution by an exchange for sodium.

Mass balance calculations indicate that the dissolved ions in the I-1 and I-4 waters may have come from different mineral sources. This is particularly clear from the calcite-gypsum ratios.

General Conclusions

The initial appraisal of chemical data for the Fred Creek aquifer measured from the winter of 1990 to winter of 1991, uncovers relationships from which fundamental conclusions may be drawn. It is apparent that: 1) the groundwater is a calcium-bicarbonate-sulfate water; 2) ion concentrations are likely a function of dissolution of minerals; 3) significant spatial variability is common in the valley with the I-1 and I-4 wells exhibiting the widest range of difference in most chemical parameters; and 4) dilution of the groundwater during recharge is indicated by the decreasing chloride content as water level rises.

The spatial and temporal variation in the aquifer requires further evaluation in order to search for the mechanisms underlying these relationships. Consequently, the next chapter deals with thermodynamics and chemical evolution of the geochemical system .

CHAPTER VII

MODELING THE GEOCHEMICAL SYSTEM

Chemical Evolution of Groundwater

It has been recognized in many groundwater basins that the movement of water along its flow path results in chemical changes in the water. Freeze and Cherry (1979) state that the normal condition is for more ions to be added to solution the longer the water is flowing. An increase in total dissolved solids and in the concentrations of most ions generally results with increased residence time between recharge and discharge. Fritz et.al. (1990) translate this relationship to a basin where recharge occurs in uplands and flow proceeds down gradient to discharge in natural springs. An increase in concentrations is reported with increasing distance from the recharge areas and therefore with decrease in elevation. The saturation index of calcite, calculated from thermodynamic relationships, also increases from high elevations to low elevations as the water flows down toward its discharge points.

Counter-trend in Fred Creek Valley

Potentiometric maps of the Fred Creek valley (Figures 24-26) show that flow should be moving south and southwest into the valley center and down the valley axis. This represents a movement from recharge points to discharge locations into the creek. Applying the groundwater evolution model to this system, there should be increasing concentrations in water samples taken progressively farther down gradient. According to the chemical analyses of six well samples and two surface waters in the middle valley, this classic relationship does not hold for the study area. The samples with the highest total dissolved solids are those from wells farther away from the discharge zones and the lowest concentrations occur very close to the creek. Every major ion except chloride is of higher concentration in the wells farthest from the creek. Because of this major deviation from normal conditions, the chemical evolution of the valley waters must be unraveled to solve the enigma.

Thermodynamics

Thermodynamic calculations consider reaction rates and the free energies of chemical species involved to determine whether a reaction can occur. Lloyd and Heathcote (1985) express that this is a way, "..to express the extent to which a water has reached chemical equilibrium with the minerals of the aquifer matrix." (Lloyd and Heathcote, 1985, p. 105). The conditions of equilibrium become an assessment of whether the solution is capable of dissolving a particular mineral phase or whether the solution is saturated with the ions derived from that phase.

The extent to which a solution has become saturated can be expressed as the product of the activity of the ions going into solution divided by the saturation constant for the dissolution equation. When expressed as a percentage, the saturation calculation is made by the following formula:

$$\% \text{ Saturation} = \frac{\text{Ion Activity Product}}{\text{Saturation Constant}} \times 100$$

$$\% \text{ SAT} = \frac{\text{IAP}}{K_s} \times 100 \qquad \text{(Eq. 9)}$$

When the saturation is less than 100%, the solution is undersaturated and saturated when greater than 100%.

For convenience of interpretation, the above relationship is expressed as the log of the ratio (but not as %) and is termed the saturation index.

$$\text{Sat. Index} = \log [\text{ IAP} / K_s] \qquad \text{(Eq. 10)}$$

Logarithmically, answers greater than zero (ie. positive values) indicate oversaturation and those less than zero (negative) indicate undersaturation conditions.

Conversion of measured concentration to activity requires the derivation of an activity coefficient which is dependent on the ionic strength of the solution. Of course, the saturation constant for each dissolution reaction to be considered must be determined from free energies of all reaction components.

These calculations have been assembled by Plummer et.al., 1976, into a computer program termed WATEQ. Upon inputting ion concentrations, temperature, pH, and other available chemical parameters, the program calculates the saturation indices of all mineral phases which would need be dissolved to produce the solution.

All water analyses were subjected to thermodynamic calculations using WATEQ4F, a recent version of the program. In addition to standard parameters, dissolved oxygen and resulting Eh values were available for many samples. These were necessary for calculation of iron oxide phases. The results of the saturation index determination are presented in table 8.1. Because of the abundance of calcium, sulfate, and bicarbonate ions, the major phases listed are calcite, gypsum and dolomite. Goethite saturation is provided for samples where dissolved oxygen values were available. Goethite was chosen as a representative phase of iron oxide.

TABLE 8

SATURATION INDICES OF SELECTED PHASES

Well	LpCO$_2$	Gypsum	Calcite	Dolomite	Halite	Goethite
(APRIL 9, 1991)						
I-1	-1.764	-1.707	-0.300	-2.171	-7.732	5.939
I-3	-0.842	-1.240	-0.648	-2.549	-7.545	5.003
I-4	-0.827	-0.592	-0.034	-2.189	-7.647	5.233
I-6	-1.049	-1.079	-0.095	-3.399	-7.557	5.213
NEB	-1.726	-1.345	0.166	-0.774	-7.511	6.250
TRIB	-1.478	-1.589	-0.050	-1.174	-7.270	6.203
(APRIL 23, 1991)						
I-1	-1.081	-1.818	-0.924	-3.128	-7.856	4.996
I-3	-1.000	-1.251	-0.387	-1.806	-7.660	5.230
I-4	-0.928	-0.696	0.279	-0.814	-7.738	5.188
I-6	-1.178	-1.025	0.130	-1.973	-7.616	5.299
NEB	-1.827	-1.485	0.253	-0.135	-7.827	5.928
TRIB	-1.623	-1.626	0.100	-0.529	-7.504	5.823
(MAY 15, 1991)						
I-1	-1.053	-1.809	-0.944	-3.335	-7.839	4.858
I-3	-1.599	-1.294	0.258	-0.575	-7.562	3.108
I-4	-0.900	-0.730	0.274	-0.577	-7.875	5.165
I-6	-1.120	-1.047	0.085	-0.643	-7.647	5.546
NEB	-1.839	-1.482	0.365	0.009	-7.695	6.229
TRIB	-1.631	-1.603	0.051	-0.624	-7.138	5.888
(NOV. 21, 1991)						
I-1	-1.149	-2.026	-0.835	-2.356	-7.904	6.589
I-4	-0.646	-0.993	-0.029	-0.837	-7.178	6.252
I-9	-0.674	-1.712	-0.169	-13445	-8.834	6.336
(FEB. 18, 1991)						
I-1	-1.866	-1.599	-0.316	-1.350	-7.671	
I-3	-0.701	-1.796	-0.704	-2.231	-7.714	5.935
I-4	-1.050	-0.732	0.381	-0.258	-7.746	5.788
I-6	-0.900	-1.637	0.012	-0.799	-7.694	6.281
NEB	-2.123	-1.525	0.208	-0.367	-7.358	6.190
I-7	-1.156	-2.032	-0.391	-1.440	-7.935	6.619
I-9	-0.684	-1.684	-0.099	-1.803	-9.167	6.212

Interpretation

In general, all samples can be classified as oversaturated in goethite and undersaturated with respect to gypsum. Calcite saturation indices varied from sample to sample and with time. Some wells produced water that was undersaturated and some that was saturated. Figures 39 and 40 show the distribution of calcite and gypsum indices graphically. The high positive values for goethite (and for all the iron oxide phases), may reflect the widespread occurrence of iron oxide staining and amorphous iron oxide crusts observed in the cores and creek exposures. Iron oxides may actually be precipitating in the groundwater. The results for gypsum show undersaturation with water at the I-4 and I-6 wells closest to equilibrium. In contrast, the calcite indices are more consistently near saturation or oversaturated, indicating that calcite is likely dissolving.

The overall classification of the water according to saturation index has limited value. What may be more useful is the use of saturation indices (S.I.) as relative measures of the change in water chemistry along flow paths in space and time. This has been attempted in published reports such as that of Plummer et.al., 1990, and Fritz, et.al., 1990. In such cases, the change in magnitude of the S.I. can be mapped and used to identify chemical trends in the aquifer.

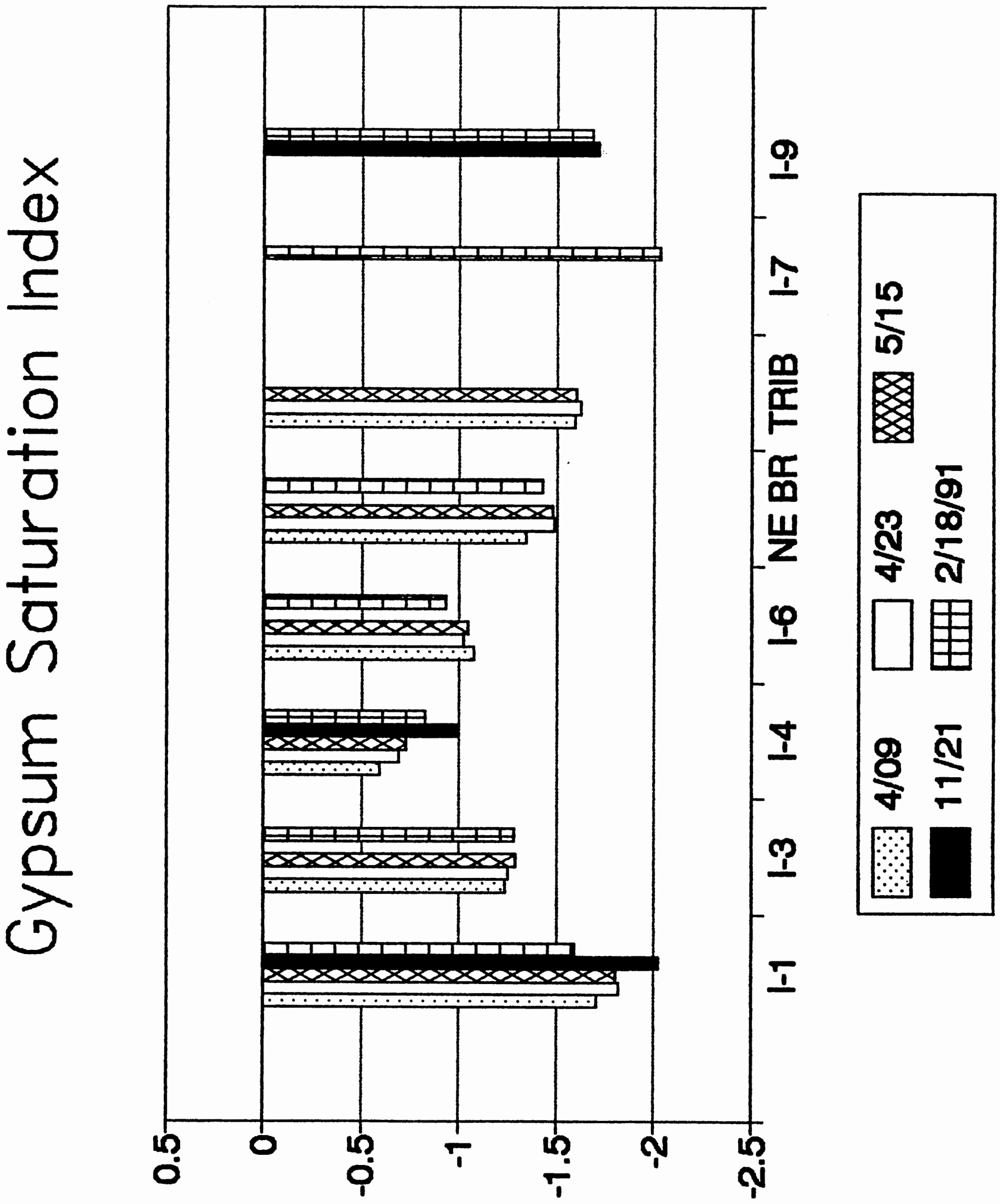


Figure 39. Graph of Gypsum Saturation Indices

Trends of S.I. Variation

There are definite changes in saturation values on a seasonal basis. Unfortunately, analyses were not made frequently enough to provide conclusive understanding of the seasonal trends. The most striking trend involves the gypsum index. In virtually all wells where multiple analyses were done, the saturation index for gypsum becomes more negative throughout the year. The may be a response to the gradual diminishing of recharge from the spring to the fall and winter causing less gypsum to be dissolved. The peak water table rise, however, occurred in May, which is in the middle of the decline of gypsum saturation.

Spatial Distribution

Seasonal trends in the calcite saturation are not obvious. Instead, significant spatial relationships appear. Well I-1 and to an extent well I-3 have samples with consistently negative (undersaturated) index values, whereas, those from wells I-4, I-6, and the NE Bridge locality have positive or barely negative values, being at or near saturation. Water from Wells I-7 and I-9 appear to be intermediate to the other values. I-7 samples are undersaturated, similar to I-1, and the one

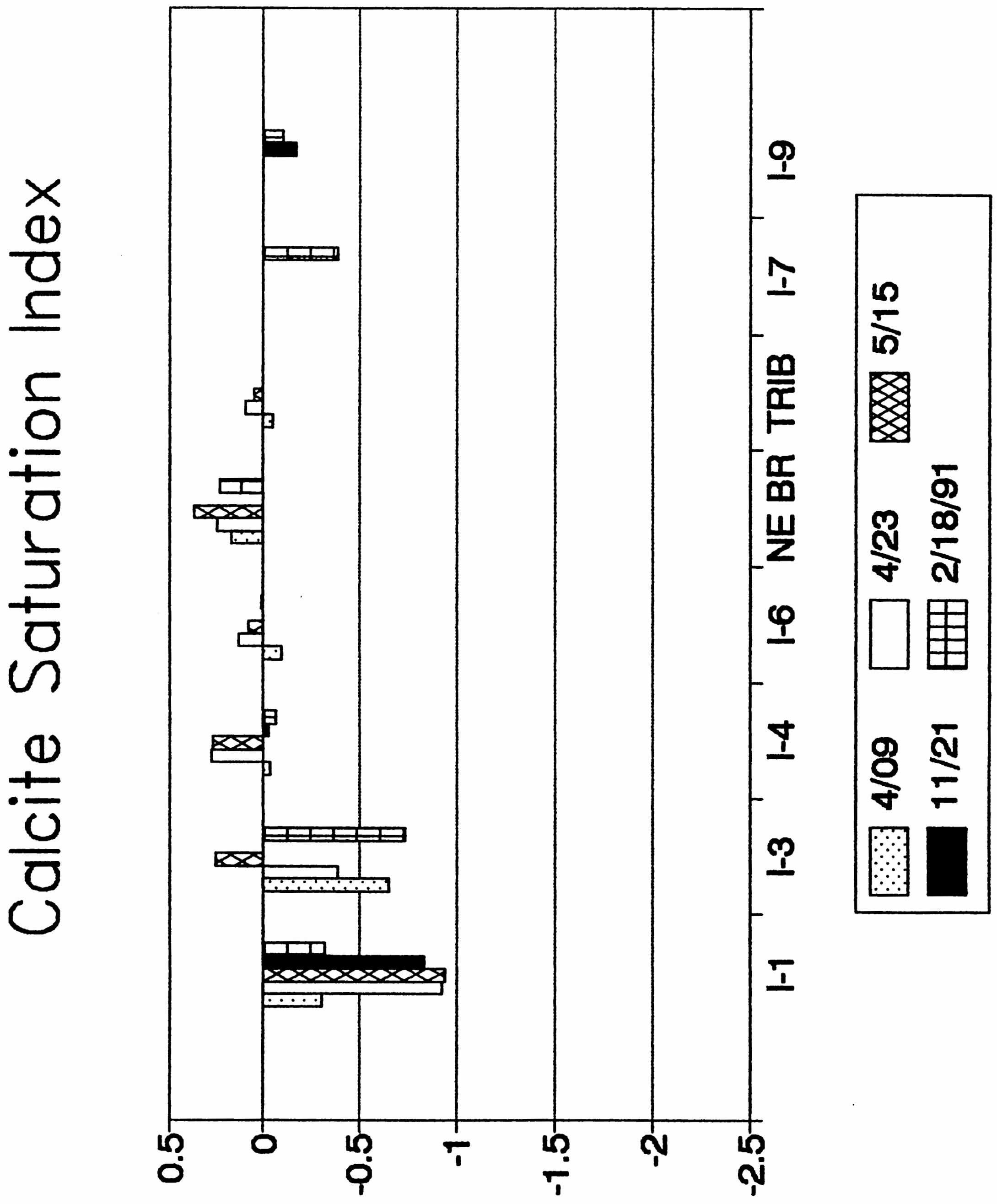


Figure 40. Graph of Calcite Saturation Indices

from well I-9 approaches saturation.

Water from well I-1 is thus shown to be substantially different from the other wells, thermodynamically with regard to calcite. It is the least saturated water, even though it is the well closest to a discharge point. The results of the mass balance calculations also showed that the I-1 well was unique in having values for calcite five time greater than those for gypsum.

By contouring the saturation index values, a broader perspective is achieved for a spatial view of the distribution. Figures 41 and 42 show calcite indices for April 1990, and February 1991; and figure 43 is a map of gypsum indices for February. In all cases, the lowest values are at the I-1 location and the highest are at the I-4. The creek water from NE Bridge always has a higher index value than the I-1 water. Samples from the I-3, -6, -7, and -9 wells have values intermediate between I-1 and I-4 so that a regular trend can be mapped.

The contour maps of the index values are very much like contour maps of the total dissolved solids values (Figures 44 and 45). The lowest TDS values were from water taken from well I-1 whereas samples from I-4 had the highest. The remaining samples can be contoured as intermediates. These trends would also be repeated for maps of individual ion concentrations of bicarbonate,

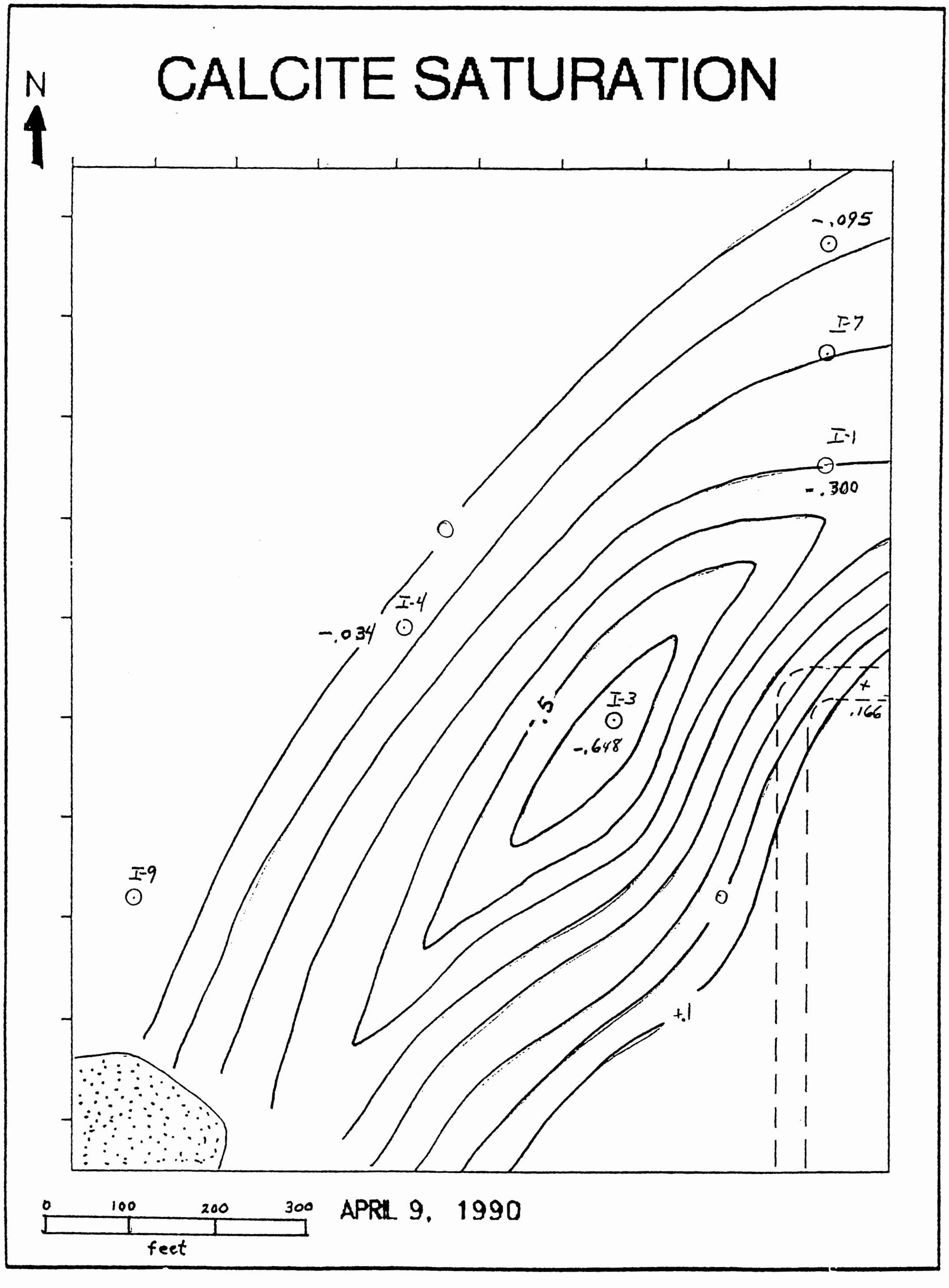


Figure 41. Map of Calcite S.I. Values for April

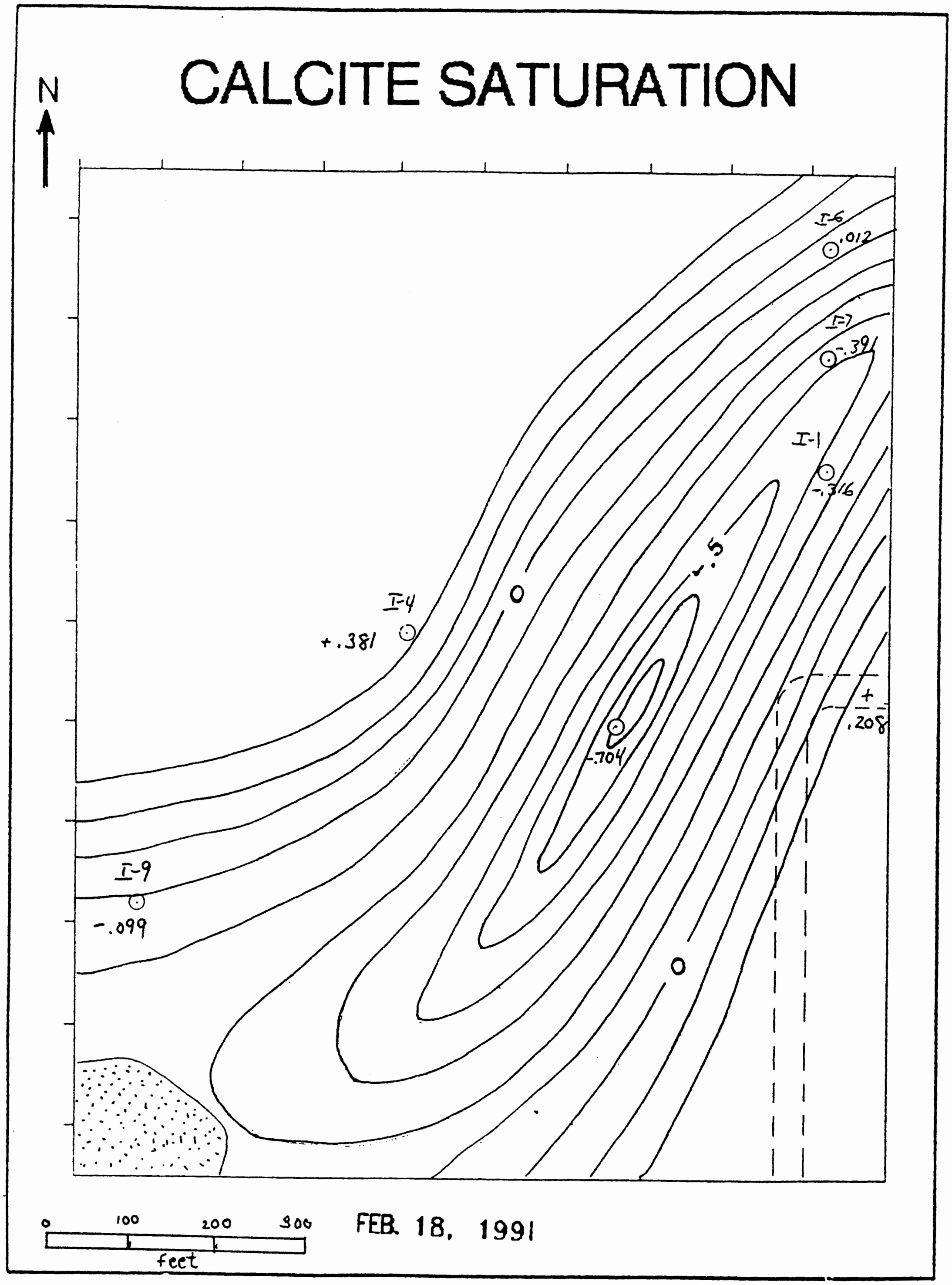


Figure 42. Map of Calcite S.I. Values for February, 1991

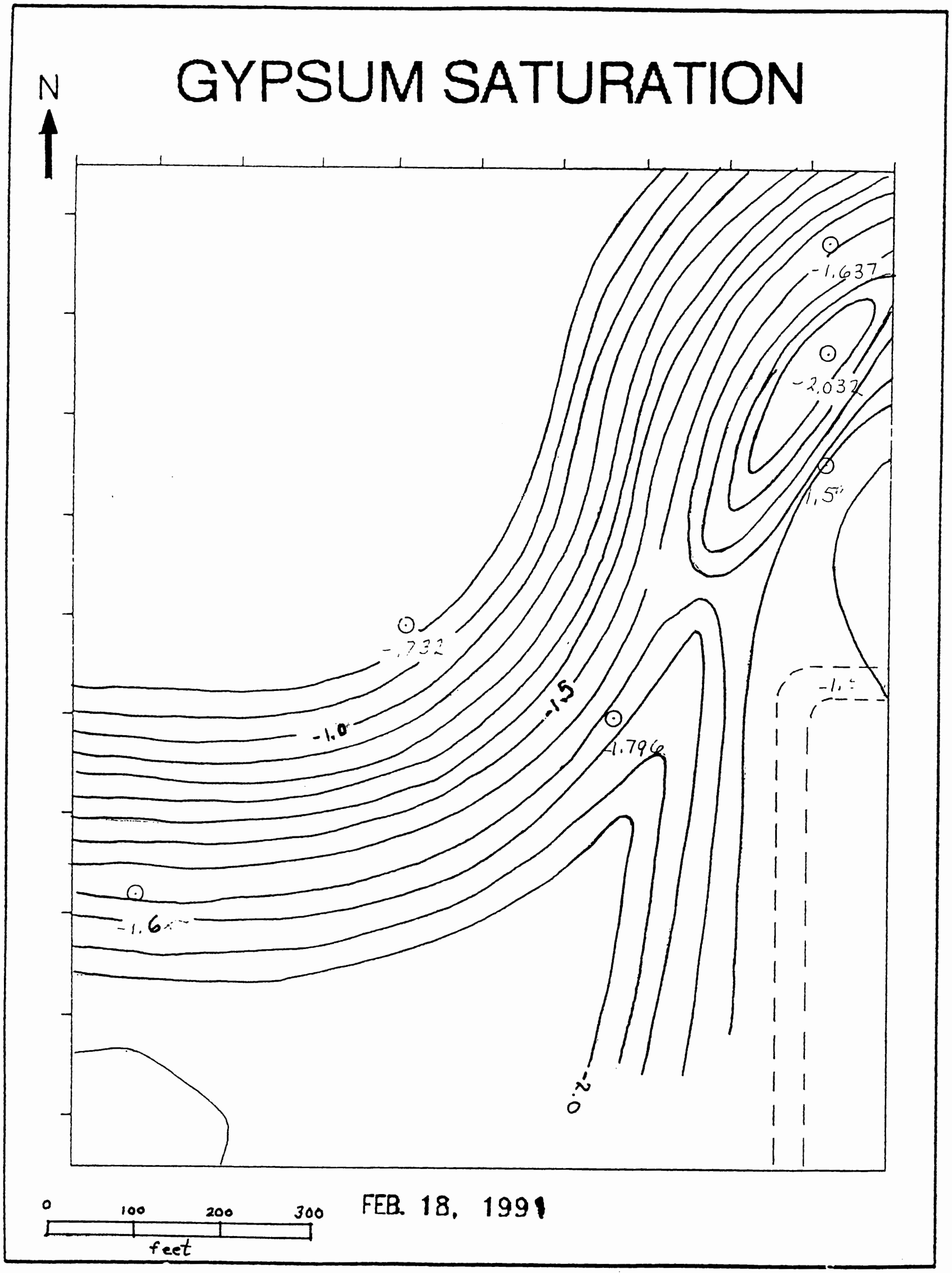


Figure 43. Map of Gypsum S.I. Values for February, 1991

sulfate, and calcium as shown by their relative concentrations illustrated in Appendix E.

The conclusion of these evaluations is that there must be a mechanism operating in Fred Creek valley which creates high concentrations at locations along the flow paths away from the creek and low concentrations in groundwater near the valley center where discharge occurs.

Mechanism for Reduction of Concentrations

There are a variety of chemical reactions which can remove ions from solution during the course of flow through an aquifer. Because the groundwater solution is charge-balanced, when one ion is removed, an observable response must be registered in some other chemical parameter. In order to reduce concentrations to the levels in well I-1, bicarbonate, sulfate, sodium, magnesium, and especially calcium must be removed in large quantities.

Calcium removal by cation exchange must be balanced by a two-fold increase in sodium. Instead of seeing this, sodium decreases along with calcium between wells. Anion adsorption could explain losses in sulfate. Several studies have documented the adsorption of sulfate to iron and aluminum oxide grains. This process is generally active in soils with low pH values. The pH of the Fred Creek groundwater does not appear compatible

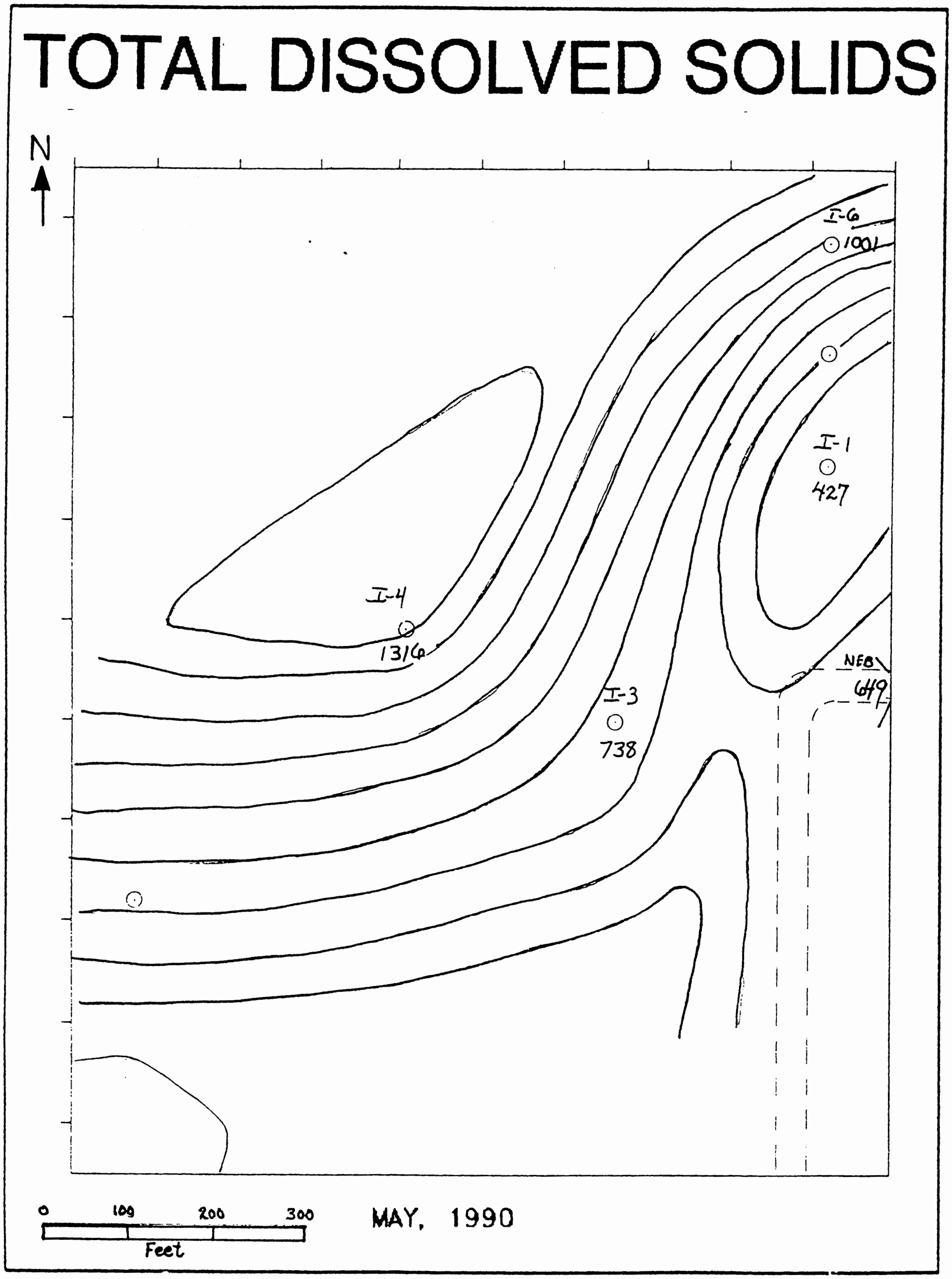


Figure 44. Map of TDS Distribution for May, 1990

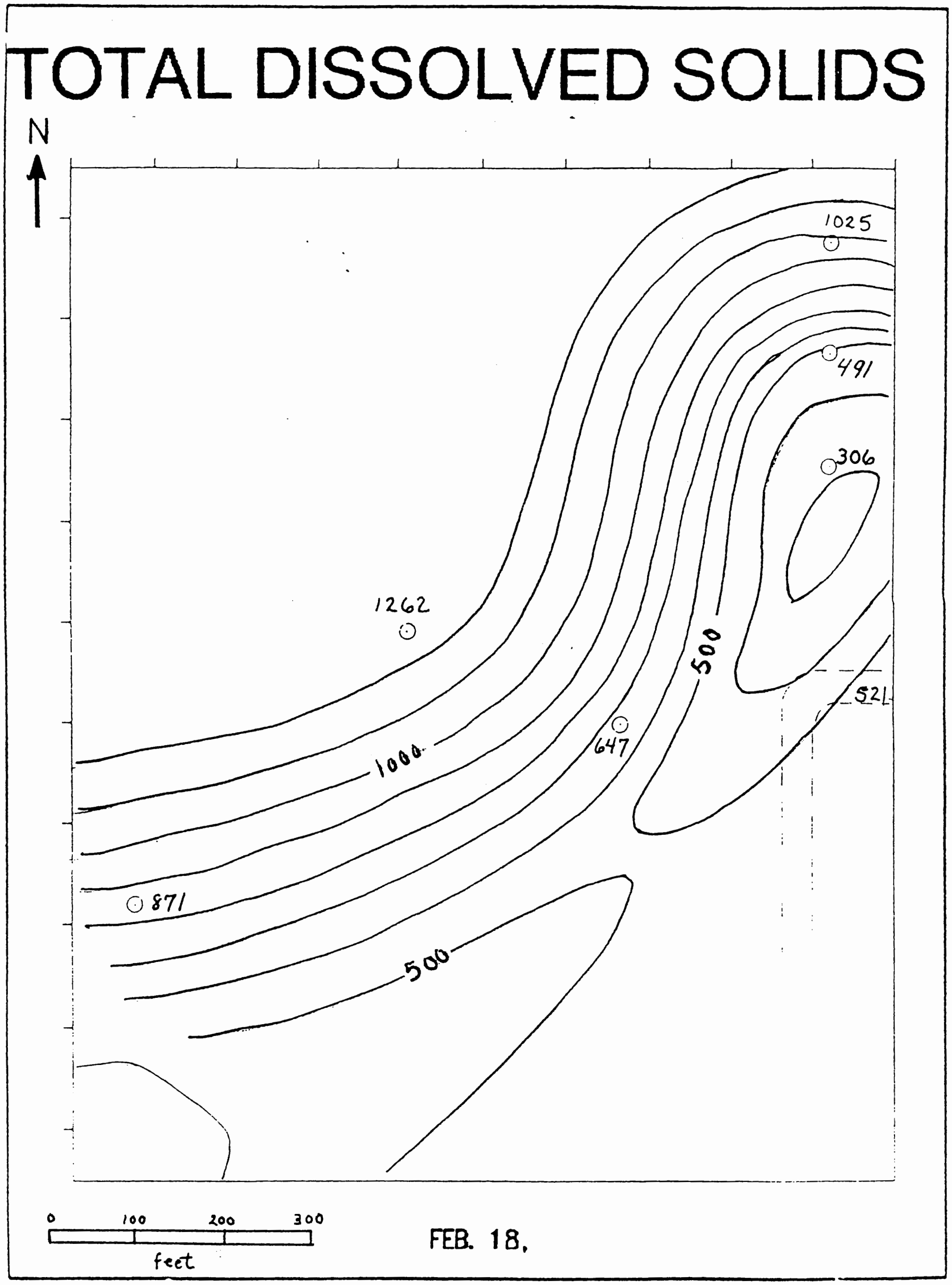


Figure 45. Map of TDS distribution for February, 1991

with this mechanism, although iron oxide is common in the matrix. Bacterial reduction of sulfate is another process which lowers concentration of sulfate. This could be operating in the aquifer; however, it would not explain the lowering of calcium and bicarbonate concentrations down gradient.

Massive precipitation events would also remove ions from solution. This does not seem likely, however, because calcite saturation indices are only positive in a few of the wells and not throughout the year. Gypsum would also have to be precipitated, and saturation indices for all wells are negative. Also, no pervasive deposits of diagenetic calcite or gypsum have been recognized in core samples.

Mixing

The only reasonable mechanism for such a reduction in concentrations is the mixing of two distinct waters, flowing together from separate sources. This would explain the intermediate values in all the wells between I-1 and I-4.

To investigate mixing, two tools can be invoked. First of all, waters that mix have a characteristic trend on triangular diagrams. For this reason, Piper plots were made for all analyses in the data base. Figure 46 is a possible mix. Other plots are included in Appendix F. Three or more analyses that plot in a

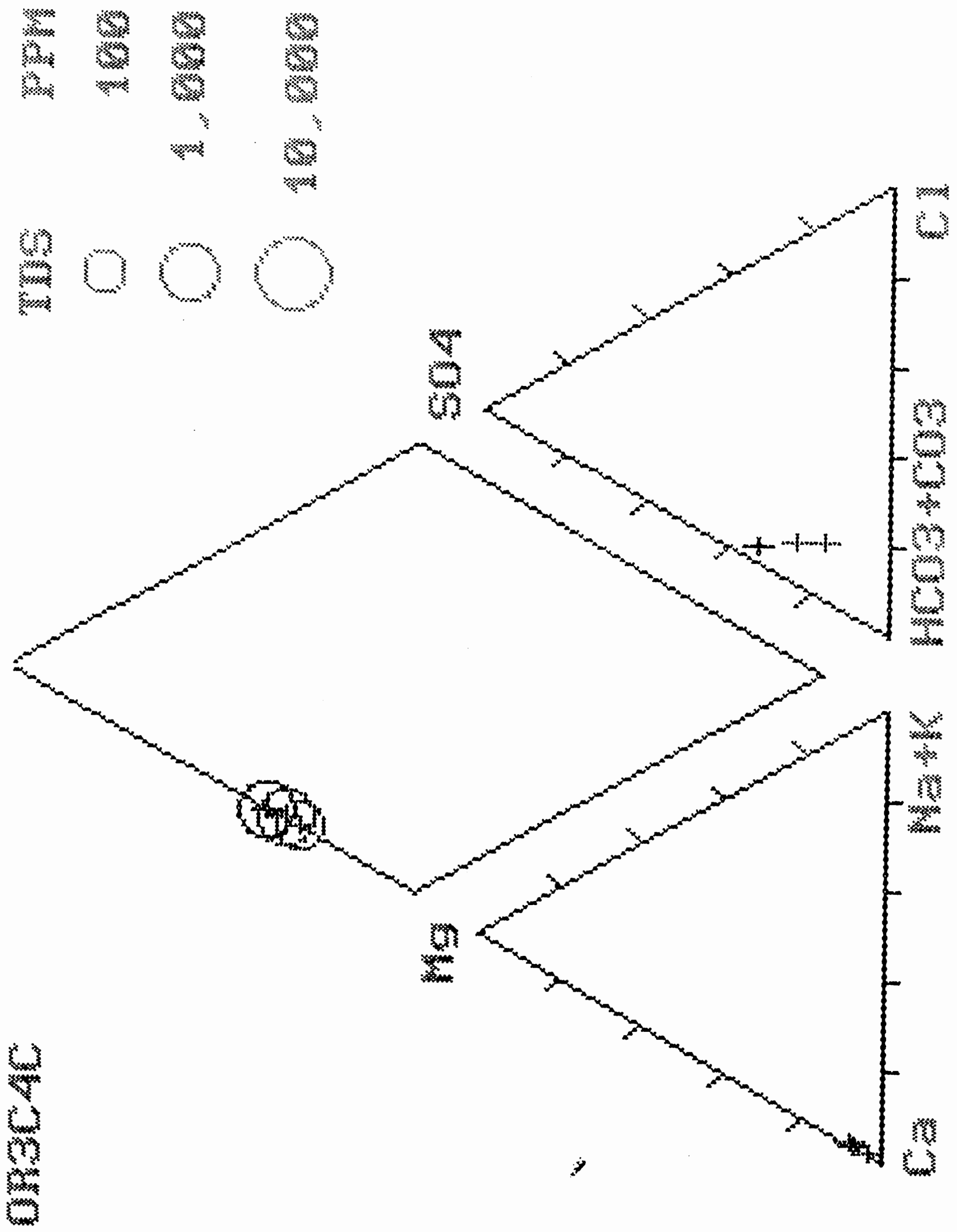


Figure 46. Piper Plot Indicating Mixing

straight line trend on each of the anion and cation triangles and the diamond plot, are candidates for mixing.

The second test for mixing is a mass balance calculation in which two analyses are used as source waters from which the third is derived. A theoretical mix is calculated from the two sources and compared to the actual water analysis, the proposed product. The two theoretical and actual values are regressed against each other and correlation coefficients (R^2) are calculated for the collective fit. If this is significant, there is likelihood that a mix has occurred.

When mixing calculations were made for a variety of combinations, the highest correlation factors came from mixes with well I-4 and I-1 as end members. Table 9 includes correlation coefficients and theoretical percentage participation from each source. Both well I-6 and I-3 fit the criteria of a reasonable product of the mixing of I-1 and I-4 with correlation values greater than .99. The theoretical percentages of I-1 and I-4 contributing to the mix are consistent for the different dates and show that I-1 has the greater influence on I-3, whereas I-4 dominates the I-6 mix.

Table 9. Results of Mixing Calculations

Date	Source	Source	Product	R^2	% S1	% S2
	1	2				
4/09	I-4	I-1	I-3	.984	28.6	71.8
4/23	I-4	I-1	I-3	.997	31.9	68.1
5/15	I-4	I-1	I-3	.997	32.1	67.9
2/18	I-4	I-1	I-3	.992	14.8	85.2
4/23	I-4	I-1	I-6	.992	59.5	40.5
5/15	I-4	I-1	I-6	.992	59.5	40.5

Even though these techniques indicate mixing is possible, the results are not completely compatible with the flow regime. Wells I-4 and I-1 are in different flow paths. Water flowing from the I-4 area could not reach the higher I-6 area to generate a mixing product. The I-4 + I-1 mix is possible with I-3 occurring where the flow paths converge.

Computer Simulation of Mixing

Trends on Piper diagrams are not definitive proofs of the proposed mixing and neither do they explain any secondary mechanisms which may be active. Mixing should produce the same order of data points on the anion trend as on the cation trend, but this does not hold for every analysis date. Even though the strongly linear trends indicate mixing, other factors may be operative in the system. A more comprehensive appraisal of the geochemistry is necessary if a reasonable model is to be constructed.

The PHREEQE Model

The U.S. Geological Survey has designed a geochemical computer program with the capability of following mass balance transfers in a dynamic system where chemical reactions and changes in concentration occur (eg. dilution, evaporation concentration, and mixing). This is accomplished while maintaining equilibrium with specified mineral phase boundaries, (Parkhurst, et.al. 1985). It is essentially a coupling of a mass balance program with a thermodynamic program with additional equations incorporated to handle pH and redox changes. (The acronym, "PHREEQE" stands for pH Reox and Equilibrium Equations.)

The equilibrium portion of Phreeqe is similar to Wateq which was discussed earlier. It is an ion association model in which dissolved species are considered as pairs of dissociated ions. The ion pairs can be modeled by means of equilibrium constants derived from dissociation reactions.

Once the input concentrations, pH, temperature, and pe values are set, chemical reactions and physical mixing can be simulated in incremental stages. Alternatively, different simulations can be linked together, with the product of the first result participating in the next event. At the end of the simulation, or at a junction in a chain simulation, the changes in concentration are reported along with the resultant pH, pe, ionic strength, electrical balance, and total alkalinity. Saturation indices can be stipulated to produce desired solutions or changes in saturation index can be monitored through a sequence of events.

The PHREEQE program has been used to model changes in water chemistry along flow paths involving calcite solubility (Plummer and Busenberg, 1982), and in the study of solution of calcite where saline and fresh waters mix (Sanford and Konikow, 1989). It is not restricted to carbonate equilibria and the thermodynamic data base may be appended to permit any species or mineral phase to be included for which thermodynamic data can be assembled.

Fred Creek Aquifer Simulations

The approach taken in modeling the Fred Creek aquifer was to build on the trends outlined by the Piper diagrams and mass balance mixing routines. The I-4 and I-1 waters were interpreted to be end members in the mixing. By varying saturation indices and monitoring the indicator parameters, episodes of mixing were designed to see whether the chemistry of the intermediate wells could be closely reconstructed.

Because the ion cross plots and trilinear plots indicate active dilution during recharge, the chemistry of the snowmelt sample was incorporated into the model. To begin with the following scenarios were modeled:

Straight Mixing Models

1. Water from the I-4 area is mixed with water from I-1 in different proportions to generate a water chemically like well I-3.
2. Water from I-4 and I-1 are mixed to produce the I-6 water type.
3. I-4 water was mixed with water like the NEB surface locality to produce both the I-3 and I-6 waters.

Dilution Models

4. The chemistry of the recharging snowmelt sample was mixed with the I-4 water to generate waters like I-3 and I-6.
5. The diluted I-4 water from one date was compared to the I-4 water at a later date.
6. Mixing and dilution were linked together to see the combined effect.

Recharging Solution Models

7. The snowmelt water was equilibrated with saturation values of the four wells to recreate concentrations of those waters.

In each case, the actual concentrations of the target water as well as pH and other criteria were compared to the computed data. Because the program provides for maintaining equilibrium with stated mineral phases, computed concentrations were recored both before and after the equilibration step. Calcite, dolomite, gypsum, halite, and CO2 were selected as the mineral phases to reflect the chemistry of the water.

Results of Computations

Mixes. Of the various simulations, the best agreement between actual and computed values occurred for mixes producing the I-3 type water. It was possible to compute concentrations within three percent of the actual for most of the seven ions and solution parameters. Taken collectively, a regression of computed versus actual values yields a correlation index (R^2) of .958 for the best mixing simulation.

Results were improved when the mix was equilibrated to mineral phases using the predetermined saturation indices for the well. Saturation index values were computed first using the WATEQ4F program and then by the PHREEQE program. Results which had been equilibrated generated concentrations which were often within 1.0% of the actual analysis. The best mix was made with 70% I-1 added to 30% I-4 to produce the I-3 water (R^2=.983).

Although mixing to produce well I-6 did not have the same precision as the I-3 product, the results were better than the other kinds of models. The R^2 value for a 70-30 mix of I-1 + I-4 to get I-6 was .867. This improved to .993 after equilibration.

Dilutions. Waters mixed with the snowmelt data to simulate dilution yielded results with greater divergence. The pre-equilibrium R^2 values were under .8, improving to .95 to .97 after equilibration. A special dilution with snowmelt was made to compare well I-4 on April 9, to the same well on April 23 when the water table was rising. The correlation in this case was .866. Finally, a 50-50 mix of I-1 and I-4 was linked to a dilution. The compound simulation gave results which were comparable to the 70-30 mix. This may indicate how a 70-30 proportion could be generated, by diluting one of the waters with recharge as the mixing proceeds.

Recharge Solution. The least successful model was the equilibration of the snowmelt without any mixing. The saturation values for the target wells were enlisted with the goal of duplicating it through dissolution of the mineral phases. Correlation values were extremely low (R^2=.415) and only improved to a maximum of .966 after equilibrium.

Complications in the Mixing Model

Whereas most ion values could be closely approximated in the mixing computations, poor results were achieved for bicarbonate. Remarkably, the bicarbonate concentrations diverged more from the target values after equilibration than before. All other ions experienced a marked convergence to the analysis as a result of equilibration.

This discrepancy points out a striking relationship in the chemical system. One explanation for this apparent bicarbonate imbalance is that the source of the sulfate ion in the groundwater is not gypsum. Microscopic examination of core samples failed to confirm the presence of gypsum. An alternate source of sulfate could be the oxidation of sulfides in the soil. For example, pyrite uncovered in coal mining operations is known to generate abundant sulfate ion when it is oxidized.

If the sulfate is derived from sulfides, the PHREEQE model will misinterpret its presence. The equilibrium equations operate on ion pairs and so, when the mixes are equilibrated, the computer assigns calcium to match the sulfate in the water. This procedure effectively robs calcium from the calcite pairing and results in an artificial over-calculation of bicarbonate.

Source of Sulfate

The above relationship explains the computational problem, but more importantly, it provides indirect evidence that gypsum is not the source of ions. To confirm this suspicion, additional tests were made. First, mixing simulations using the PHREEQE program were run on water analyses from the Stillwater, Oklahoma area. Data from Hagen (1986) and Hoyle (1988) and Ross (1988) for groundwater in the Ashcroft Siltloam were used. Although the same procedures were followed as for Fred Creek mixes, the Stillwater data did not produce a bicarbonate discrepancy. This indicated that the problem was not in the mechanics of the program but was a response to the input data.

For further confirmation, core samples from Fred Creek were tested for the presence of sulfides. The sodium azide-iodine test was chosen from Feigl (1958) as a definitive test for insoluble sulfides. The common mineral pyrite is not readily soluble, and cannot be identified by tests which rely on detecting hydrogen sulfide gas. Instead, in the chosen test, the sulfide ion acts as a catalyst in a reaction between sodium azide (NaN_3) and iodine. In the presence of sulfide, the chemical reaction occurs which liberates nitrogen gas. Even small grains of sulfide minerals will cause the formation of nitrogen gas bubbles in the solution.

First the test was run on a ground specimen of pyrite to confirm that it worked. Next, controls of granulated halite and quartz sand were tested. They gave negative results. Finally, core samples from wells I-4, I-1 and I-3 were tested. Many samples responded positively to the test with the least response occurring in the I-1 samples. Silt size grains and grain coatings caused the liberation of bubbles in the test solution. Although these samples appear reduced by the pervasive dark gray color, no opaque or metallic pyrite grains had been previously recognized. The results of the tests indicate that sulfide is present in a finely disseminated state throughout much of the area.

Consequences of Sulfide Oxidation

Hem (1985) describes the oxidation of pyrite as a significant source of sulfate ions for groundwaters. The pyrite is associated with highly reduced sediments such as coal sequences and certain marine shales. The oxidation reaction releases hydrogen ions to the water, increasing the acidity and in extreme cases, acid mine drainage occurs. Moran et al. (1978), describe widespread pyrite oxidation in west-central North Dakota associated with lignite deposits which supply sulfate to the groundwater. The reaction they report (Chem Eq. 2) yields 4 hydrogen ions for every molecule of pyrite oxidized. Kennedy (1986), cites a complex of four reactions involving the bacteria _Thiobacillus ferroxidans_ and states that five hydrogen ions are released for every pyrite molecule. In either case, there is a proliferation of acidity.

$$4FeS_2 + 15O_2 + 14H_2O \text{ ---> } 4Fe(OH)_3 + 16H^+ + 8SO_4^= \qquad \text{(Chem Eq. 2)}$$

If the source of the dissolved sulfate in the vicinity of well I-4 is pyrite, there should be an indication of the extra H^+ and also the Fe^{+2} which are generated. The pH of the I-4 water ranged from 6.4 to 6.7 throughout the year and was not as low as the I-1 or

I-3 wells. The area of high sulfate is near the valley wall where limestone and calcareous siltstone subcrop the terrace. The release of H^{+} ions would be countered by dissolution of limestone resulting in a buffering of the solution. The highest concentrations of both calcium and bicarbonate are recorded from the I-4 and I-6 wells which also have the highest sulfate levels.

$$H_3O^{+} + CaCO_3 \text{ ---> } Ca^{2} + HCO_3^{-} + H_2O$$

(Chem Eq. 3)

The ferrous iron released when pyrite is oxidized would become mobilized and form iron oxides where oxidizing conditions develop. Iron oxide staining and cementing crusts pervade much of the alluvium. Sieve analysis showed that much of the sand-size fraction from many wells is actually aggregated silt and very fine sand, cemented by iron oxide crusts. Although quartz dominates the deposit, iron oxides cover and cement most grains.

$$2FeS_2 + 2H_2O + 7O_2 \text{ ---> } 2Fe^{2} + 4SO_4^{=} + 4H^{+}$$

(Chem Eq. 4)

$$4Fe^{2} + O_2 + 4H^{+} \text{ ---> } 4Fe^{3} + 2H_2O$$

(Chem Eq. 5)

$$Fe^{3} + 3H_2O \text{ ---> } Fe(OH)_3 + 3H^{+}$$

(Chem Eq. 6)

In the computer manual for the PHREEQE program (Parkhurst, el.al., 1985), an example of pyrite oxidation is presented. The format of the example is to add one mole of oxygen in small increments to pure water and then set it in equilibrium to pyrite, goethite, gypsum, and calcite. By the point where 0.1 mole of oxygen is added, concentration levels and saturation indices are attained which are comparable to the I-4 well. The pe of the model (4.0) is even lower than used for the I-4 well (13.88), based on dissolved oxygen content, indicating there is adequate oxidation potential for the generation of sulfate.

Oxidation of electron donors such as organic carbon and hydrogen sulfide is considered the earliest stage of redox reaction in an open groundwater system (Champ, et.al. 1979, Stumm and Morgan, 1981). Whereas, ions are susceptible to reduction along a flow path in an anoxic environment, there is a sequence of oxidation which occurs in open oxidizing systems. Stumm and Morgan (1981) report that dissolved organic carbon is first to be oxidized, followed by H_2S, Fe^{++}, NH_4^+, and Mn^{++}. The product of the first is CO_2 which becomes dissolved in the water as HCO_3 and the sulfides are oxidized to $SO_4^=$.

Stoichiometry of the Reactions

Beyond the inferences made from the computer modeling and the identification of sulfides in the core samples, it is important to explore the reactions involved to see whether the source of sulfate in water can be predicted stoichiometrically. Hem (1985) states that simple solution reactions may be studied as a function of the concentrations of the ion products until the groundwater has become saturated with a particular mineral phase. Thereafter, the concentrations are governed by the chemical equilibrium of the mineral phases that could precipitate or alter solubility of other minerals.

For recharging waters subject to the oxidizing sequence described earlier, the dominant reactions would be: a) oxidation of sulfides producing sulfate and hydrogen ions (Chem Eq. 2), b) solution of limestone by low pH water (Chem. Eq. 3), and c) solution of limestone by carbonic acid formed when carbon dioxide is dissolved (Chem. Eq. 1). The product of sulfide oxidation is 2 H^+ ions for every $SO_4^=$ ion. In turn, the 2 H^+ ions yield 2 Ca^{+2} and 2 HCO_3^-. The concurrent process of carbonic acid solution of limestone produces 2 HCO_3 ions and 1 Ca^{+2} ion. If no other processes are involved, the resulting concentrations should be 1 mole of $SO_4^=$, 3 moles of Ca^{+2}, and 4 moles of HCO_3^-.

In order to compare the actual analyses to the theoretical results, a triangular plot was made of relative concentrations of Ca + Mg, HCO_3, and SO_4, expressed as percent of total milliequivalents. In addition to the Fred Creek data, analyses were selected from Hem (1985) depicting Ca and SO_4 dominant waters and from Moran et.al. (1978), including waters where sulfide oxidation was postulated as a source of sulfate. Also, analyses from Thomas and Glover (1989) were used for plots of water from the Blaine Gypsum aquifer of southwest Oklahoma. This plot is shown in Figure 47.

Subdivision of the triangle plot into sectors identifies waters which result from combinations of the various reactions involved. Simple gypsum solution is represented by analyses plotting near the junction of 50% Ca + Mg and 50% HCO_3 (point 4, Fig. 47). Limestone solution by carbonic acid is indicated at the junction of 50% Ca + Mg and 50% HCO_3 (point 1, Fig. 47), whereas mere solution of CO_2 yields the high HCO_3 values at the lower left apex. Sulfide oxidation without solution of carbonates should plot at the SO_4 apex. If pH values are below 4.0, bicarbonate will not be detected and so carbonate solution by sulfuric acid will plot on the "0" line of HCO_3.

The theoretical concentrations for sulfide oxidation and resulting limestone solution by acidified water (2 meq. SO_4 + 4 meq. Ca + 2 meq. HCO_3) plot at the mid-point of the 50% Ca line (point 3, Fig. 47). The addition of carbonic acid solution of limestone to the above process produces a water (2 meq. SO_4 + 6 meq. Ca + 4 meq. HCO_3) which plots on the 50% Ca line but closer to the Ca-HCO_3 base (point 2, Fig. 47). The combination of gypsum and limestone dissolution produces 2 meq. SO_4 + 4 meq.Ca + 2 meq. HCO_3 falling on the mid-point of the 50% Ca line.

The Fred Creek data plots in a tight cluster around the theoretical value for combined sulfide oxidation and

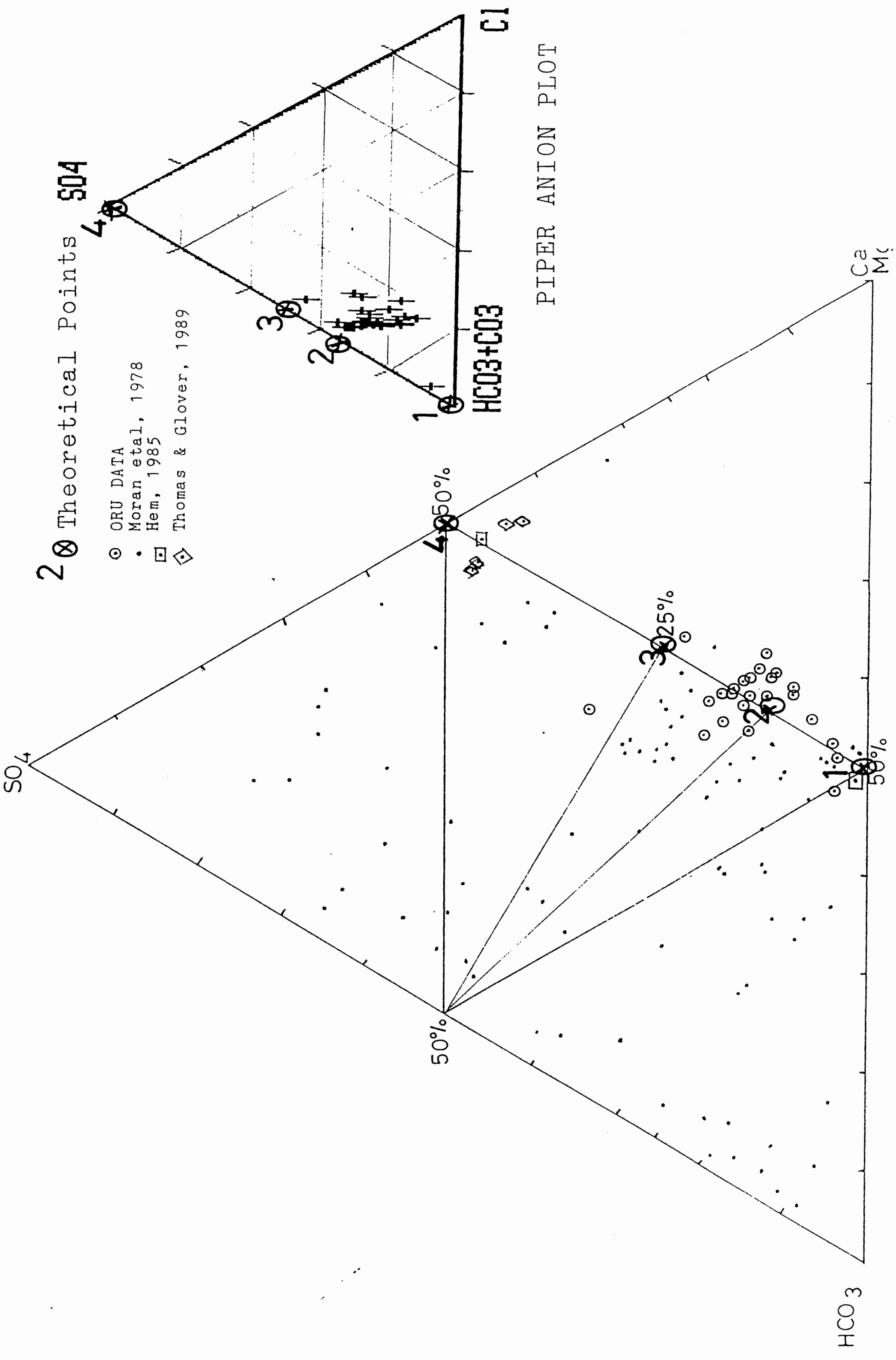


Figure 47. Triangular Diagram of Sulfate, Bicarbonate, and Calcium Plus Magnesium

carbonic acid solution. Only one of the twenty analyses plots closer to the theoretical proportions for sulfide oxidation-limestone solution without carbonic acid.

One analysis from Hem (1985) and four from Thomas and Glover (1989) plot in the gypsum solution sector. These are all waters from gypsum aquifers.

The data from Moran et.al. (1975) is scattered throughout the triangle below the 50% Ca line. Many values fall near the ORU data, some are concentrated near the HCO_3 apex, a few are in the limestone solution area and some in the gypsum solution area.

The distribution of the ORU and North Dakota data compared to those from gypsum aquifers shows that waters containing sulfate can be separated according to the source reactions of the sulfate. Figure 48 contains the major sectors where products of sulfide-carbonate reactions plot. There is a definite separation of gypsum solution from sulfide oxidation-carbonic acid solution of limestone. Transitional values do occur between sectors which may indicate the progression of waters through the oxidation sequence in a recharging system. The separation is adequate, however, to make a distinction between sulfate sources and may serve as a general test for distinguishing gypsum and sulfide derived sulfates.

In order to put these trends in a familiar format, the same reaction proportions were located on the anion

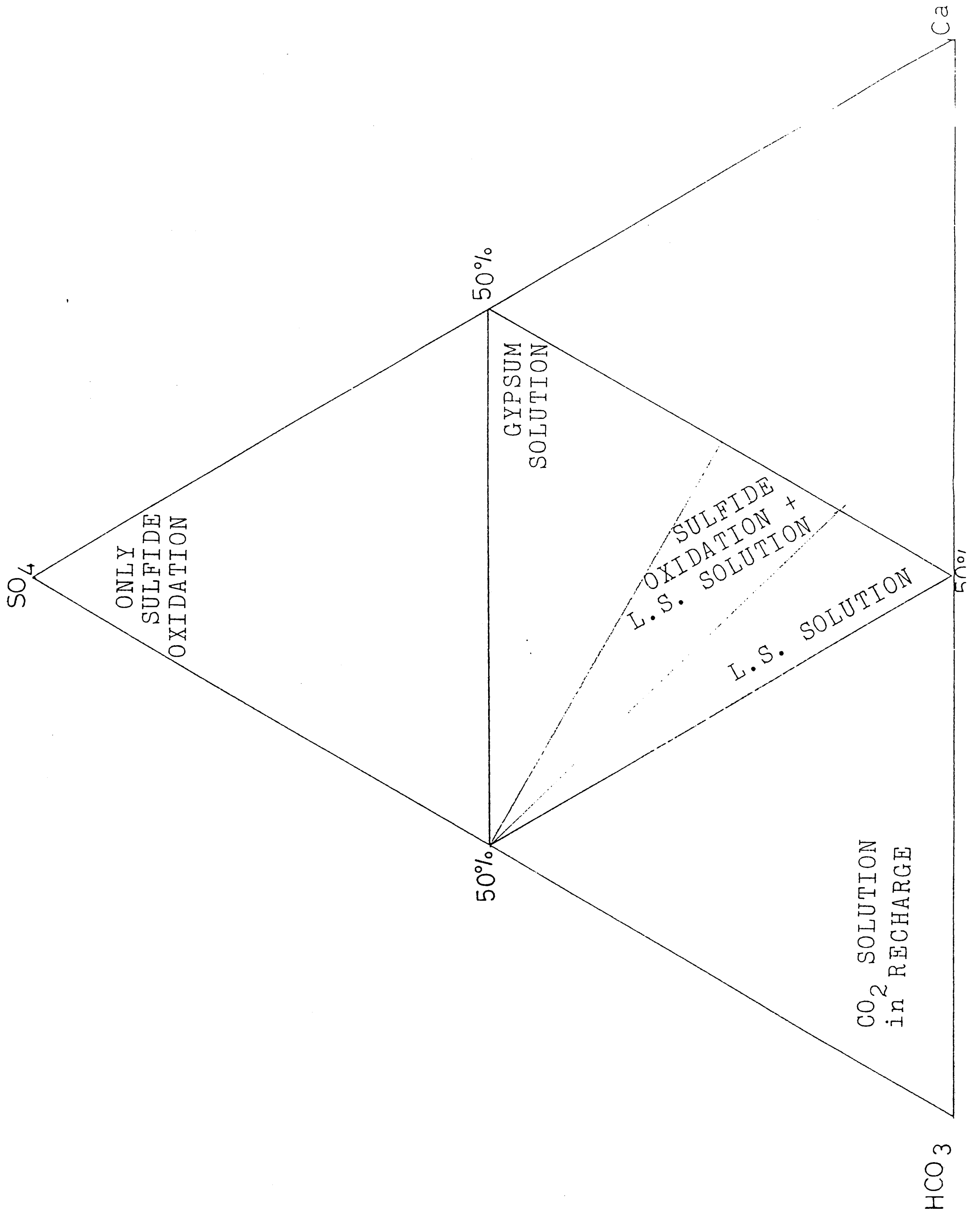


Figure 48. Reaction Locations on Triangular Plot

portion of a Piper plot (also on Figure 47). If chloride is negligible, theoretical points 1 through 4 are located in the same relative spacing as on the other diagram. The trend of data points should be directed toward the lower third of the 0% Cl line (point 2) if sulfide oxidation in conjunction with carbonic acid dissolution of limestone has occurred.

Simple gypsum solution should be located near point 4 and trends of mixed gypsum and limestone solution would point toward the sulfate apex. Sulfate origin should be discernable on an anion plot; however, varying chloride content may mask the simple trends. It is therefore recommended to make the Ca-SO_4-HCO_3 plot for greater certainty of interpretation.

Conclusions

Computer modeling of the thermodynamic conditions in the aquifer supplements the interpretations drawn from simpler techniques and clarifies the geochemical model. The results of applying the PHREEQE model lead to the following conclusions:

1.) High concentrations of sulfate in the I-4 area are caused by oxidation of sulfides in the Quaternary terrace. The associated release of hydrogen ions triggers the accelerated solution of limestone so that calcium and bicarbonate levels are also very high. The increase in SO4, Ca, and HCO3 significantly raises the

TDS levels as well as the specific conductance.

2.) High concentration water (I-4) flows toward the discharge point and mixes with low concentration water (I-1) moving down the axis of the valley. The mixing results in intermediate concentrations in the intervening well (I-3).

3.) Dilution of the groundwater by spring recharge modifies the mix. The result is a best agreement for a mix of 30% I-4 water with 70% I-1 water.

4.) The waters continue to adjust to the mineral phases while mixing and calcite can be dissolved or precipitated to bring about the final equilibration. Some amount of equilibration is always needed to attain the best match of the data but complete equilibrium is never attained.

5.) A similar relationship occurs between the I-6, I-7, and I-1 wells on a separate flow path. The location of the high concentration waters of oxygenated recharge waters is a critical factor in generating the elevated concentration of sulfate, calcium, and bicarbonate. Even though sulfides are identified throughout the aquifer, only those being oxidized will release sulfate to the groundwater.

CHAPTER VIII

WATER QUALITY

Major Ions

Some areas of south Tulsa withdraw groundwater from terrace and river alluvium for domestic use and irrigation. The chemical quality of the water varies within the aquifer and treatment needs vary accordingly. Table 10 lists the major ions from the Fred Creek aquifer which exceed federal drinking water standards and also, concentration ranges for other ions which may degrade the quality of drinking water.

The high total dissolved solids values are caused by elevated Ca, HCO3 and SO4 concentrations. High Na and Cl concentrations are not a problem in the alluvial groundwaters which are far enough from the river. The river water and groundwater close to it are commonly too saline to be used without treatment. Depending on use, the high hardness and sulfate values would need to be reduced to a more desirable level. The remaining major ions and pH levels fall within acceptable limits.

TABLE 10

WATER QUALITY OF FRED CREEK AQUIFER

ION/PARAMETER	CONCENTRATION RANGE mg/l	MCL	PRIORITY POLLUTANT
pH	6.2 - 7.5	5-9	---
TDS	306 - 1359	250	---
SULFATE	25 - 375	250	No
NITRATE	1.8 - 14.5	45	No
	TRACE METALS ug/L		
CADMIUM	3 - 10	10	Yes
COPPER	10 - 50	1000	Yes
IRON (total)	<10 - 950	300	No
LEAD	Below Detection	50	Yes
MANGANESE	<60 - 3900	100	No
SILVER	Below Detection	50	Yes
ZINC	10 - 50	5000	Yes

TABLE 11

WATER QUALITY OF NEARBY WATERS

ION/PARAMETER	OWRB s. 17 7-5-88	OWRB s. 33 7-5-88	ARK. R. 11th St. 5-31-88	S. HILLS T-1 11-15-91	M-COMP
pH	7.5	6.2	8.5	6.3	6.5
TDS	214	163	1370	280	407
SULFATE	52	20	260	41	55
NITRATE	2.8	33.6	1.8	4.8	6.6
		TRACE METALS ug/L			
CADMIUM	5	5	<1	n.a.	n.a.
COPPER	10	39	2	n.a.	n.a.
IRON (total)	78	122	30	1118	350
LEAD	45	45	<5	n.a.	n.a.
MANGANESE	10	10	80	60	100
SILVER	NA	NA	<1		
ZINC	10	105	<10		

Minor Ions

In addition to determining major ion concentrations, analyses were made for nitrate, total iron, total manganese, and also for selected trace metals. The first three ions were analyzed with wet chemical methods whereas atomic absorption spectrometry was used to test for the presence of silver, lead, copper, zinc, and cadmium.

Nitrate

Samples collected during the spring and fall of 1990 and also in February of 1991 were all evaluated for the minor ions. Nitrate was selected because of the national concern over increasing levels of nitrate being detected in groundwater. Nitrate is derived from the oxidation of ammonium by nitrifying bacteria in the soil. The ammonium may be derived from the hydrolysis of fertilizers or by bacterial action on decaying organic matter. Some nitrates are applied directly to croplands as fertilizers. Application exceding plant need results in leaching to shallow aquifers or washing into streams. Poorly timed application of fertilizer may encourage pollution because plant growth is not adequate during dormant seasons to uptake all the nitrate.

In urban areas, nitrate pollution can be generated by homeowners using improper application management or by the high volume use of fertilizer on golf courses. Masters theses by Hagen (1986), Ross (1988), Hoyle (1988), and Froneberger (1989) report phases of a project in Stillwater, Oklahoma where the groundwater under a residential lot was monitored for nitrate derived from downward leaching of fertilizer. Concentrations reached levels which exceed the USEPA maximum contaminant level of 45 mg/l (as NO3) but the concentrations varied widely with depth and with time.

The monitor wells on the ORU campus are located in unimproved grass fields. No fertilizers are applied to the fields as they are merely used for jogging and exercise. The only on site nitrate contribution would come from decay of vegetable material when the clover and short grasses die back in winter and from animal droppings. For much of the year of study, a flock of 50 Canadian geese adopted the campus lake area for a home. Their foraging habits drove them repeatedly across the field study area in a manner similar to a grazing herd of cattle. They definitely contributed to the nitrogen budget of the field, but the effects of this have not been detected so far.

The nitrate concentration from all samples ranged from 1.76 to 14.5 mg/l (as NO3) with a mean value of 7.0 mg/l. The highest concentrations occurred in the I-6 well and the "Tributary" locality. Well I-6 is the closest well to residential development and the stream designated "Tributary" is fed by runoff collected through storm sewer pipes from a neighborhood. One high level was recorded in the I-1 well in November. This well is across the street from several homes. The lowest values were always found in the I-3 and I-4 wells and the "Northeast Bridge" surface locality. These two wells are isolated, farther from home lots where fertilizer would be used. All samples had nitrate values below the federal recommended maximum of 45 mg/l as NO3.

Water quality of well samples for residential areas 1.5 miles south and 7 miled southeast of the ORU campus and from a golf course and public school campus 1.5 miles north are provided in Table 11. The nitrate values from these outlying areas are all within the maximum acceptable limit. The highest value, 39 mg/l, is from the farther residential area.

Iron and Manganese

Iron and manganese do not pose health hazards in drinking water but elevated concentrations cause staining and undesirable taste. Iron and manganese oxide crusts are common in the Fred Creek alluvium. They were probably deposited in the stream bed as grain coatings and laminae. The mean total iron concentration was 218 ug/l and the manganese concentration mean was 780 ug/l for the wells that had detectable levels (12 of

29 analyses were less than detection limit). For the most part, samples were within the acceptable range. One of the highest iron values came from the well with steel casing which appears to be actively corroding. A scum of iron oxide is always present at the top of the standing water.

Trace Metals

Five trace metals were investigated with atomic absorption spectroscopy. A preliminary project undertaken in the spring of 1990 evaluated lead, cadmium, and silver but detected no absorption for any sample. A second project was run during the spring of 1991. Preliminary analyses of lead, copper, zinc, silver, and cadmium gave no measurable results, so the samples were concentrated by a ten to one factor. The concentrated samples showed no measurable lead or silver, but values for zinc, copper, and cadmium were determined. Ranges are listed in Table 10.

According to Hem (1985), copper, zinc, and cadmium can be dissolved from natural sources but they can also be leached from construction materials. Copper plumbing supplies corrode under acidic conditions and zinc and cadmium are used as paint additives and in the galvanizing process for iron. They could be found in a variety of materials used in residential construction.

The I-3 well was highest in zinc and copper and also had cadmium levels as high as any well. The levels are all below federal maximum contaminant levels and do not pose any threat. There is an iron sanitary sewer line 41 feet north of well I-3 which is buried at a depth just above the current water table. The distribution of trace metals is actually fairly consistent among the wells sampled. This implies that there is a source in the mineralogy of the sediment.

Waters from the comparison areas listed in Table 11 had concentrations of cadmium, copper, and zinc which were similar to the Fred Creek aquifer samples. Whereas lead was below detection in Fred Creek analyses, the outlying areas had measureable levels.

Organic Chemicals

To appraise the potential for organic contamination, tests were made for two broad indicators, total organic carbon (TOC) and total organic halogen (TOX). This approach was taken as a reconnaissance level evaluation because the cost of compound-specific testing is very great.

Total organic carbon was analyzed in the I-1, -3, -4, and -7 wells in July of 1990. Elevated levels of TOC can indicate the presence of petroleum derived hydrocarbons. This test was chosen because it has been used widely in field studies as a general indicator for contamination (Brouwer, et.al. 1984). Organic carbon in the water may also come from natural sources through the leaching of humic constituents from the top soil. Substantially high levels must therefore be detected in order to merit further testing. Suspect wells or areas can be highlighted and more complete testing for hydrocarbons can be limited to those alone. Spruill, 1988, presented a field study where refinery wastes had contaminated the soil and groundwater aquifer on the flood plain of the Arkansas River in southwest Kansas. A statistical evaluation of TOC levels compared to the number of actual hydrocarbons identified was made. There was a significant correlation between them when the TOC level was above a background level of 6 mg/l.

The results of the TOC analysis at Fred Creek are listed in table 12 along with total organic halogen. Three of the four wells have comparable levels, near 15 mgl but the I-7 well recorded 46 mg/ TOC. Compared to the study by Spruill (1988), a level of 46 mg/l could indicate hydrocarbon presence whereas levels as low as 15 mg/l may be background.

TABLE 12

RECONNAISSANCE TESTS FOR ORGANIC COMPOUNDS

SAMPLE LOCATION	TOC	TOX
	mg/l	mg/l
Well I-1	16.0	0.036
Well I-3	16.0	0.048
Well I-4	14.0	0.051
Well I-7	46.0	0.199
NE Bridge	----	0.063
Lake Evelyn	----	0.059

There are two possible sources for hydrocarbons in the campus area. The primary one is a battery of gasoline storage tanks buried a few hundred feet northwest of well I-4 in the bedrock hill of the north valley divide. The water with the highest TOC level is much farther from the source than the intervening I-4 and I-3 wells. Samples from the nearby wells only have background levels of TOC.

Another possible source is one or more plugged and abandoned oil well locations east and west of the study area at distances of 0.4 miles. Only the well to the east is upgradient and located near the colluvium zone as the base of the divide (Figure 6). Pollution from oil wells is often accompanied by high levels of sodium and chloride from the subsurface brines associated with crude oil. All the wells in the Fred Creek valley have quite low sodium and chloride levels and so an oil well source is doubtful.

To be more certain of the presence of hydrocarbons, a more specific reconaissance test could be run. The test for benzene, toluene, and xylene is often used for detecting oil related hydrocarbons. This would be an economical step, short of a comprehensive test for a suite of organic compounds.

The total organic halogen test was run as a broad indicator for any chlorinated solvents. The same wells as before were tested (Table 12) as well as samples from two surface locations. All but one sample had less than 0.065 mg/l TOX. The I-7 well had almost 0.2 mg/l, which was 3 to 5 times higher than other samples. Because this well also had the highest TOC readings, it is identified as a candidate for further testing.

Well I-7 was cased with steel casing so that a comparison could be made with the water in wells cased with PVC. Curiously I-7 had the highest levels of both TOC and TOX. The steel pipe was slotted with a power saw and lubricating oil was used during sawing. Although the pipe was cleaned with soapy water and rinsed with boiling water, some oil could have remained. Before an expensive suite of tests is ordered for well I-7, the TOC and TOX tests should be repeated on recent samples to see if levels are still high after 9 months. The very low levels of TOX in the PVC cased wells implies that there is no problem with leaching of organics from the pipe.

Although tests for contamination were not inclusive of all possible pollutants, the water quality appears mainly limited by the high hardness and pockets of high sulfate concentration. The I-6 well, at the northeast corner of the campus, adjacent to residential tracts, had cadmium at levels higher that the USEPA maximum contaminant level. Otherwise, the water can be characterized as undesirable, but not contaminated by toxic compounds. Further testing for organics should be done to complete the assessment.

The published analyses from the residential wells and the samples analyzed from the golf course show results which are within the same range as most of the ions tested from the Fred Creek aquifer. Based on this comparison, the range of values determined for Fred Creek samples most likely represents natural variation from sedimentary sources.

In the future, more complete tests will be done by the OWRB for the I-4 and I-1 wells. It is also hoped that the mass spectrometer at ORU may be used to test for other hydrocarbons in all wells.

CHAPTER IX

RESULTS AND CONCLUSIONS

Hydrogeologic Conclusions

As a result of investigation of the sedimentologic, stratigraphic, and hydrogeologic character of the Fred Creek Valley, a variety of conclusions can be made regarding the aquifer. Following are pertinent observations and conclusions which have come out of this study:

1.) The Fred Creek Valley aquifer is actually a combination of Quaternary terrace deposits, younger Quaternary stream alluvium, and highly weathered siltstone of the Pennsylvanian, Nowata Shale.

2.) The three units are in hydraulic continuity with each other.

3.) Although Fred Creek Valley opens into the Arkansas River flood plain, the water table in the river aquifer is much lower than that in the valley. Drainage of the sandy flood plain deposits by deepened flood control channels may have lowered the water table to the point where it is virtually separated from the valley aquifer.

4.) The Fred Creek aquifer is in equilibrium with the creek and discharges to it along its course. After the creek flows onto the river flood plain, it becomes a losing stream.

5.) The sediments of the valley and the weathered bedrock are dominated by quartz silt with subordinate amounts of clay and iron oxides. The hydraulic conductivity, transmissivity, and storativity values are low because of the small grain size.

6.) Evapotranspiration during the growing season causes a major drain on the groundwater which is at least equal to the water lost by discharge.

7.) The most demonstrable episodes of recharge occurred during a time of snow melting.

8.) Low soil moisture zones were often encountered several feet below the surface when drilling wells. Recharge by downward piston flow is not considered a consistent process in the aquifer.

9.) The most rapid response to recharge events was recorded in the well closest to the valley wall.

Hydrogeologic Model

From these conclusions, a hydrogeologic model can be constructed. The block diagram of Figure 49 illustrates this model.

Pleistocene erosion of the Pennsylvanian bedrock

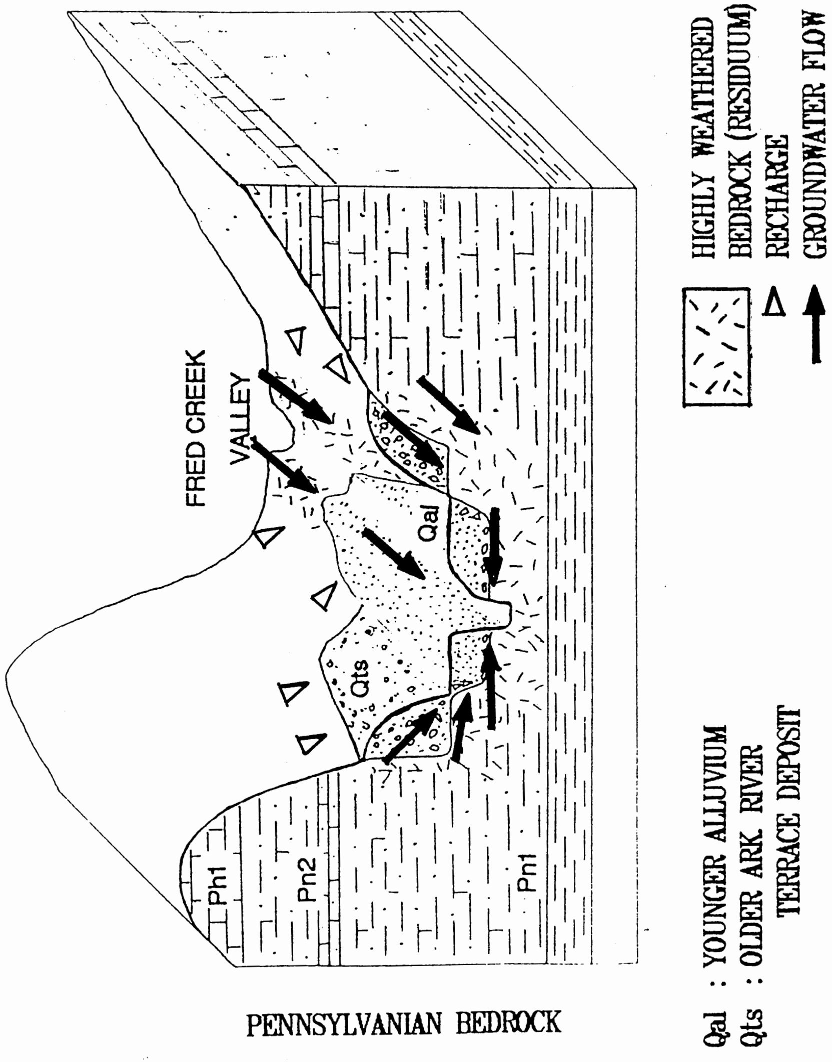


Figure 49. Block Diagram of Fred Creek Valley Showing Flow Paths

cut down to the lower Nowata Shale and the valley floor became covered by a deposit of lag gravel derived from the Seminole Formation sandstone beds. The lower valley was within reach of flood waters of the ancient Arkansas River. Overbank and backwater deposits from the river are now preserved as discontinuous terraces. Some of the terrace deposits were swampy, accumulating considerable amounts of organic matter in a reducing environment.

While exposed in the valley floor, the Nowata siltstones became deeply weathered, losing much of the calcareous matrix by solution. With rejuvenation of the Arkansas River, the creek cut down through the terrace deposits and eventually became choked with its own sediment. The result of these events was a system of three porous deposits in contact with each other.

Water recharges the present day aquifer along the valley perimeter where colluvium zones serve as high permeability collection sites. Although low permeability away from the colluvium inhibits recharge from rain episodes, snow melt releases water more gradually and deeply penetrating infiltration reaches the water table. Groundwater flows down the center of the valley through the weathered bedrock zone and alluvium and also flows from the valley walls in toward the axis of the valley.

Groundwater discharge keeps the creek flowing throughout the year except in the upper reaches where the water table drops below the creek bed level. Discharge also maintains the level of the man-made lake unless the water table drops too low by end of summer.

Geochemical Conclusions

Following are the primary conclusions which have been drawn from the geochemical relationships:

1.) The Fred Creek groundwater is dominated by calcium and bicarbonate ions which is fairly typical of a recharging system where dissolution is active.

2.) A subordinate portion of the aquifer has higher concentrations of Ca^{2}, HCO_3^-, and $SO_4^{=}$, than in the central valley, even though the areas are hydraulically connected.

3.) Mapping of total dissolved solids, conductivity, ion concentrations, and saturation indices show that there are trends of transition between the anomalous area and the main valley.

4.) Trilinear plots show possible indications of mixing waters.

5.) Cross plots of Chloride versus water elevation indicates episodes of dilution.

6.) Geochemical modeling supports both mixing and dilution but suggests that sulfate is not derived from gypsum dissolution.

7.) Chemical tests of core samples identify pyrite in the reduced sediments of well I-4.

8.) Sulfate derived from oxidation of sulfides can be distinguished from that coming from gypsum solution if limestone solution is a concurrent reaction. This is possible using a triangular plot of percentage concentrations of sulfate, bicarbonate, and calcium plus magnesium.

Geochemical Model

A geochemical model can also be fashioned to explain the observations. Water recharges the upper valley beyond the limits of alluvium deposits. Solution of CO_2 that builds up in the soil drops the pH of the recharging water so that it can dissolve some calcite from the bedrock but the groundwater flowing through the bedrock zone is characterized by low levels of total dissolved solids.

Snow melt charged with dissolved oxygen infiltrates the reduced terrace deposits and reacts with finely disseminated pyrite grains (Figure 50). As a result of the oxidation of the iron sulfide, $SO_4^{=}$, Fe^{+2}, and H^+ ions are taken into solution. The prolific generation of H^+ causes a drop in pH which triggers calcite dissolution in the valley wall area. The net result is a significant increase in the concentration of sulfate, calcium, and bicarbonate ions in solution and a buffering of the pH. Oxidation of sulfide is an early

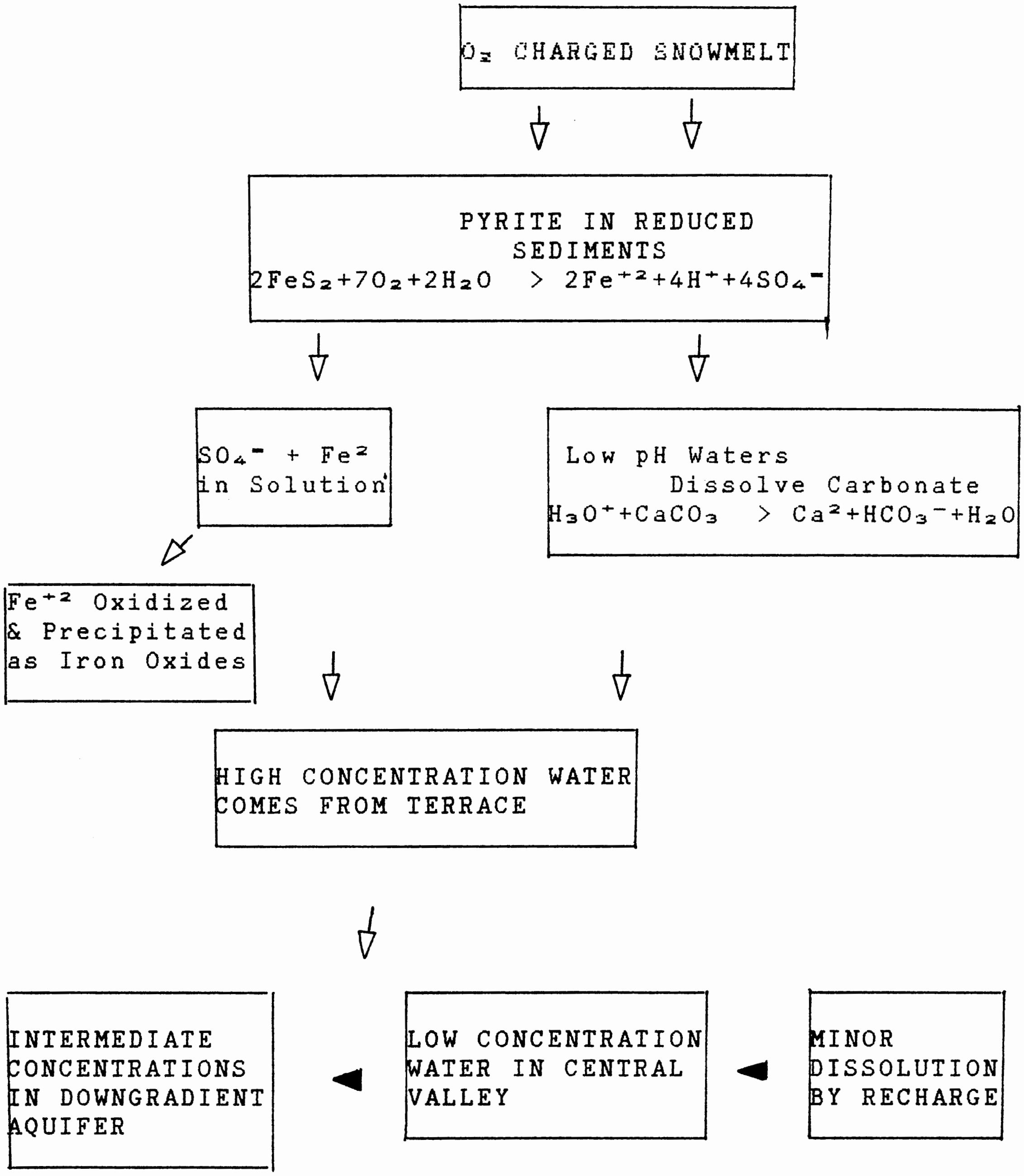


Figure 50. Geochemical Model

step in chemical evolution for recharging water in an open groundwater system (Stumm and Morgan, 1981).

Moving down gradient, the high concentration water mixes with the lower concentration water of the valley, resulting in intermediate concentrations. The waters are still undersaturated, so dissolution of soluble minerals continues. Recharge reaching the water table by way of macropores serves to dilute the mixture.

Major production of sulfate occurs in the winter when snowmelt recharges the terrace by piston flow. For the remainder of the year, sulfate levels drop due to dilution. Calcium solution tracks that of sulfate but bicarbonate remains high through the growing season due to the addition of plant generated CO_2 to the groundwater.

This model explains the counter trend in water concentrations and is compatible with the widespread occurrence of iron oxides throughout the aquifer. Pyrite oxidation is generally reported in association with coal mining operations, but wider occurrences have also been studied in reduced sediments of the Plaines States (Moran, 1978). Although sulfate in groundwater in most frequently linked to solution of gypsum, oxidation of pyrite may be more common than realized.

Characterization of groundwater for determination of background levels in monitoring situations may become complicated by localized mineralogies. It is important to recognize the multiple sources of common ions. Sufficient data must be gathered to explain divergence from normal trends in geochemistry but geochemical modeling can greatly enhance interpretation.

Water Quality

The quality of the groundwater is limited by the high sulfate and TDS levels. The quality is lowest near where oxidizing recharge waters are reacting with sulfide bearing sediments. Quality improves as water from different portions of the aquifer mix down gradient. Levels of trace metals for which tests were made are within federal and state limits and dissolved nitrate is well within the acceptable range. Based upon general tests for organic carbon and organic halogens, significant contamination by organic chemicals is not indicated; however, more definitive tests are needed to assess the specific concentrations. Overall, water in the Fred Creek aquifer does not appear to be contaminated. Due to the diluting effects of mixing, water that discharges to the creek or flows underground to the Arkansas River flood plain does not degrade the quality of other water sources in the area.

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APPENDIX A

DESCRIPTION OF CORE SAMPLES

DEPTH	DESCRIPTION
WELL I-1	
2	SOD
14	md. brn CLAY
19	md. brn. SNDY CLAY
25	brn/blk, fn. SAND, calc cem?
32	ylw brn/brn fn. SAND % sndy CLAY
36	brn. fn SAND w/ blk clay
42	vy dk brn/blk fine SANDY CLAY (A zn)
46	blk fn. SAND & CLAY
54	blk fn. sandy clay
60	dk. fn sandy, incr. in CLAY
69	dk brn. fn SAND
76	A.A. w/ incr. in clay
84	md. brn, fn SAND, ylw & brn mottles
92	gray & md. brn, fn. SAND, w/ ylw-brn
99	A.A. w/ blk Sh. clasts & SS. cobbles
107	gry & ylw brn. fn. SAND, clalyey
115	ylw brn to brn fn sndy clay, moist
120	A.A.
128	A.A. sndy clay
136	A.A. w. blk Sh. clasts. vy wet @ btm
147	brn SANDY CLAY, very wet **
158	A.A. dripping wet
167	brn & gray; red brn w/ blk weath. Sh
176	A.A. lost 1/2 sample, wtr in barrel
180	A.A.
185	A.A. very muddy
	standing water @ 11'6" (138")

WELL I-2	50' s. of SEWER LINE AT S. BANK OF CK DESCRIPTION
0-16"	Dark surf soil, good A horizon
6-18"	Md brn, fn Snd & clayey Snd, some yellw brn
18-24"	Brn/yell brn w/ some black clasts clay incr. to fn sndy Clay
24-30"	A.A. w. few ss cobbles (1" diam)
30-37"	Slightly darker, still has a lot of clay.
37-42"	Hard spot, md brn fn Snd, very loose, 1
42-47"	A.A.
47-52"	A.A. recov 2 pieces iron stained SS
52-60"	A.A. md brn w. some pockets of yllw brn sdy Loam; sev iron stained SS cobl
60-66"	A.A. w/o cobbles, good loam but dry
66-76"	Brn sdy Loam, loose
76-90.5"	Brn fn Snd, slightly loamy
90-96"	Brn fn Snd w/ some black mottles
96-112	Good fn Snd, somewhat more moist
112-127"	Dark brn moist sand
127-137"	A.A.
137-140"	Hit hard layer, some SS in barrel some moist clay
140-144"	SS & gravel
148"	Cannot penetrate sandstone
T.D. 12'4"	

WELL I-3	DESCRIPTION
0-6"	Md. brn to yllw brn fn sd. to clayey sd.; orange sand at base
6-12"	Orange md. Sd. (fill); dk. brn sdy clay at base.
12-18"	Dk. brn. fn sndy Loam w/ some rootlets
18-24"	AA w/ dk brn to blk clay clasts HARD DIGGING !
24-28"	Md brn fn Sd. & sdy Loam, dry & powdery
28-34"	A.A. - HARD DRILLING !
34-40"	A.A.
40-46"	A.A.
46-59"	FAST DRILLING, md. brn Loam
59-65"	Dried wood, becoming sandier, md. dk. brn
65-71"	A.A. fn. snd, md/dk brn w/ few ironstone pebbles.
71-75"	A.A. w/ black clay clasts
75-81"	A.A. silty
81-91"	A.A., slightly damp, FAST DRLG
91-102"	WOOD; fn sndy loam & dk gray clay and damp silt
102-111"	Dk gray clay w/ red orng, pockets becoming lt. gray sndy clay, damp, very plastic, easy drlg
111-118"	Gray-green sndy clay, very plastic
118-127"	Gray green fn sndy clay, moist & plastic w/ some yllw-brn
127-133"	Gray /yllw brn. fn sndy clay; moist
133-145"	Bubbling while drlg; md. brn & yllw brn fn/md clayey Snd; SATURATED
145-158"	No Sample
158-166.5	Yllw brn to orng fn/md Sd some is clay rich
166.5-178	Md. brn clayey Snd
178-182.5	Lost Sample
182.5-196	Half barrel full; Brn clayey Snd
196-200"	Half barrel full
200-207'	A.A.
T.D. PIPE	

WELL I-4

DEPTH	DESCRIPTION
0-15"	Drk brn, clay loam, few drk red clasts
15-20"	Same w/ a ss. cobble
20-28"	Dk brn to ylw brn clay loam
28-38"	Md brn & ylw brn fn sdy clay loam
38-57"	Md brn loamy clay
57-64"	Dk gry clay & Fn sdy clay
64-66"	Vy dk clayey loam w/ ss.cobbles
66-72.5"	Vy dk black loam
72-82"	Black clay & loam
82-86"	Black sandy clay
86-96"	AA black loam
96-107"	Blk loam & brn sdy clay loam
114-120"	Dk brn & orange brn sdy clay loam
125-133"	Gry & lt ylw brn mott clayey fn sand
133-143"	Gray & ylw brn clayey sand
150-155"	Mostly gray w/ ylw brn clayey fn sd
155-164"	Very gray & moist
168-173"	Gray fn sdy CLAY
173-183"	Sandy clay, gray & brn
183-190.5	AA w/ weath. ylw brn ss. & gravel
	A=gray sd B= gravel & ss.
190.5-195	Ylw brn snd & ss. 4 cm. dia, angular
195-204"	
204"	Md orang brn clay, very plastic w/ charc
210-218"	some weath. dk red spots
	AA. reddish brn clay
218-227"	Clay w/ frags of ss., CLAY is dry
T.D. 228"	and impermeable
19 ft.	

WELL I-5	E. side Fred Ck. just N. of Trib
	DESCRIPTION
0-18"	FILL, brn clay
18-30"	Dk brn A horizon
30-32"	Md brn B horizon
32-41"	A.A.
41-48"	Gray brn Snd, HARD DRILLING, DRY
48-58"	Vy lt brn / gry silty Loam
58-64"	A.A. vy lt brn/gray silty Loam
64-68.5"	Gray brn Silt w/ oxidized pockets yellw brn
68.5-72"	Yllw brn to brn oxidized sdy Silt
72-75"	Sndy Silt w/ many concretions
75-81"	Silty Snd. w/ incr in clay
81"	STOPPED BY A BOULDER

WELL I-6	NE corner of campus
	DESCRIPTION
0-6"	Md/dk brn clayey silt (Fill?)
6-15"	Brn/red brn silty clay
15-20"	Dk brn clayey silt loam (A zone)
45-51"	Dk/md brn clayey Silt (spl)
51-62"	Yllw brn /brn fn sndy Clay
62-68'	A.A.
68-75"	Mang. nod. in crusts in yllw brn clay sndy Clay
75-80	A.A.
80-90	A.A. w/ abund. mang crusts & laminat
96-99	A.A.
125"	Spl
128-137"	Fe mang. concret, Wtr Tbl
137-144"	Spl
144-156	Md. brn fn sndy clay
156-163	Fn sandy Clay, md brn w/ some SS pebb yllw brn & red brn debris
163-168"	Md brn sdy Clay w/ weathered SS Clay clods are dry inside (imperm)
168-172"	Dominantly Clay
T.D. 14'5	STANDING WATER @ 10'2"

WELL I-7	HALF WAY BETWEEN I-1 & I-6 DESCRIPTION
0-6"	Red rn/brn loam & sndy Loam
6-12"	A.A.
24-30"	Dk brn to black soil (A horizon) Clay loam to loamy Clay
42-48"	Black loam ClayBlack loamy Clay
48"	Md dk brn loamy clay (lighter than above - 2 ft. A zone)
52-58"	Mixed red brn & dk brn sdy loamy Clay
60-65"	Lt brn & rd brn mottled, sdy clay Loam (typical aquifer)
65-71"	Rd brn sdy clay Loam w/ mang. nodules & some ironstone colluvium
71-76"	Lg. angulary pieces iron SS.
76-81"	Lt. brn, loamy sand
81-92.5"	Snd & SS colluv. some cobbles are rounded
92-98"	Spl
99"	Gray & tan fn sndy Loam
99-104.5"	A.A. but moist, clay sdy Loam
112-117"	Spl
124"	A.A. w/ more Clay
132"	A.A. but damp
133.5"	STANDING WATER
138-144"	Dk brn gravel, wet
144-150"	Saturated; dk brn fn gravel to crs Snd
165"	More colluvium
166-172	Spl
182-187"	Spl
T.D. 19'	Casing 18'6" only

WELL I-9 135 paces SW of I-4, due N of Lk. Ev.

	DESCRIPTION
0-6"	Dark brn fn Sandy Loam
6-30"	Mottled brown & rd brn silt Loam
30"	Sandstone cobbles, manganese crust
	Like cobb in ck. bank. Hard Drilling
42"	Brn silt Loam
48"	Wood Fragments
54"	Dk brn loam, some clay
	Easy drilling from 54" down.
66"	Vy dark clay Silt w/ roots
	Black clay looks like swamp deposit
90"	Black clay, easy drilling
102"	Sandy black clay
114"	Black, clayey Sd, vy easy drilling
120-126"	Still black clayey Snd
132-138"	Some gray sand in black Snd
156-159"	Lt. gray and tan Sand, moist
162-163.5	Yellow brn & gray WET SAND
	WATER @ 13'7"
168"	Very sndy, yllw brn
180-185"	Orange SAND

T.D. 17'3CONTINUED CAVE-IN AT BTM
CSG to 15'10"

FRED CK NE BRIDGE; W. bank EXCAVATED CHANNEL
120 paces to Pennsylvanian Shale,

2.5' Fissile Shale, weathered, gray to tan
Cut out laterally to S.
Could be faulted agains terrace silt
Silt to south is gray and tan mottled like lower aquifer in wells

15 paces of Bend in Creek
Base of bank is about 1 ft. above Shale, down stream

1 ' Yllw brn Silt

3' Gravel lens, lens is concave downward
Cobbles are rounded and 1-4" in diam
Lens grades upward

11' Brn and gray Silt
Pockets of gray silt, lack iron stain
Gray pockets are 9" long & vertical
No trace of calcareous minerals
Manganese crusts associated with some lenses

GAS TANK EXCAVATION, TOP OF HILL

36" Top soil

4" Calcareous siltstone

8 ft Silty Shale

WELL G-1	DESCRIPTION
0	Dk. brn CLAY LOAM
6	vy fn Sdy CLAY LOAM, dk brn
12	dk brn, CLAYEY LOAM
18	dk brn, LOAMY CLAY
24	
30	BLACK SILTY CLAY
36	BLACK SILTY CLAY w/ dk red pockets
42	A.A.
48	md dk brn CLAYEY SILT, dry hrd drlg
72	mottled Dk brn CLAYEY SILT w/ red and gray patches, better drlg
80	
96	md brn SILTY CLAY w/ red patches
102	md brn SILTY CLAY, frly hard drlg
108	
114	orange SILTY CLAY
120	orange brn CLAY
130	orange SILT, moist
136	orange SILT w/ blk lamina (Mn), vy moist
144	orange/brn mott. SILTY CLAY
150	moist clay after hard streak
156	orange SAND
162	fn SAND, orange/tan, some moist
164	md grn dry, loose SAND, tan
170	dry SAND
192	dry SAND
204	sli moist SAND
218	saturated SAND
223	SAND, DRIPPING WET
234	TD. CONSTANT CAVING AT BTM.

WELL G-2	132 PACES N. of G-1
12-16	Surf. fill w/ L.S. cobbles; dk brn silt
16-24	Md ylw brn sand, only sli moist, vy lse
46-51	Ylw brn SAND, A.A. w/ dk brn clay lam
51-58	SAND - more moist than above
58-63	Dk Brn clayey sand
63-72	SAND, md. brn, MOIST
72-74	Black, organic rich CLAY
74-77	Black Clay A.A.
77-82	A.A., Good Drilling
82-88	DkBrn Clay, not as dark as above
88-95	A.A.
95-99	Dk Brn Silty CLAY
99-104	Md Brn Clay
106-112	Md Brn Silty Clay
112-120	Clayey SILT
120-125	Fn sdy, silt clay, md brn
125-133	
133-138	Red/brn CLAY slow drilling
138-144	A.A. red brn clay
144-152	Red brn sandy clay
152-156	A.A. very slow drilling
156-161	A.A. Sli sandy
161-165	A.A. w/ dk gray clay pockets
165-170	Mix Rd/orang SAND & dk brn Clay silt
170-176	A.A.
176-179	
179-185	ORANGE SAND
185-190	Tan to Orange SAND
190-194	Md grnd SAND, VERY DRY & LOOSE
194-200	DRY SAND
200-206	Light tan SAND
206-209	A.A.
209-214	Rd/Orng loose SAND, sli moist
214-220	SATURATED SAND (18'- 18' 4")
220-226	A.A.
226-231	A.A.
231-237	A.A. Lost some spl
237-242	A.A.
242-247	A.A. btm hole caving
247-253.5	A.A.

TD 21'1.5"   STNDG WTR 19'5.75"

WELL II-1 North Bank, South of LRC, mouth of crk

0-6	Md. brn/ylw brn Loam
6-9	Rd-brn, Sndy Loam & rd/ylw brn clayey loam, moist
10-15	A.A. w/ 2" cobble (Fill)
20-23	Dark Brown fn sdy Loam, moist
23-31	Vy dk brn, clay w/ roots
31-37	Dk. brn. clayey Loam
38-42	A.A. - sample
50-55	Md. brn, less dark, moist
55-60	Rd/brn fn sdy Loam
60-63	Ylw/rd brn sdy Silt
63-66	Red brn Silt (Very Dry)
70-76	A.A., Silt, very dry
76-80	A.A. Very Slow Drilling
80-83	A.A.
84-90	Ylw brn clayey Silt, Very Dry
90-93	A.A.
102-104	Lt/md brn, clayey silt, Dry
104-105	A.A.
108-114	Lt/md brn clay & clayey SILT, less dry
114-123	Md brn Silty Clay, Less dry than above
125-130	Rd brn silty Clay - moist
130-135	Rd brn Clay, quite moist
135-142	Md. Brn moist Clay
142-146	Gray & Brn Clay
146-153	A.A. moist Clay
153-161	Very damp silty clay
	Standing Water @ 13'5"
161-168	Saturated Clayey Silt, ylw brn
170-180	Gray/tan Clay & Silt
192-197	A.A.
200	Greenish gray Clay, plastic

TD 17'4"

WELL I-8	N. end of Rugby Field
0-3"	Brn silt; mod. moisture
3-6"	Brn Loam
6-9"	Ylw brn to rd brn Clay, hard drlg
9-12"	A.A., Silty Clay
12-16"	Ylw brn Silty Clay
16-19"	A.A. w/ some gray Clay & Fe Oxide - Fill?
19-21"	Dark Brown Clayey Silt - A-Zone
21-26"	A.A. dark Brown
30-32"	Brn Silty Clay, lighter; still hrd drlg
32-35"	A.A. lt. brn
35-42"	A.A. lt. ylw brn Silty Clay w/ some dk rd/brn Fe stain, Hard Drlg
42-44"	A.A.
50-53.5"	Lt brn to ylw brn Clayey Silt
53.5-57"	A.A. Clayey Silt - dry
57-62"	A.A.
62-64"	A.A.
64-68"	A.A. Hard Drilling continues
70-76"	A.A. Dry
76-80"	Lt brn to ylw brn Clayey Silt; somewhat moist
80-82"	A.A.
86-92"	A.A. Lt brn/ylw brn Silty Clay, moist Fair Drilling
92-97"	A.A., cool, moist lt brn silty Clay Good Drilling
102-108"	Silty Clay, tan & gray w/ dk rd brn pockets- MnO crusts; Nowata?
108-111"	A.A. tan & gray mottled silty Clay
111-116"	A.A. w/ incr in dk rd brn clumps appears laminated
116-122"	A.A. dk brn & tan laminated Clay
122-127"	A.A.
132-137"	A.A. vy moist and plastic
137-142"	Tan Sandy Clay, very damp
142-148"	Saturated, Clayey Sand, tan Standing Water @ 12' 1/2"
170-178"	A.A.
178-185"	A.A.
185-196"	A.A.
TD 16'	

APPENDIX B

GRAIN SIZE ANALYSES

Sieve and Pipette Analysis

Percent Composition

SAMPLE	Mdn. Sz		CLAY	CRS SLT	TOT SLT	FN SND	TOT SND
			Well I-1				
2-14	.04	mm	23.04	35.89	46.96	20.33	29.99
19-25	.04	mm	22.36	41.94	53.37	17.71	24.28
32-36	.05	mm	21.37	44.99	56.62	16.61	22.01
42-46	.02	mm	32.38	39.51	57.29	7.47	10.33
54-60	.025	mm	32.81	24.23	38.84	27.48	28.35
69-76	.04	mm	28.06	19.43	32.69	31.84	39.26
84-92	.07	mm	20.69	18.32	27.69	31.29	51.61
99-107	.025	mm	29.01	35.12	53.27	15.4	17.72
115-120	.04	mm	20.34	36.65	48.54	28.89	31.13
128-136	.025	mm	25.4	35.7	55.73	15.42	18.88
147-158	.01	mm	32.66	28.29	55.25	10.82	12.09
180-185	.03	mm	26.22	28	43.63	24.7	30.15

Well I-6

SAMPLE	Mdn. Sz		CLAY	CRS SLT	TOT SLT	FN SND	TOT SND
0-6	.05	mm	14.7	32.57	46.99	24.12	38.32
15-20	.025	mm	24.81	43.89	65.45	6.13	9.73
80-90	.01	mm	32.78	35.52	57.71	7.65	9.51
117-123	.015	mm	27.55	37.6	62.43	8.18	10.03
137-144	.02	mm	26.79	33.54	56.46	13.94	16.74
144-156	.015	mm	30.65	31.04	53.32	12.93	16.02
168-172	.007	mm	40.54	21.46	44.51	12.53	14.95

GRAIN SIZE ANALYSIS BY SIEVE

SIZE RANGE in mm.

Well	Sample	>4.0	>1.0	>.65	>.25	.25-.065	<.065
		% COMPOSITION					
I-1	36- 42	1.08	0.25	19.82	5.76	68.65	4.45
I-1	99-107	0.23	1.70	1.06	3.86	70.42	22.73
I-1	176-180	1.41	1.90	1.90	10.91	55.84	28.04
I-2	120-127	0.00	0.55	1.79	31.94	47.29	18.44
I-3	145-158	1.96	6.83	8.16	26.85	35.68	20.52
I-4	155-164	0.39	2.82	2.25	17.60	58.21	18.72
I-6	117-123	0.19	1.93	2.34	5.83	67.08	22.63
I-9	180-186	0.19	0.84	40.30	47.51	9.52	1.66

APPENDIX C

WATER TABLE ELEVATIONS AND RAINFALL DATA

DATE	I-1	I-3	I-4 (FEET)	I-6	I-7	I-9
SURFACE ELEVATION	651.50	649.00	652.00	656.00	653.00	649.00
WATER ELEVATION						
2/24	640.00	637.08				
26		638.00				
3/03			638.42	645.83		
12			638.67	647.29		
26				648.17		
4/02	642.29	638.92	641.08	647.67		
09	642.04	638.83	640.83	646.92		
16	642.21	639.00	640.83	647.08		
23	643.67	639.83	642.00	649.92		
30	643.88	640.08	642.33	650.25		
5/07	644.13	640.42	643.21	650.75		
14	643.50	639.92	642.58	648.96		
21	643.25	639.83	642.21	648.50		
28	642.83	639.46	641.75	647.46		
6/04	642.50	639.25	641.38	646.67		
11	642.29	639.00	641.04	645.96		
18	641.92	638.96	640.75	645.13		
25	641.63	638.75	640.50	644.54		
7/02	641.29	638.50	640.25	643.88	641.88	
09	641.04	638.33	640.00	643.17	641.67	
16	640.79	638.25	639.75	642.79	641.38	
23	640.69	638.25	639.46	642.50	641.25	
30	640.50	638.17	639.33	642.33	641.04	
8/06	640.38	637.96	639.17	642.04	640.88	
13	640.38	638.08	639.04	641.83	640.79	
20	640.29	637.88	639.00	641.67	640.67	
27	640.02	637.77	638.82	641.77	640.50	
9/03	639.75	637.71	638.67	641.67	640.25	
10	639.58	637.63	638.50	641.71	640.08	
17	639.83	637.75	638.50	641.67	640.21	
24	640.17	638.00	638.67	642.00	640.63	
10/01	640.17	638.04	638.65	642.17	640.65	
08	640.25	638.08	638.71	642.67	640.71	
15	640.25	638.04	638.73	643.08	640.75	
22	640.21	638.00	638.67	642.71	640.67	
29	640.10	637.92	638.60	642.46	640.58	
11/05	640.34	638.02	638.62	642.71	640.75	
12	640.12	637.96	638.67	643.08	640.71	
19	640.08	638.00	638.58	642.92	640.62	635.08
27	640.08	638.04	638.58	643.00	640.62	635.00
12/03	640.08	638.13	638.54	642.33	640.67	634.96
11	639.96	637.98	638.50	642.29	640.63	634.92
17	640.31	637.83	638.54	642.33	640.88	634.96
26	640.25	637.92	638.57	643.17	640.85	634.87
1/09		638.17	638.50	643.67	641.04	635.00
16	640.67	638.38	639.04	644.46	641.42	635.04

DATE	I-1	I-3	I-4	I-6	I-7	I-9
22	640.69	638.33	639.33	644.71	641.46	635.21
31	640.54	638.46	639.21	644.37	641.33	635.04
2/06	640.50	638.21	639.17	643.92	641.29	635.00
13	640.58	638.29	639.08	643.83	641.33	635.00
18	640.52	638.25	639.08	643.67	641.25	635.02
27	640.50	638.29	639.08	643.46	641.21	634.83
3/06	640.46	638.25	639.00	643.38	641.21	634.79
13	640.44	638.21	639.00	643.42	641.21	634.75
19	640.50	638.21	638.96	643.54	641.21	634.77
27	640.54	638.25	639.00	643.92	641.27	634.77
4/25	640.58	638.31	639.08			
5/17	640.98	638.46	639.17	644.83	641.83	635.08

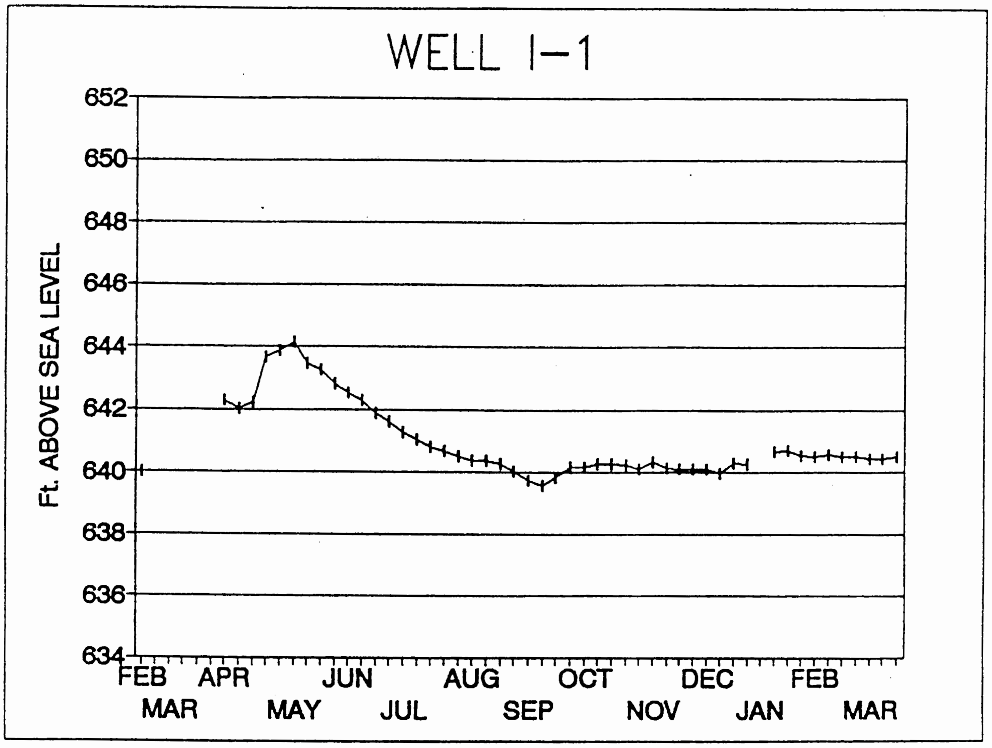
WELL I-8 SURFACE ELEV: 648.50

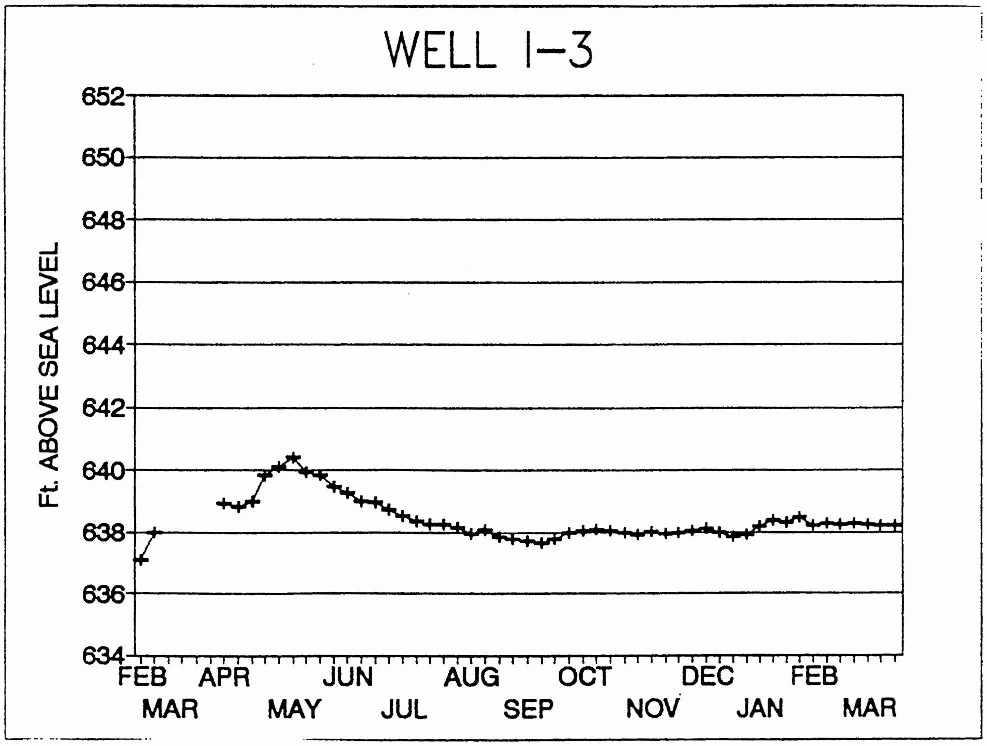
WELL	I-8
3/19	636.46
3/27	636.48
4/25	636.60
10	636.53
17	636.77

RAINFALL RECORDED BY USGS RAIN GAUGE

DATE	MONTH	RAIN	DATE	MONTH	RAIN
03	JAN	1.48	05	JUL	0.12
16		0.59	06		0.28
17		0.13	07		0.18
18		0	21		0.26
19		1.69	11	AUG	0.2
21		0	12		1.15
01	FEB	0.26	17	SEP	0.69
15		2.92	01	OCT	
21		2.12	03		0.85
28		1.77	08		0.54
06	MAR	1.08	09		0.1
11		2.47	03	NOV	0.36
14		2.8	05		1.37
23		0.33	02	DEC	0.49
25		0.3	16		0.24
28		0.35	17		1.29
02	APR		27		0.12
10		0.96	28		0.08
16		0.49	29		0.16
17		1.36		1991	
18		0.62	01	JAN	0.15
19		0.13	02		0.17
20		1.33	05		0.47
24		0.21	06		0.1
25		0.52	08		0.28
26		1.26	09		0.07
27		0.52	10		0.39
02	MAY	2.9	14		0.07
03		0.22	15		0.41
11		0.58	18		0.16
15		0.79	06	FEB	
18		0.82	01	MAR	0.13
19		0.65	02		0.27
26		0.25			
30		0.7			
02	JUN	0.29			
09		1.55			
10		0.12			
18		0.17			
19		0.2			
24		0.2			

INDIVIDUAL PLOTS OF WATER ELEVATION


WELL I-1
Ft. ABOVE SEA LEVEL
652
650
648
646
644
642
640
638
636
634
FEB
APR
JUN
AUG
OCT
DEC
FEB
MAR
MAY
JUL
SEP
NOV
JAN
MAR


WELL I-3
Ft. ABOVE SEA LEVEL
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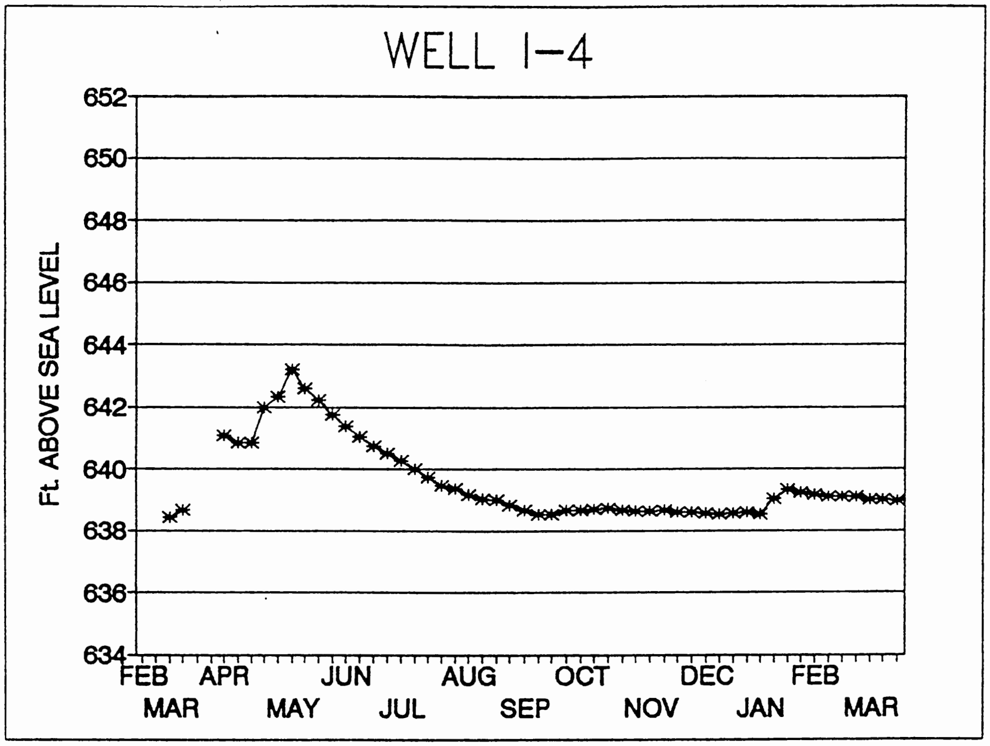
650
648
646
644
642
640
638
636
634
FEB
APR
JUN
AUG
OCT
DEC
FEB
MAR
MAY
JUL
SEP
NOV
JAN
MAR


WELL I-4
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650
648
646
644
642
640
638
636
634
Ft. ABOVE SEA LEVEL
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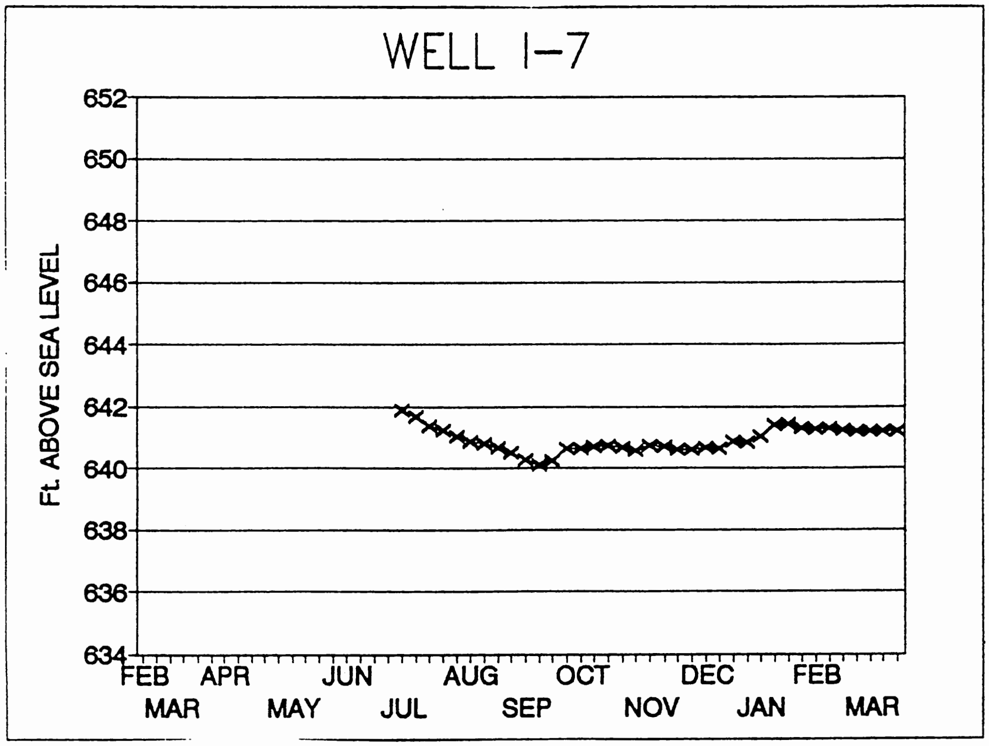
APR
JUN
AUG
OCT
DEC
FEB
MAR
MAY
JUL
SEP
NOV
JAN
MAR


WELL I-7
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642
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638
636
634
Ft. ABOVE SEA LEVEL
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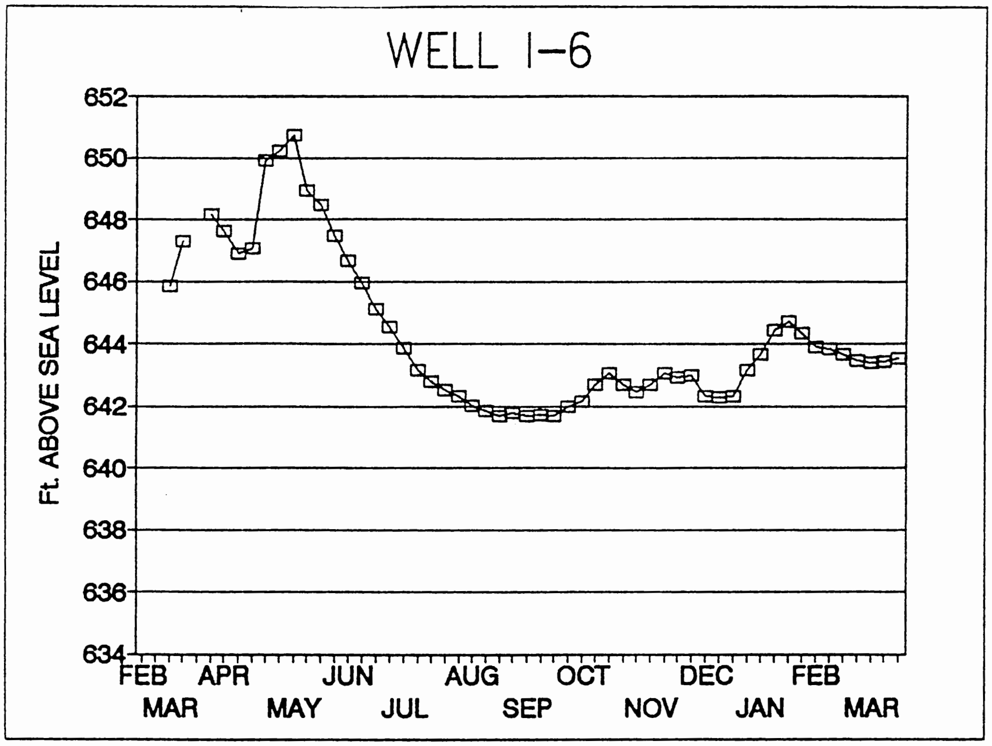
APR
JUN
AUG
OCT
DEC
FEB
MAR
MAY
JUL
SEP
NOV
JAN
MAR


WELL I-6
Ft. ABOVE SEA LEVEL
652
650
648
646
644
642
640
638
636
634
FEB
APR
JUN
AUG
OCT
DEC
FEB
MAR
MAY
JUL
SEP
NOV
JAN
MAR

APPENDIX D

AQUIFER TEST DATA and PLOTS

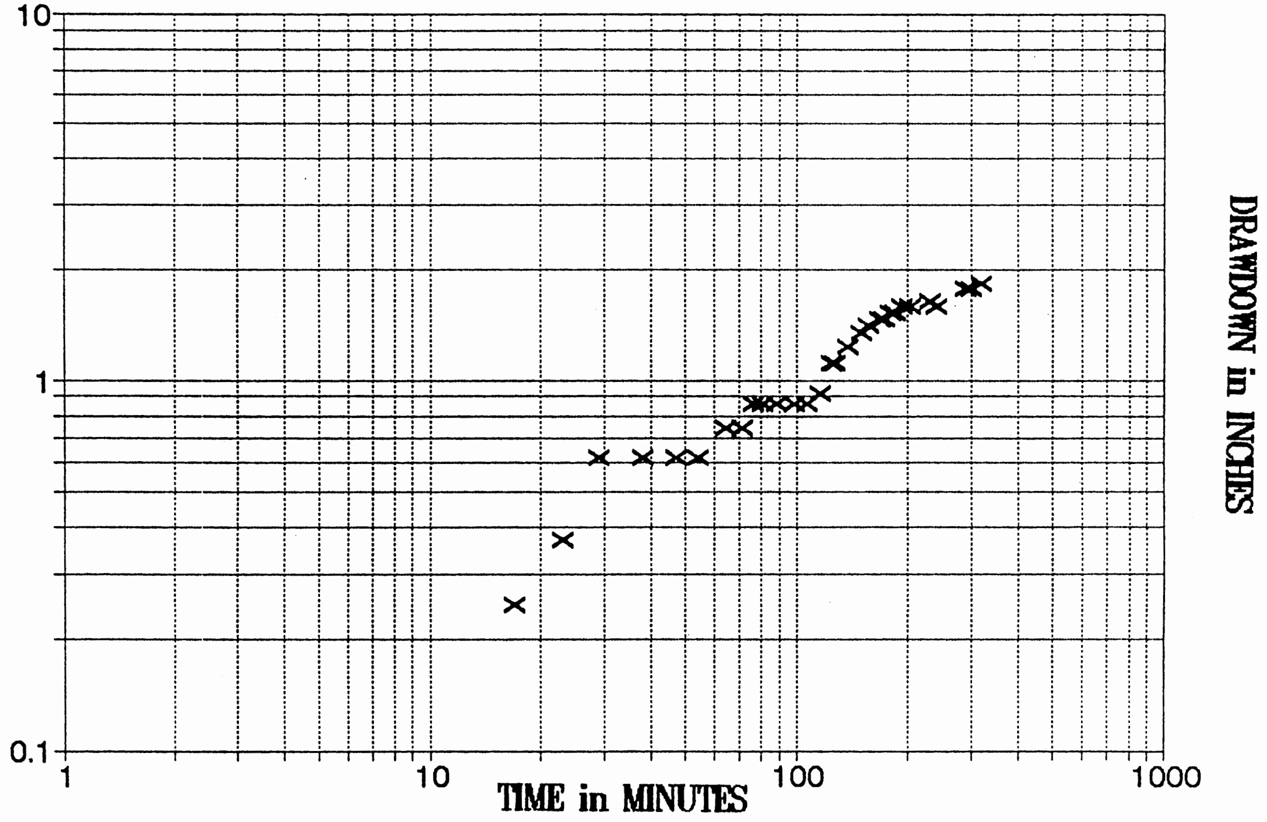
DRAWDOWN DATA from AQUIFER TEST

OBS WELL I-11 (21')

PUMP TIME	DRAWDWN inches	ft	CORR. ft.	inches
0	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00
17	0.25	0.02	0.02	0.25
23	0.38	0.03	0.03	0.37
29	0.63	0.05	0.05	0.62
38	0.63	0.05	0.05	0.62
47	0.63	0.05	0.05	0.62
54	0.63	0.05	0.05	0.62
64	0.75	0.06	0.06	0.74
71	0.75	0.06	0.06	0.74
76	0.88	0.07	0.07	0.87
81	0.88	0.07	0.07	0.87
88	0.88	0.07	0.07	0.87
99	0.88	0.07	0.07	0.87
107	0.88	0.07	0.07	0.87
116	0.94	0.08	0.08	0.93
125	1.13	0.09	0.09	1.11
128	1.13	0.09	0.09	1.11
138	1.25	0.10	0.10	1.23
151	1.38	0.11	0.11	1.36
158	1.44	0.12	0.12	1.42
169	1.50	0.13	0.12	1.48
174	1.50	0.13	0.12	1.48
181	1.56	0.13	0.13	1.54
186	1.56	0.13	0.13	1.54
194	1.63	0.14	0.13	1.60
204	1.63	0.14	0.13	1.60
231	1.69	0.14	0.14	1.66
240	1.63	0.14	0.13	1.60
289	1.81	0.15	0.15	1.78
300	1.81	0.15	0.15	1.78
317	1.88	0.16	0.15	1.84

TIME DRAWDOWN PLOT

WELL I-11



OBS WELL I-10 (63.5')

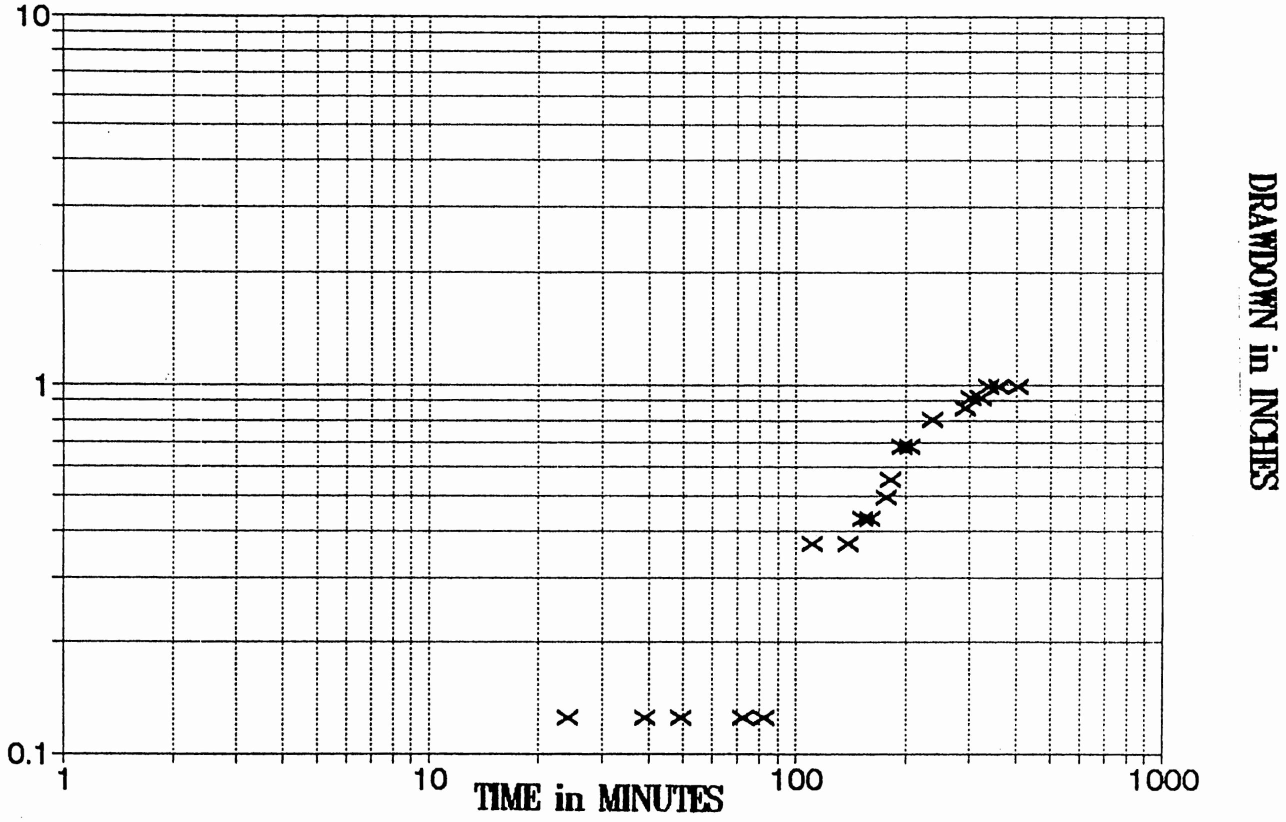
PUMP TIME	DRAWDWN inches	ft	CORR. ft.	inches
18	0.01	0.00	0.00	0.01
24	0.13	0.01	0.01	0.12
39	0.13	0.01	0.01	0.12
49	0.13	0.01	0.01	0.12
72	0.13	0.01	0.01	0.12
82	0.13	0.01	0.01	0.12
111	0.38	0.03	0.03	0.37
139	0.38	0.03	0.03	0.37
154	0.44	0.04	0.04	0.44
160	0.44	0.04	0.04	0.44
178	0.50	0.04	0.04	0.50
182	0.56	0.05	0.05	0.56
196	0.69	0.06	0.06	0.68
206	0.69	0.06	0.06	0.68
236	0.81	0.07	0.07	0.81
292	0.88	0.07	0.07	0.87
302	0.94	0.08	0.08	0.93
319	0.94	0.08	0.08	0.93
337	1.00	0.08	0.08	0.99
357	1.00	0.08	0.08	0.99
404	1.00	0.08	0.08	0.99

DISTANCE DRAWDOWN (DD @ 235min)

Dist	DrwDwn
21.0	1.69
42.5	0.81
17.0	1.22

TIME DRAWDOWN PLOT

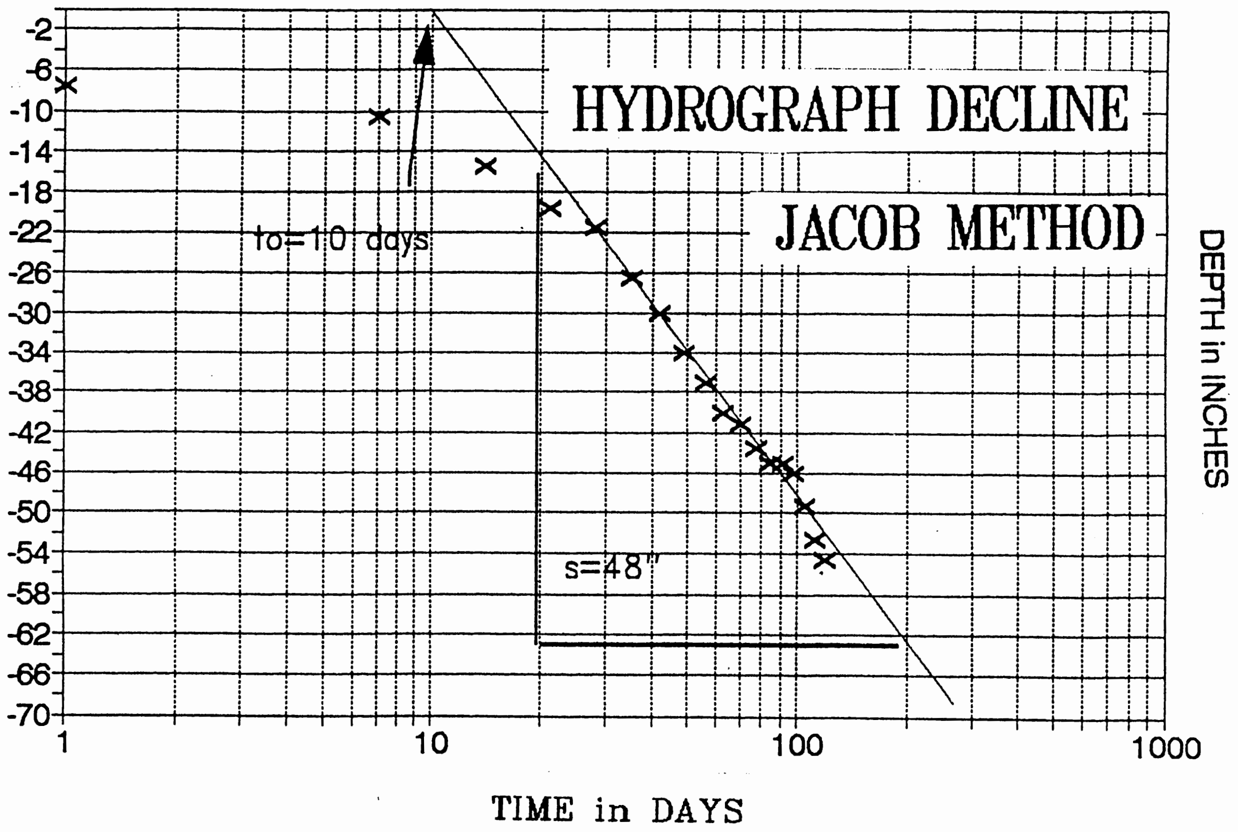
WELL I-10



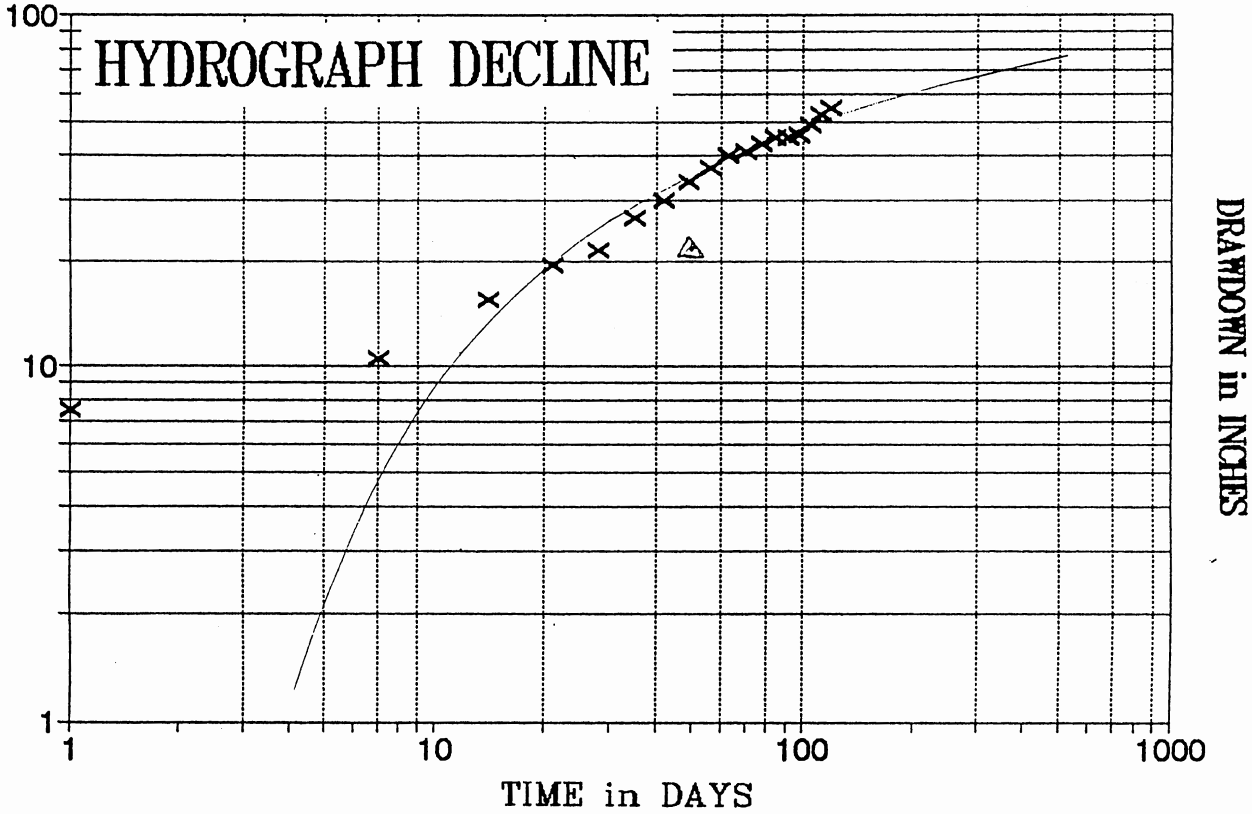
HYDROGRAPH DECLINE DATA USED FOR CALCULATION OF TRANSMISSIVITY

WATER LEVEL	DECLINE	CUMULATIVE DECLINE	DATE	ELAPSED TIME
(INCHES)				(DAYS)
-96.0	7.5	7.5	5/14	1
-99.0	3.0	10.5	21	7
-104.0	5.0	15.5	28	14
-108.0	4.0	19.5	6/04	21
-110.5	2.5	22.0	11	28
-115.0	4.5	26.5	18	35
-118.5	3.5	30.0	25	42
-122.5	4.0	34.0	7/02	49
-125.5	3.0	37.0	09	56
-128.5	3.0	40.0	16	63
-129.75	1.25	41.25	23	70
-132.0	2.25	43.5	30	77
-133.5	1.5	45.0	8/06	84
-133.5	0.0	45.0	13	91
-134.5	1.0	46.0	20	98
-137.75	3.25	49.25	27	105
-141.0	3.25	52.5	9/03	112
-143.0	2.0	54.5	10	119

TIME DRAWDOWN PLOT



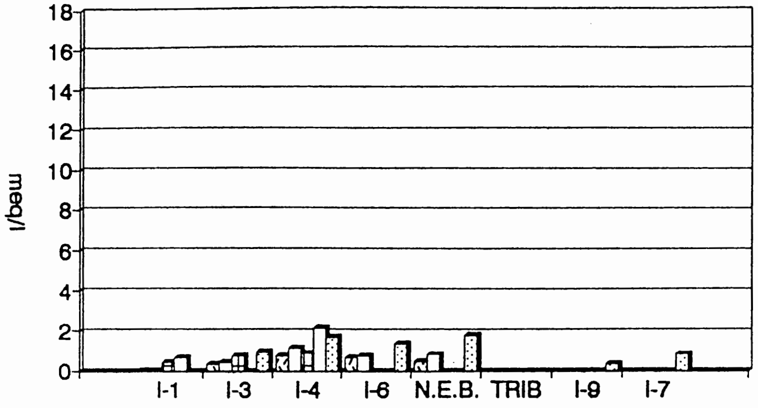
TIME DRAWDOWN PLOT



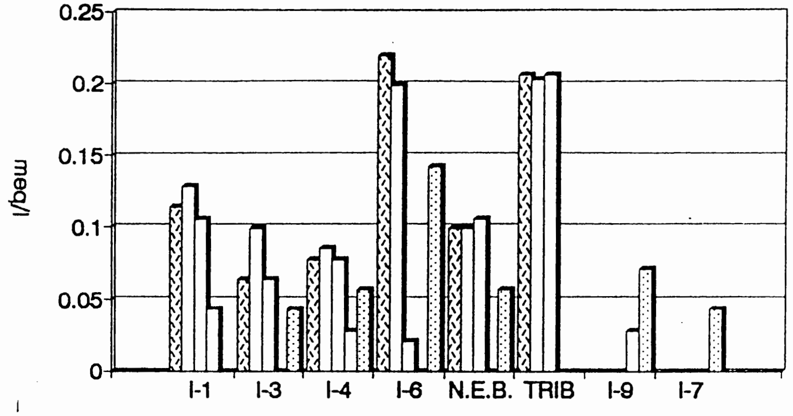
APPENDIX E

RESULTS OF CHEMICAL ANALYSIS

SODIUM

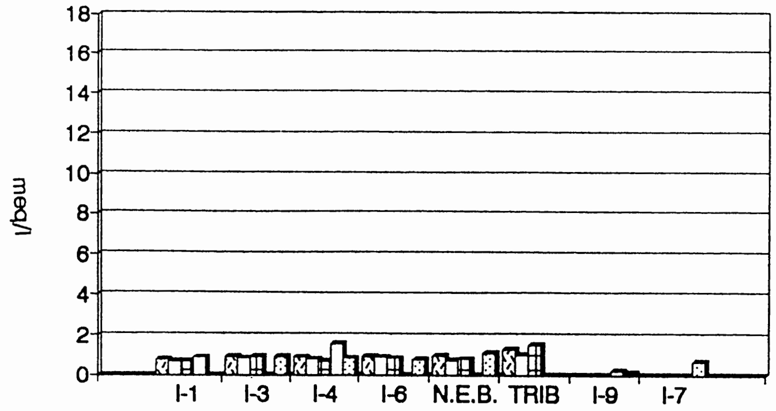


NITRATE

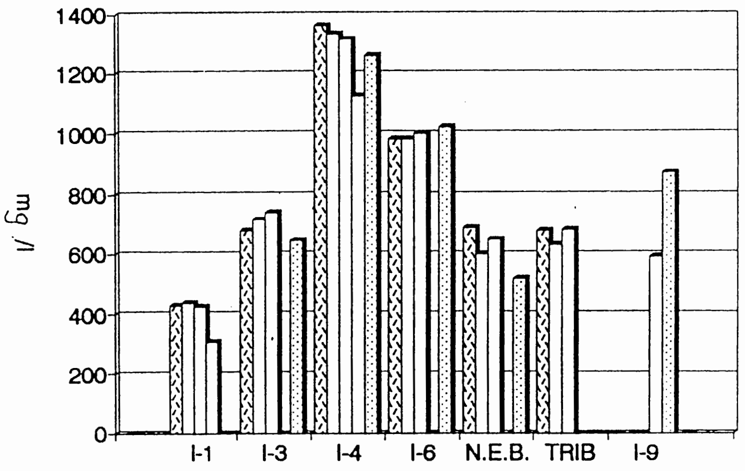


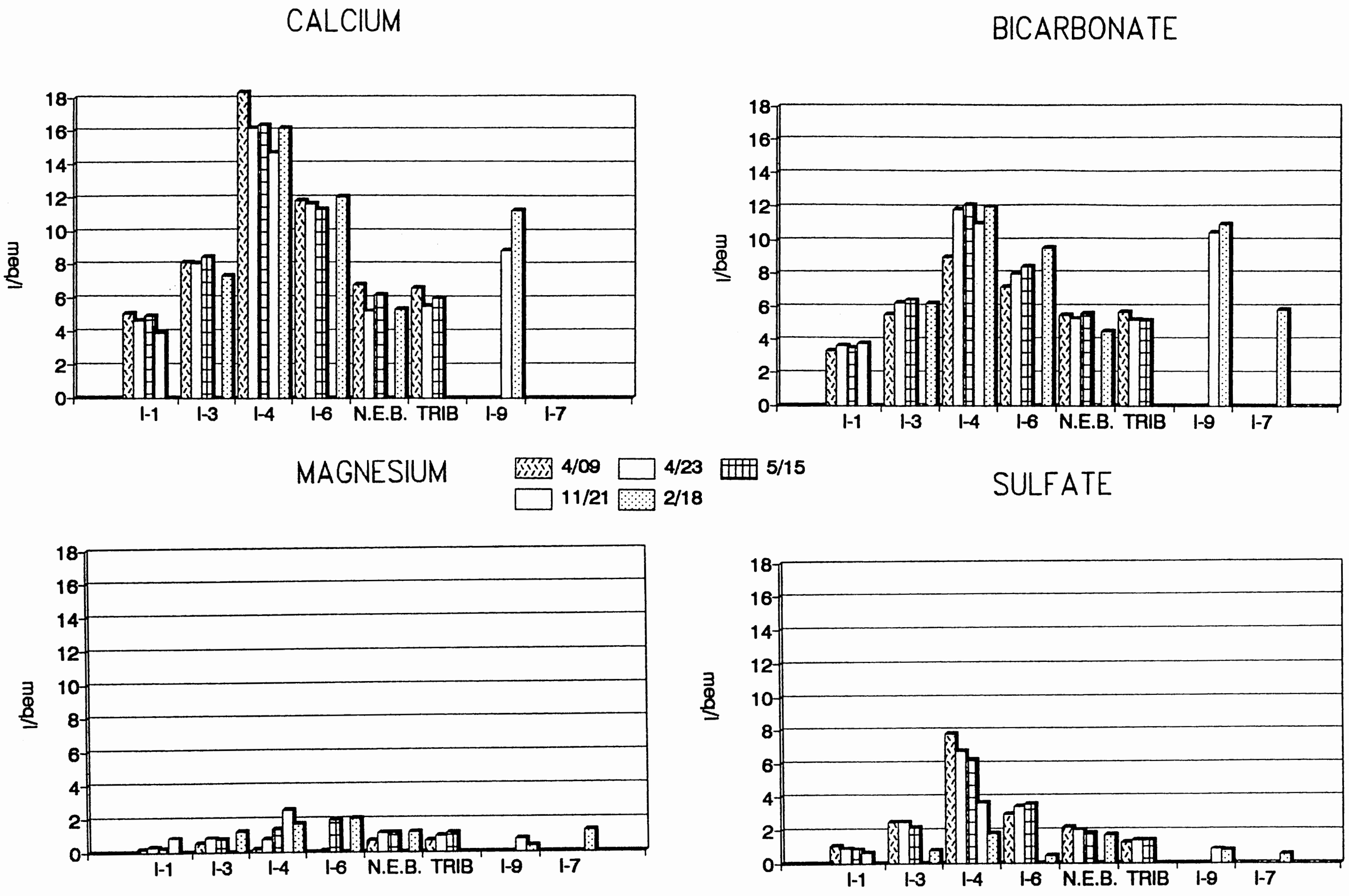
▨ 4/09 ☐ 4/23 ▥ 5/15
☐ 11/21 ░ 2/18

CHLORIDE



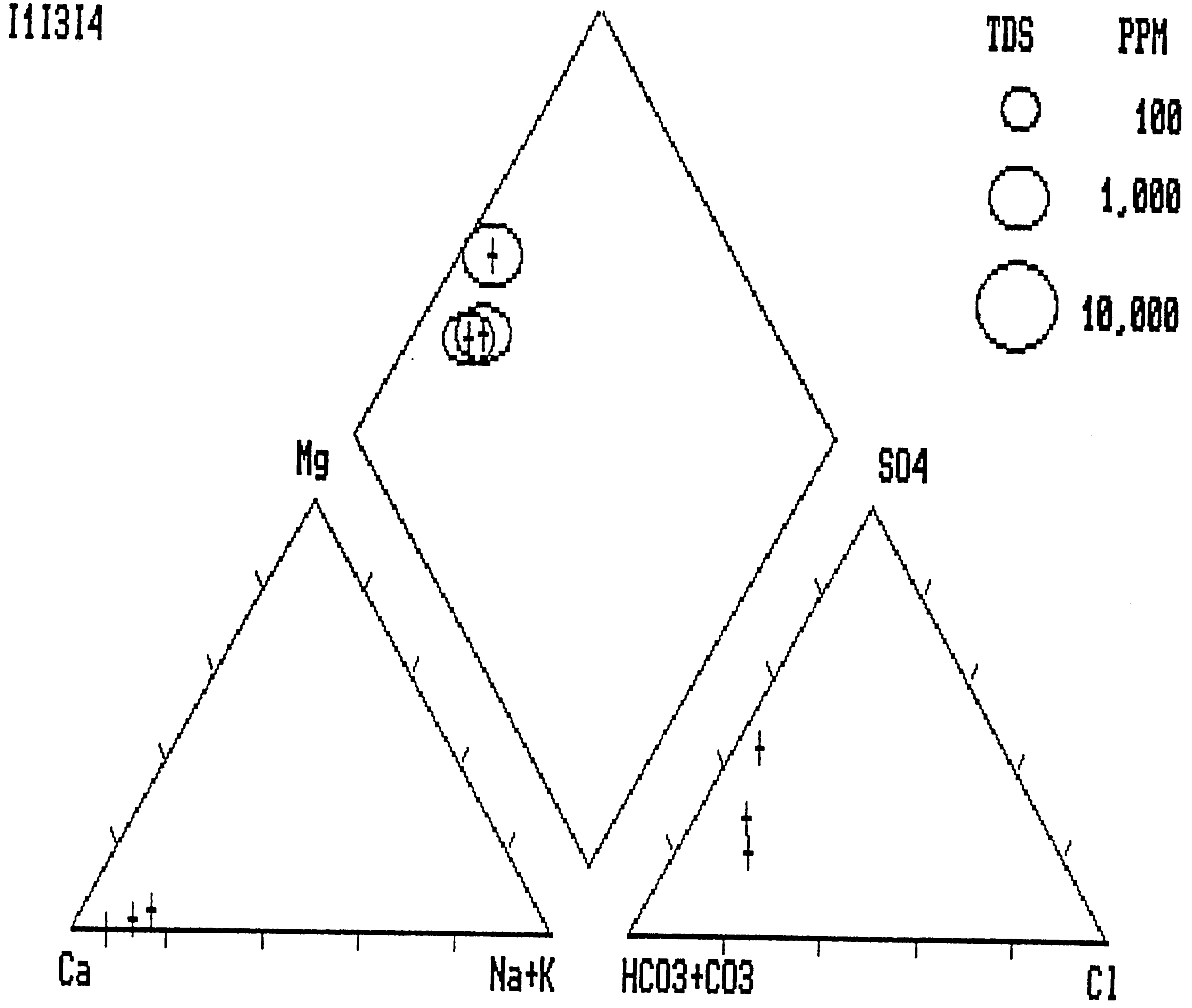
Total Dissolved Solids

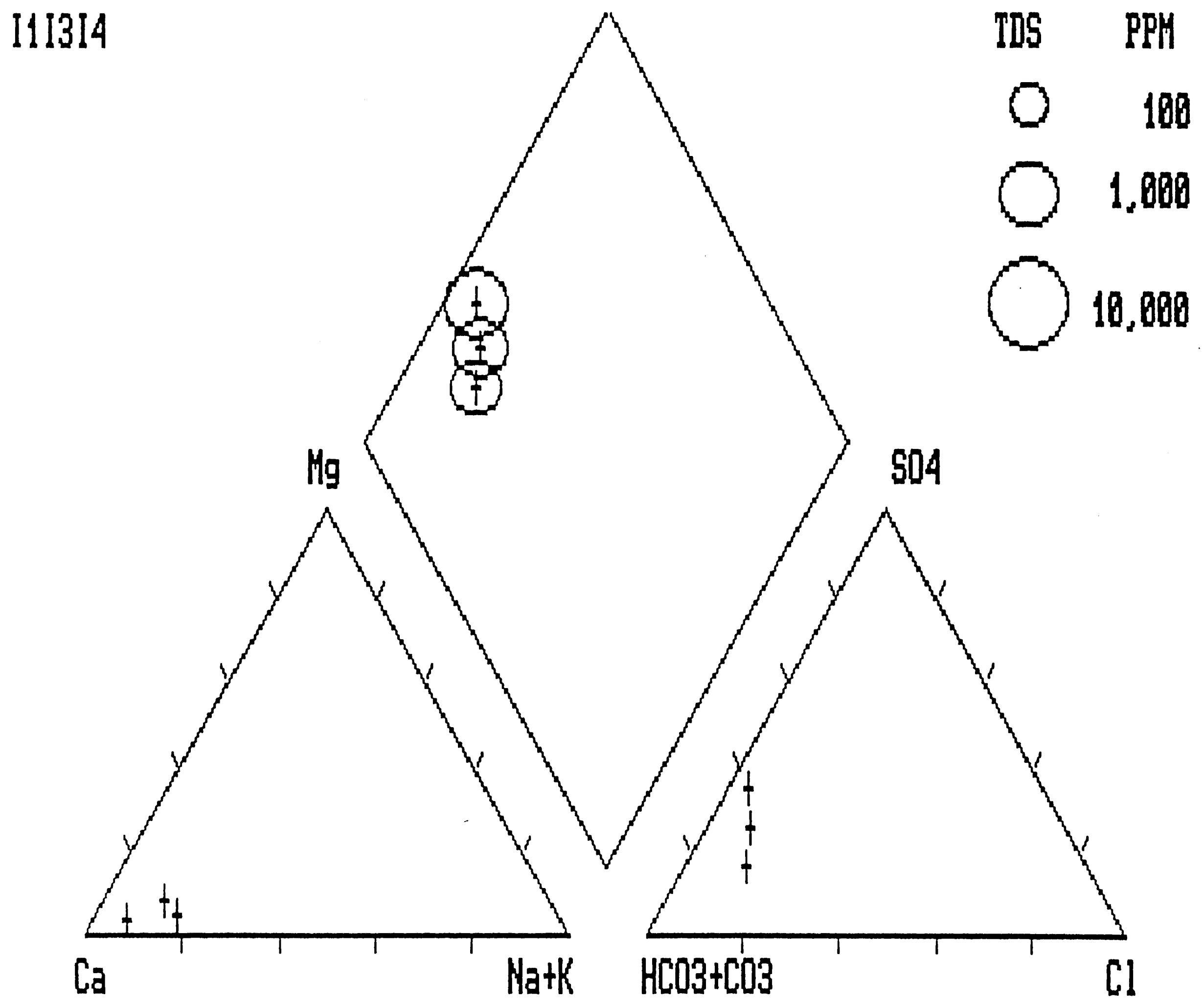


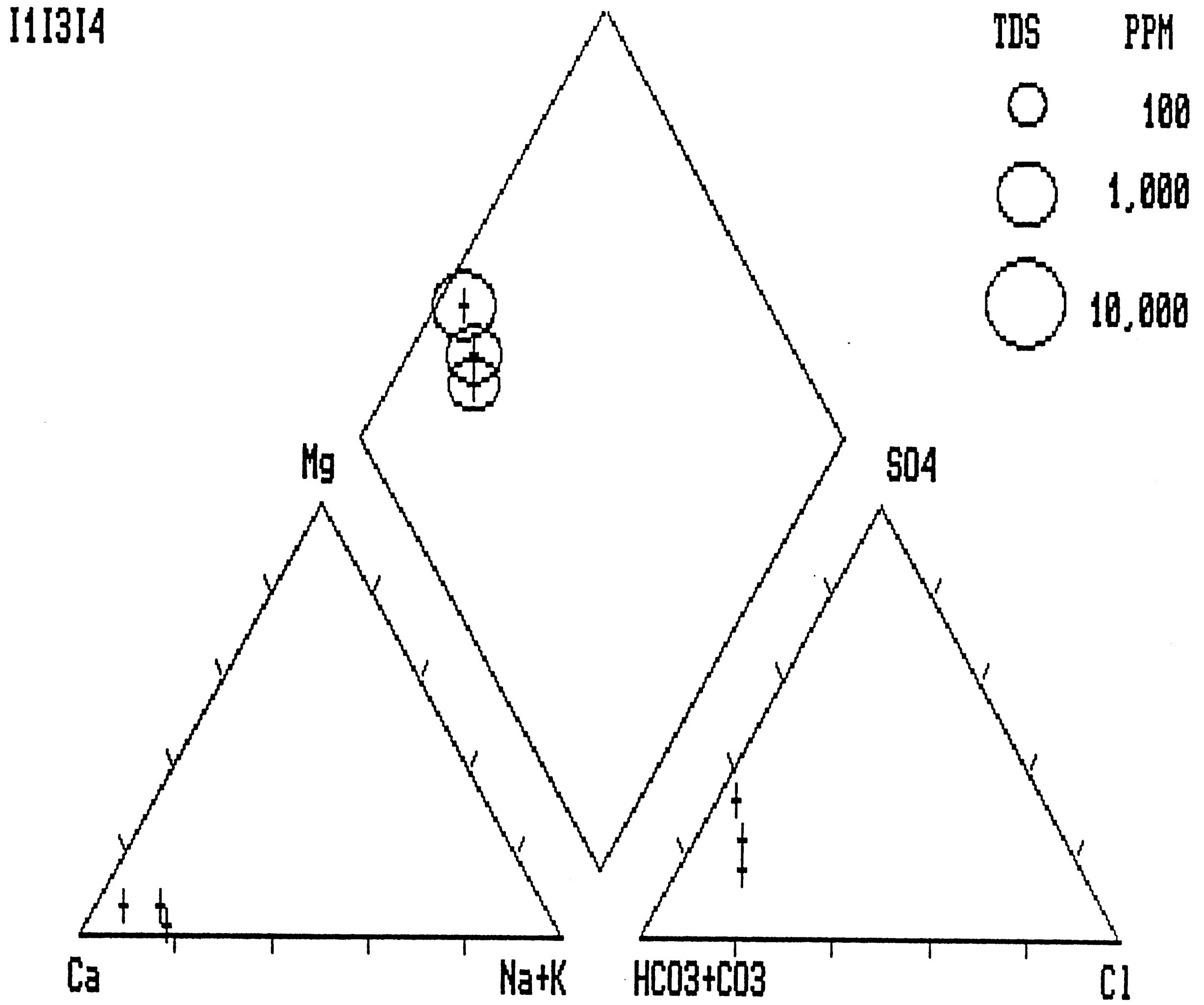

CALCIUM
BICARBONATE
MAGNESIUM
SULFATE
meq/l
0
2
4
6
8
10
12
14
16
18
I-1
I-3
I-4
I-6
N.E.B.
TRIB
I-9
I-7
4/09
4/23
5/15
11/21
2/18

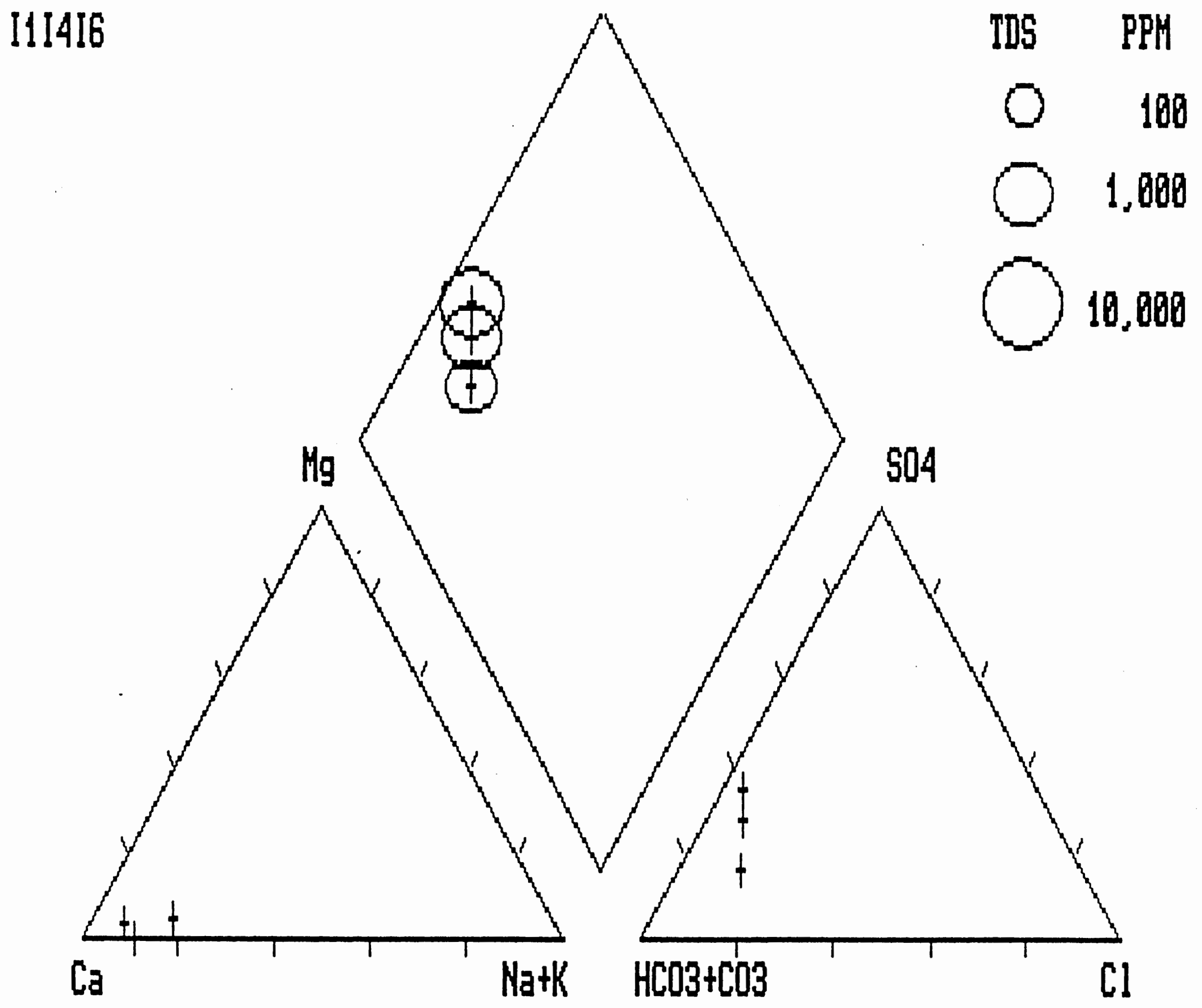
APPENDIX F

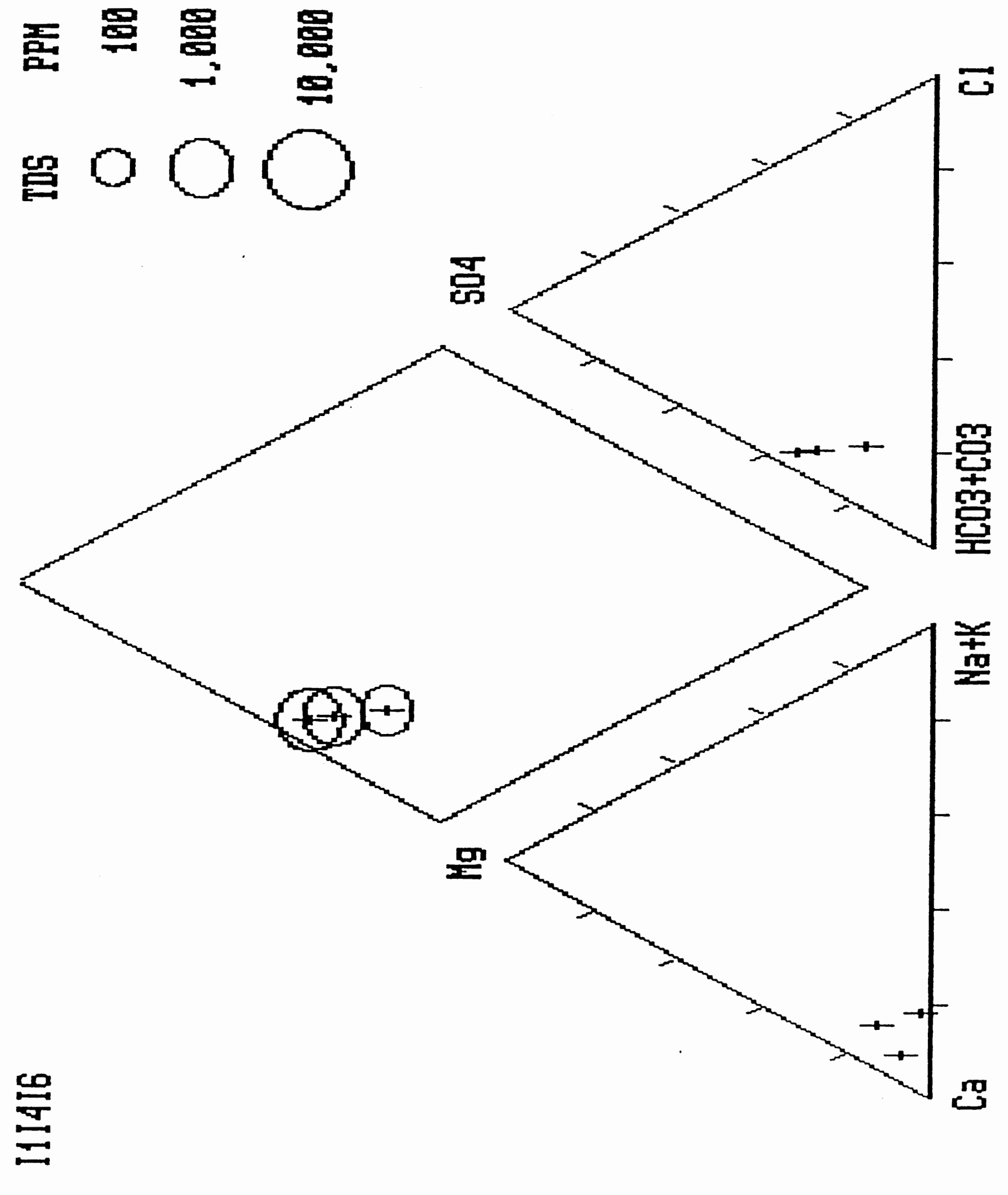
PIPER DIAGRAMS


I1I3I4
TDS
PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl


I1I3I4
TDS
PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl


I1I3I4
TDS PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl


I1I4I6
TDS
PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl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TDS
PPM
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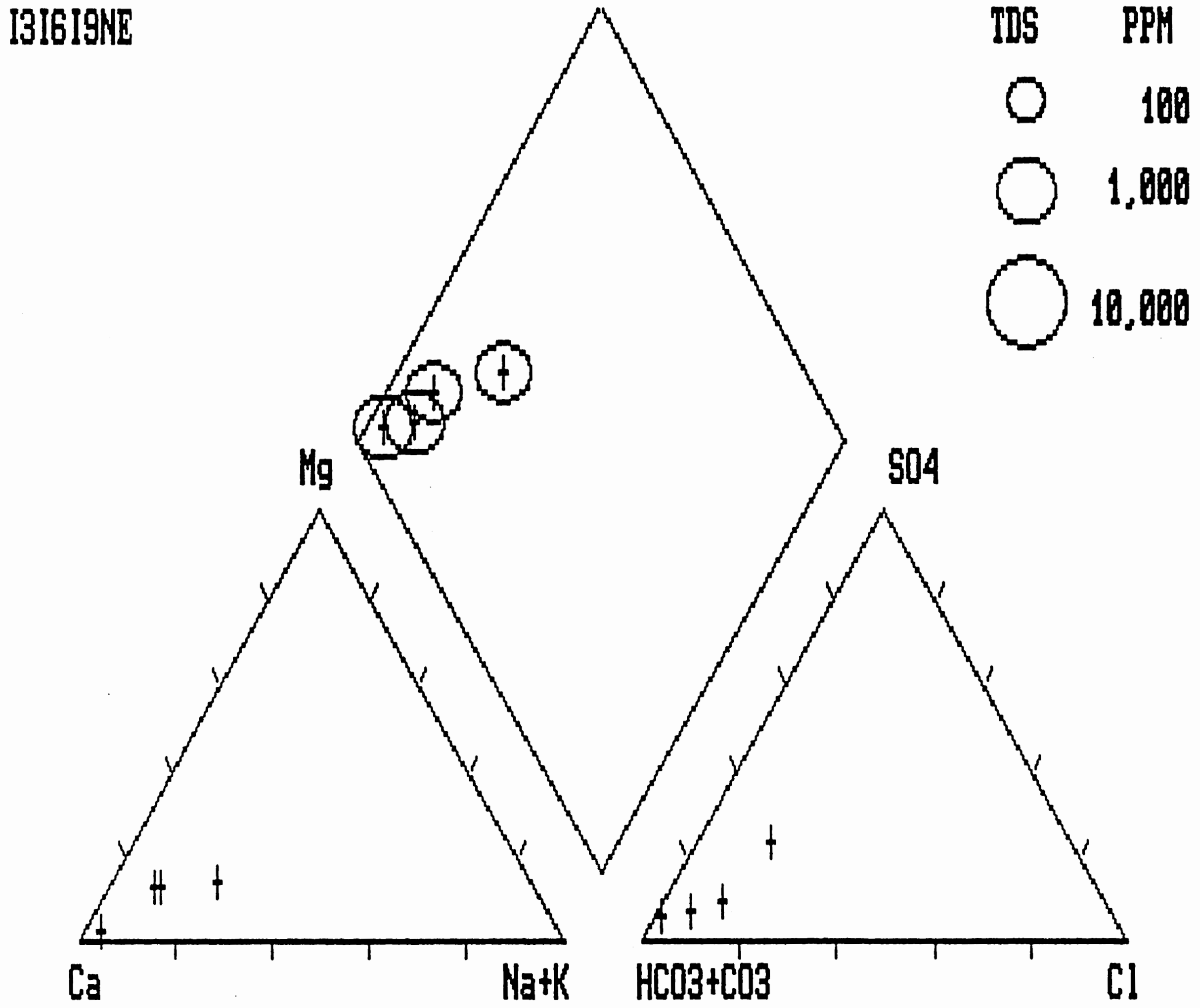
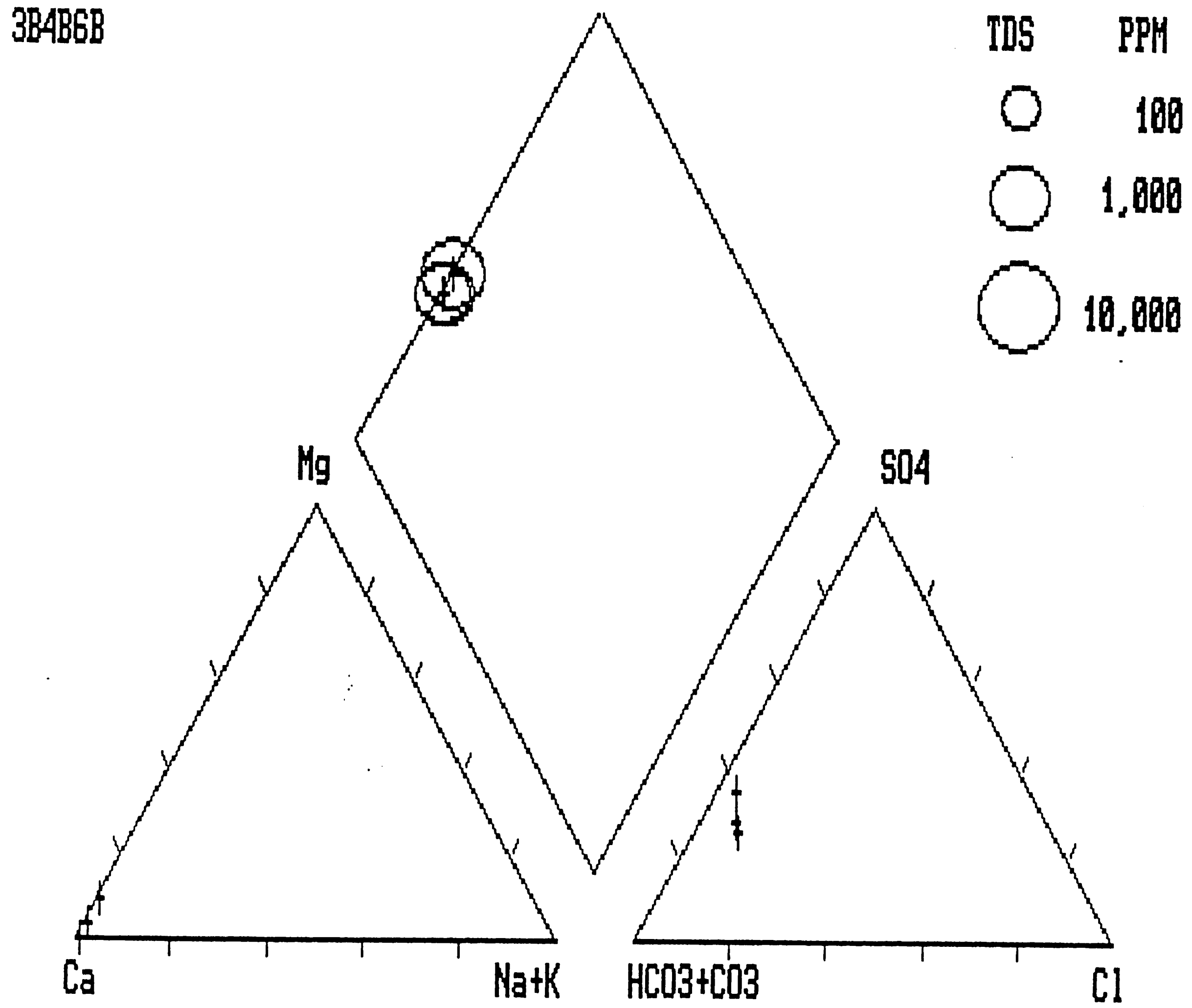
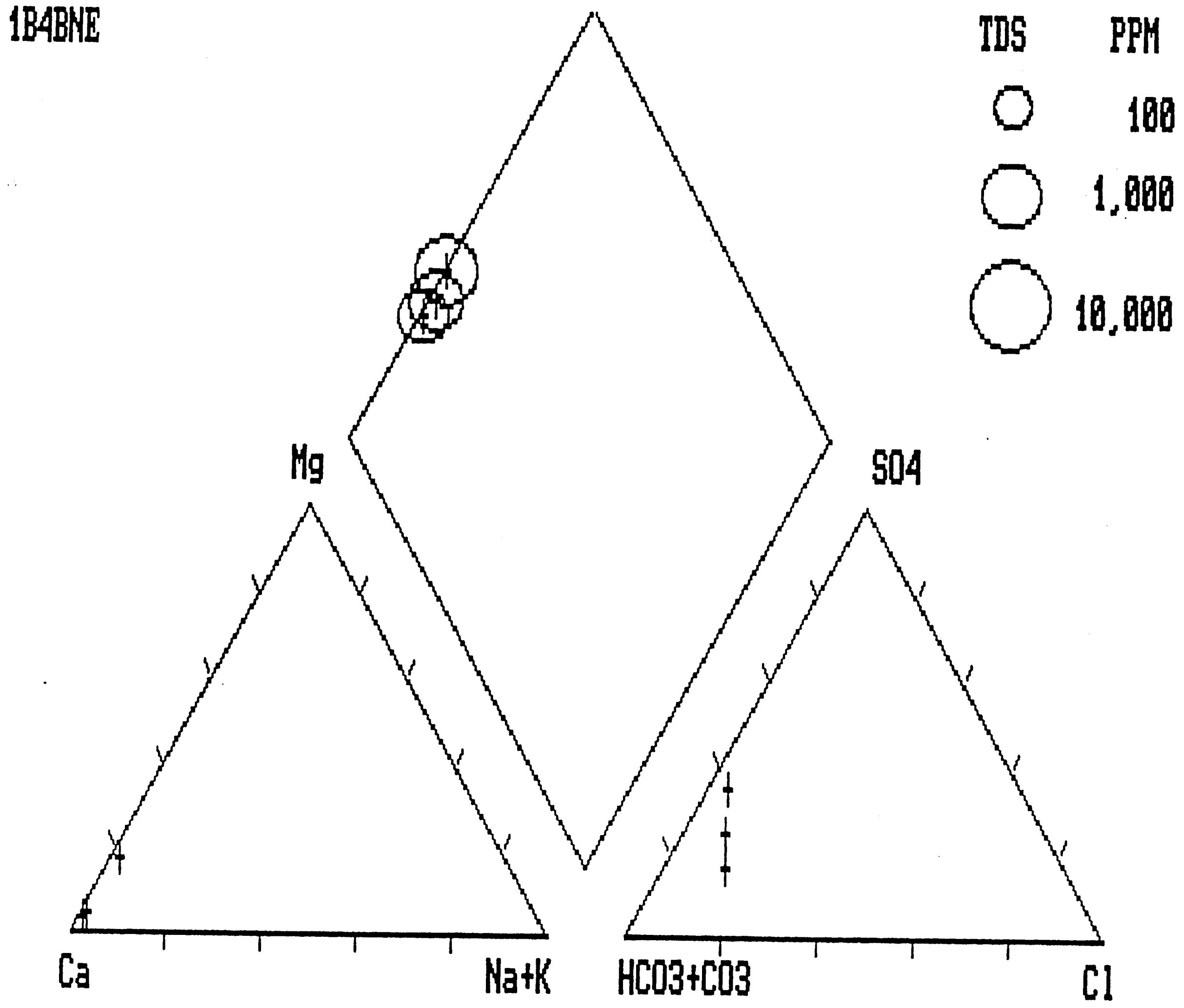
1,000
10,000
SO4
Cl
HCO3+CO3
Mg
Na+K
Ca


I3I6I9NE
TDS
PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl


3B4B6B
TDS
PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl


1B4BNE
TDS
PPM
100
1,000
10,000
Mg
SO4
Ca
Na+K
HCO3+CO3
Cl

APPENDIX G

RESULTS OF PHREEQE MODELING

	Molality of Standard	Computed Molality	% Dif	After Equilib.	% Dif
I6 APR23		MIX I-1 with I-4 (50-50 mix)			
Ca	-2.237	-2.2827	2.00	-2.2547	0.79
Mg	-4.431	-3.5858	-23.57	-4.5023	1.58
Na	-2.8768	-2.9711	3.17	-2.8959	0.66
K	-4.2907	-4.4156	2.83	-4.4156	2.83
Cl	-3.0579	-3.1513	2.96	-3.0421	-0.52
HCO3	-2.099	-1.9245	-9.07	-1.9514	-7.56
SO4	-2.7646	-2.7195	-1.66	-2.7551	-0.34
NO3	-3.7014	-3.9725	6.82	-3.9725	6.82
pH	6.8			6.7928	-0.11
ion str	0.018			0.0177	-1.69
e Bal	0.000568			-0.00031	282.20
Thor	0.053949			0.055814	3.34
T.alk	0.007961			0.00828	3.85
T.Carbon	0.010659				
		R^2=.847		R^2=.992	
I6 APR23		40-60 mix			
Ca	-2.237	-2.2372	0.01	-2.2602	1.03
Mg	-4.431	-3.5476	-24.90	-4.5088	1.73
Na	-2.8768	-2.9624	2.89	-2.8945	0.61
K	-4.2907	-4.4099	2.70	-4.4099	2.70
Cl	-3.0579	-3.1426	2.70	-3.0435	-0.47
HCO3	-2.099	-1.8901	-11.05	-1.9502	-7.63
SO4	-2.7646	-2.6568	-4.06	-2.7509	-0.50
NO3	-3.7014	-3.9902	7.24	-3.9902	7.24
pH	6.8			6.7954	-0.07
ion str	0.018			0.0176	-2.27
e Bal	0.000568			-0.00051	210.65
Thor	0.053949			0.056024	3.70
T.alk	0.007961			0.008318	4.29
T.Carbon	0.010659				
		R^2=.837		R^2=.991	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I6 APR23		60-40 mix			
Ca	-2.237	-2.3335	4.14	-2.2492	0.54
Mg	-4.431	-3.6278	-22.14	-4.4958	1.44
Na	-2.8768	-2.9799	3.46	-2.8974	0.71
K	-4.2907	-4.4215	2.96	-4.4215	2.96
Cl	-3.0579	-3.1601	3.23	-3.0406	-0.57
HCO3	-2.099	-1.9619	-6.99	-1.9527	-7.49
SO4	-2.7646	-2.7928	1.01	-2.7592	-0.20
NO3	-3.7014	-3.9555	6.42	-3.9555	6.42
pH	6.8			6.7902	-0.14
ion str	0.018			0.0178	-1.12
e Bal	0.000568			-0.00011	615.63
Thor	0.053949			0.055607	2.98
T.alk	0.007961			0.008242	3.41
T.Carbon	0.010659				
		$R^2=.858$		$R^2=.992$	
I6 APR23		Mix 70-30			
Ca	-2.237	-2.391	6.44	-2.2437	0.30
Mg	-4.431	-3.6743	-20.59	-4.4893	1.30
Na	-2.8768	-2.9888	3.75	-2.8988	0.76
K	-4.2907	-4.4275	3.09	-4.4275	3.09
Cl	-3.0579	-3.1691	3.51	-3.0391	-0.62
HCO3	-2.099	-2.0029	-4.80	-1.9539	-7.43
SO4	-2.7646	-2.881	4.04	-2.7632	-0.05
NO3	-3.7014	-3.9392	6.04	-3.9392	6.04
pH	6.8			6.7876	-0.18
ion str	0.018			0.0179	-0.56
e Bal	0.000568			9.13E-05	-521.3
Thor	0.053949			0.055406	2.63
T.alk	0.007961			0.008206	2.98
T.Carbon	0.010659	$R^2=.867$		$R^2=.993$	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I6 APR23		MIX I4	w/ NEB	EQUIL	
Ca	-2.237	-2.2704	1.47	-2.2835	2.04
Mg	-4.431	-3.319	-33.50	-4.5772	3.19
Na	-2.8768	-3.2306	10.95	-2.9261	1.68
K	-4.2907	-4.6884	8.48	-4.6884	8.48
Cl	-3.0579	-3.4107	10.34	-3.0062	-1.72
HCO3	-2.099	-1.9467	-7.82	-1.9735	-6.36
SO4	-2.7646	-2.6598	-3.94	-2.7281	-1.34
NO3	-3.7014	-4.0346	8.26	-4.0346	8.26
pH	6.8			6.7944	-0.08
ion str	0.018			0.017	-5.88
e Bal	0.000568			-0.00112	150.62
Thor	0.053949			0.054212	0.49
T.alk	0.007961			0.007974	0.16
T.Carbon	0.010659				
		R^2=.704		R^2=.987	

MIX SNOW w/ I-4 50-50 DILUTION

Ca	-2.237	-2.3881	6.33	-2.263	1.15
Mg	-4.431	-3.6861	-20.21	-4.4418	0.24
Na	-2.8768	-3.2148	10.51	-2.9335	1.93
K	-4.2907	-4.6139	7.00	-4.6139	7.00
Cl	-3.0579	-3.3644	9.11	-3.0053	-1.75
HCO3	-2.099	-2.0119	-4.33	-1.9531	-7.47
SO4	-2.7646	-2.7709	0.23	-2.7493	-0.56
NO3	-3.7014	-4.3701	15.30	-4.3704	15.31
pH	6.8			6.8176	0.26
ion str	0.018			0.0175	-2.86
e Bal	0.000568			-0.00078	173.06
Thor	0.053949			0.055462	2.73
T.alk	0.007961			0.008361	4.78
T.Carbon	0.010659				
		R^2=.794		R^2=.954	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I6 APR23		90-10 DILUTION			
Ca	-2.237	-3.0515	26.69	-2.2471	0.45
Mg	-4.431	-4.1705	-6.25	-4.4199	-0.25
Na	-2.8768	-3.8048	24.39	-2.9695	3.12
K	-4.2907	-4.9584	13.47	-4.9584	13.47
Cl	-3.0579	-3.8058	19.65	-2.9696	-2.97
HCO3	-2.099	-2.3903	12.19	-1.9548	-7.38
SO4	-2.7646	-3.4688	20.30	-2.762	-0.09
NO3	-3.7014	-5.0684	26.97	-5.0684	26.97
pH	6.8			6.811	0.16
ion str	0.018			0.0178	-1.12
e Bal	0.000568			-0.00034	265.26
Thor	0.053949			5.4805	99.02
T.alk	0.007961			0.008285	3.91
T.Carbon	0.010659				
		R^2=.736		R^2.861	
I6 APR23		30-70 DILUTION			
Ca	-2.237	-2.2447	0.34	-2.271	1.50
Mg	-4.431	-3.5603	-24.46	-4.4528	0.49
Na	-2.8768	-3.0776	6.52	-2.9155	1.33
K	-4.2907	-4.5088	4.84	-4.5088	4.84
Cl	-3.0579	-3.2441	5.74	-3.023	-1.15
HCO3	-2.099	-1.901	-10.42	-1.9522	-7.52
SO4	-2.7646	-2.6249	-5.32	-2.7428	-0.79
NO3	-3.7014	-4.224	12.37	-4.224	12.37
pH	6.8			6.821	0.31
ion str	0.018			0.0174	-3.45
e Bal	0.000568			-0.00099	157.12
Thor	0.053949			-0.05581	196.67
T.alk	0.007961			-0.0084	194.76
T.Carbon	0.010659				
		R^2=.797		R^2=.970	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
DISSOLVE MINERALS W/ RECHARGE (EQUILIBRATE SNOWMELT)					
I1 APR23		SNOW DIL			
Ca	-2.6315	-4.0588	35.17	-2.6728	1.55
Mg	-3.854	-4.4826	14.02	-3.8998	1.17
Na	-3.017	-4.3615	30.83	-3.1196	3.29
K	-4.4459	-5.115	13.08	-5.118	13.13
Cl	-3.1973	-4.0583	21.22	-3.0951	-3.30
HCO3	-2.4391	-2.579	5.42	-2.1479	-13.56
SO4	-3.3696	-5.9825	43.68	-3.3385	-0.93
pH	6.4			6.4195	0.30
ion str	0.0081			0.0077	-5.19
e Bal	0.000696			-0.00024	395.92
Thor	0.031162			0.031205	0.14
T.alk	0.003638			0.003782	3.80
		R^2=.415		R^2=.966	
I3 APR23		SNOW DIL			
Ca	-2.3942	-4.0588	41.01	-2.4055	0.47
Mg	-3.3768	-4.4826	24.67	-3.3873	0.31
Na	-2.9064	-4.3615	33.36	-3.0065	3.33
K	-4.6376	-5.115	9.33	-5.115	9.33
Cl	-3.0869	-4.0583	23.94	-2.9875	-3.33
HCO3	-2.2049	-2.579	14.51	-1.969	-11.98
SO4	-2.903	-5.9825	51.48	-2.8952	-0.27
pH	6.5			6.5059	0.09
ion str	0.0141			0.0139	-1.44
e Bal	0.000517			-0.00024	319.76
Thor	0.050477			0.050592	0.23
T.alk	0.006239			-0.00634	198.48
		R^2=.289		R^2=.989	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I4 APR23					
Ca	-2.0918	-4.0588	48.46	-2.0675	-1.18
Mg	-3.4213	-4.4826	23.68	-3.3897	-0.93
Na	-2.9295	-4.3615	32.83	-3.0293	3.29
K	-4.3874	-5.115	14.22	-5.115	14.22
Cl	-3.1097	-4.0583	23.37	-3.0093	-3.34
HCO3	-1.9264	-2.579	25.30	-1.7784	-8.32
SO4	-2.47	-5.9825	58.71	-2.4882	0.73
pH	6.7			6.6885	-0.17
ion str	0.0258			0.0263	1.90
e Bal	-0.00132			-0.00024	-460.90
Thor	0.087974			0.086129	-2.14
T.alk	0.011847			0.011638	-1.80
		R^2=.204		R^2=.973	
I6 APR23		SNOW DIL			
Ca	-2.237	-4.0588	44.89	-2.2451	0.36
Mg	-4.431	-4.4826	1.15	-4.4238	-0.16
Na	-2.8768	-4.3615	34.04	-2.9779	3.40
K	-4.2907	-5.115	16.12	-5.115	16.12
Cl	-3.0579	-4.0583	24.65	-2.9602	-3.30
HCO3	-2.099	-2.579	18.61	-1.9601	-7.09
SO4	-2.7646	-5.9825	53.79	-2.762	-0.09
pH	6.8			6.808	0.12
ion str	0.018			0.0178	-1.12
e Bal	0.000568			-0.00024	341.44
Thor	0.053949			5.4233	99.01
T.alk	0.007961			0.008189	2.78
		R^2=.197		R^2=.947	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
COMPOSITE	MIX &	DILUTE	FIRST		
I3 APR23	50-50	Dil. I4	Result w/	I-1	
Ca	-2.3942	-2.3881	-0.26	-2.493	3.96
Mg	-3.3768	-3.6861	8.39	-3.762	10.24
Na	-2.9064	-3.2148	9.59	-3.1047	6.39
K	-4.6376	-4.6139	-0.51	-4.5218	-2.56
Cl	-3.0869	-3.3644	8.25	-3.2729	5.68
HCO3	-2.2049	-2.0119	-9.59	-2.0778	-6.12
SO4	-2.903	-2.7709	-4.77	-2.9744	2.40
NO3	-4.0025	-4.3701	8.41	-4.0695	1.65
pH	6.5	6.582	1.25	6.505	0.08
ion str	0.0141	0.0138	-2.17	0.011	-28.18
e Bal	0.000517	-0.00078	166.50	-4.1E-05	1372.1
Thor	0.050477	0.0493	-2.38	0.040232	-25.46
T.alk	0.006239	0.00614	-1.58	0.00489	-27.58
T.Carbon	0.01062				
		R^2_1=.946	(IONS)	R^2_1=.957	
		R^2_2=.997	(ALL VALUES)	R^2_2=.998	
I6 APR23		Dil. I4	Result w/I-1		
Ca	-2.237	-2.3881	6.33	-2.493	10.27
Mg	-4.431	-3.6861	-20.21	-3.762	-17.78
Na	-2.8768	-3.2148	10.51	-3.1047	7.34
K	-4.2907	-4.6139	7.00	-4.5218	5.11
Cl	-3.0579	-3.3644	9.11	-3.2729	6.57
HCO3	-2.099	-2.0119	-4.33	-2.0778	-1.02
SO4	-2.7646	-2.7709	0.23	-2.9744	7.05
NO3	-3.7014	-4.3701	15.30	-4.0695	9.05
pH	6.8	6.582	-3.31	6.505	-4.53
ion str	0.018	0.0138	-30.43	0.011	-63.64
e Bal	0.000568	-0.000777	173.06	-4.1E-05	1497.6
Thor	0.053949	0.049302	-9.43	0.040232	-34.09
T.alk	0.007961	0.006142	-29.62	0.00489	-62.80
T.Carbon	0.010659				
		R^2_1=.794		R^2_1=.859	
		R^2_2=.988		R^2_2=.992	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I3 APR23		MIX I4 w/ NEB			
Ca	-2.3942	-2.2704	-5.45	-2.4517	2.35
Mg	-3.3768	-3.319	-1.74	-3.481	2.99
Na	-2.9064	-3.2306	10.04	-2.9515	1.53
K	-4.6376	-4.6884	1.08	-4.6884	1.08
Cl	-3.0869	-3.4107	9.49	-3.0369	-1.65
HCO3	-2.2049	-1.9467	-13.26	-1.9915	-10.72
SO4	-2.903	-2.6598	-9.14	-2.856	-1.65
NO3	-4.0025	-4.0346	0.80	-4.0346	0.80
pH	6.5			6.5162	0.25
ion str	0.0141			0.0132	-6.82
e Bal	0.000517			-0.00112	146.08
Thor	0.050477			0.049611	-1.75
T.alk	0.006239			0.006193	-0.75
T.Carbon	0.01062				
		R^2=.943		R^2=.990	
I3 APR23	70-30	MIX NEB+I4		EQUIL	
Ca	-2.3942	-2.3692	-1.06	-2.4499	2.27
Mg	-3.3768	-3.284	-2.83	-3.4946	3.37
Na	-2.9064	-2.9699	2.14	-2.9154	0.31
K	-4.6376	-4.1047	-12.98	-4.1047	-12.98
Cl	-3.0869	-3.1505	2.02	-3.0704	-0.54
HCO3	-2.2049	-2.0408	-8.04	-2.0039	-10.03
SO4	-2.903	-2.7672	-4.91	-2.8556	-1.66
NO3	-4.0025	-4.0215	0.47	-4.0215	0.47
pH	6.5			6.5107	0.16
ion str	0.0141			0.0132	-6.82
e Bal	0.000517			-0.00073	170.67
Thor	0.050477			0.048489	-4.10
T.alk	0.006239			0.006029	-3.48
T.Carbon	0.01062				
		R^2=.948		R^2=.939	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I4 APR23		Mix 4/9 + Snow			
Ca	-2.0918	-2.3344	10.39		
Mg	-3.4213	-4.2549	19.59		
Na	-2.9295	-3.1706	7.60		
K	-4.3874	-4.5917	4.45		
Cl	-3.1097	-3.3238	6.44		
HCO3	-1.9264	-2.0543	6.23		
SO4	-2.47	-1.7088	-44.55		
NO3	-4.0692	-4.4079	7.68		
pH	6.7				
ion str	0.0258				
e Bal	-0.00132				
Thor	0.087974				
T.alk	0.011847				
T.Carbon	0.016804	R^2=.866			

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I-3 APR 9 50-50 I-4 & I-1					
Ca	-2.392	-2.2325	-7.14	-2.3686	-0.99
Mg	-3.5861	-4.1066	12.67	-3.5621	-0.67
Na	-2.8507	-2.9179	2.30	-2.9179	2.30
K	-4.4457	-4.4948	1.09	-4.4948	1.09
Cl	-3.0308	-3.0982	2.18	-3.0982	2.18
HCO3	-2.2549	-1.9552	-15.33	-1.9321	-16.71
SO4	-2.9031	-2.6546	-9.36	-2.9215	0.63
NO3	-3.9445	-4.0183	1.84	-4.0183	1.84
pH	6.3			6.2877	-0.20
ion str	0.0137			0.0138	0.72
e Bal	0.00102			0.001645	37.99
Thor	0.055166			0.054433	-1.35
T.alk	0.00556			0.005415	-2.68
T.Carbon	0.011836	R^2=.947		R^2=.983	
I-3 APR 9 70-30 Mix					
Ca	-2.392	-2.3441	-2.04	-2.3743	-0.75
Mg	-3.5861	-4.1066	12.67	-3.5678	-0.51
Na	-2.8507	-2.9323	2.78	-2.9323	2.78
K	-4.4457	-4.5624	2.56	-4.5624	2.56
Cl	-3.0308	-3.1124	2.62	-3.1124	2.62
HCO3	-2.2549	-2.0212	-11.56	-1.931	-16.77
SO4	-2.9031	-2.8133	-3.19	-2.9178	0.50
NO3	-3.9445	-3.9873	1.07	-3.9873	1.07
pH	6.3			6.2905	-0.15
ion str	0.0137	R2c=.958		0.0137	0.00
e Bal	0.00102	R2e1=.983		0.001448	29.55
Thor	0.055166	R2e2=.9986		0.054654	-0.94
T.alk	0.00556			0.005445	-2.11
T.Carbon	0.011836	R^2=.958		R^2=.983	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I-3 APR 9				EQUIL	
Ca	-2.392	-2.949	18.89	-2.3801	-0.50
Mg	-3.5861	-4.1067	12.68	-3.5736	-0.35
Na	-2.8507	-2.9472	3.27	-2.9472	3.27
K	-4.4457	-4.4101	-0.81	-4.4101	-0.81
Cl	-3.0308	-3.127	3.08	-3.127	3.08
HCO3	-2.2549	-2.099	-7.43	-1.9298	-16.85
SO4	-2.9031	-3.0657	5.30	-2.9139	0.37
NO3	-3.9445	-3.9584	0.35	-3.9584	0.35
pH	6.3			6.2933	-0.11
ion str	0.0137			0.0136	-0.74
e Bal	0.00102			0.001267	19.49
Thor	0.055166			0.054881	-0.52
T.alk	0.00556			0.005477	-1.51
T.Carbon	0.01184	R^2=.891		R^2=.976	
I-3 APR 9	50-50	I4 & SNOW		EQUILIBR	
Ca	-2.392	-2.3344	-2.47	-2.3881	-0.16
Mg	-3.5861	-4.2549	15.72	-3.5816	-0.13
Na	-2.8507	-3.1706	10.09	-3.1706	10.09
K	-4.4457	-4.5917	3.18	-4.5917	3.18
Cl	-3.0308	-3.3238	8.82	-3.3238	8.82
HCO3	-2.2549	-2.0543	-9.76	-1.929	-16.89
SO4	-2.9031	-1.7088	-69.89	-2.9128	0.33
NO3	-3.9445	-4.4079	10.51	-4.4079	10.51
pH	6.3			6.296	-0.06
ion str	0.0137			0.0131	-4.58
e Bal	0.00102			0.000951	-7.22
Thor	0.055166			0.054636	-0.97
T.alk	0.00556			0.005499	-1.11
T.Carbon	0.011836	R^2=.779		R^2=.947	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I-3 APR 9	.9 SNOW + .1 I-4				
Ca	-2.392	-3.0017	20.31	-2.4161	1.00
Mg	-3.5861	-4.4265	18.99	-3.6096	0.65
Na	-2.8507	-3.77	24.38	-3.7700	24.38
K	-4.4457	-4.9485	10.16	-4.9485	10.16
Cl	-3.0308	-3.7829	19.88	-3.7829	19.88
HCO3	-2.2549	-2.4101	6.44	-1.9239	-17.20
SO4	-2.9031	-3.4069	14.79	-2.8974	-0.20
NO3	-3.9445	-5.1062	22.75	-5.1062	22.75
pH	6.3			6.3089	0.14
ion str	0.0137			0.0123	-11.38
e Bal	0.00102			2.16E-06	-47082.1
Thor	0.055166			0.055303	0.25
T.alk	0.00556			0.005638	1.38
T.Carbon	0.011836	R^2=.912		R^2=.834	
I-6 APR 9		60-40 MIX			
Ca	-2.2296	-2.1858	-2.00	-2.238	0.38
Mg	-5.3853	-4.1065	-31.14	-5.3882	0.05
Na	-2.8506	-2.9108	2.07	-2.9108	2.07
K	-4.313	-4.3822	1.58	-4.3822	1.58
Cl	-3.0308	-3.0913	1.96	-3.0913	1.96
HCO3	-2.1451	-1.9257	-11.39	-1.95	-10.01
SO4	-2.836	-2.5928	-9.38	-2.8331	-0.10
NO3	-3.6572	-4.0346	9.35	-4.0346	9.35
pH	6.6			6.605	0.08
ion str	0.0176			0.0172	-2.33
e Bal	0.002025			0.00175	-15.72
Thor	0.05425			0.054158	-0.17
T.alk	0.00716			0.00725	1.23
T.Carbon	0.011099	R^2=.800		R^2=.983	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
I-3 APR 9		SNOW ANALYSIS EQUILIRATED			
Ca	-2.392	-4.0588	41.07	-2.4232	1.29
Mg	-3.5861	-4.4826	20.00	-3.6167	0.85
Na	-2.8507	-4.3615	34.64	-4.3615	34.64
K	-4.4457	-5.115	13.09	-5.115	13.09
Cl	-3.0308	-4.0583	25.32	-4.0583	25.32
HCO3	-2.2549	-2.5757	12.45	-1.9225	-17.29
SO4	-2.9031	-5.9825	51.47	-2.8934	-0.34
pH	6.3			6.3121	0.19
ion str	0.0137			0.0121	-13.22
e Bal	0.00102			-0.00024	533.82
Thor	0.055166			0.05548	0.57
T.alk	0.00556			0.005674	2.01
T.Carbon	0.011836	R^2=.283		R^2=.679	
I-4 APR 9		SNOW ANALYSIS EQUILIBRATED			
Ca	-2.0374	-4.0588	49.80	-2.071	
Mg	-4.1064	-4.4826	8.39	-4.1401	
Na	-2.8838	-4.3615	33.88	-4.3615	
K	-4.3611	-5.115	14.74	-5.115	
Cl	-3.0648	-4.0583	24.48	-4.0583	
HCO3	-2.0477	-2.5757	20.50	-1.8166	
SO4	-2.4079	-5.9825	59.75	-2.3923	
pH	6.5			6.5162	
ion str	0.0264	R2c=.136		0.0244	
e Bal	0.002137	R2e1=.783		-0.00024	
Thor	0.083812	R2e2.977		0.08533	
T.alk	0.008961			0.009223	
T.Carbon	0.014992				

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
WELL C4	6/22/86	50-50 MIXA4-C4		EQUIL	
Ca	-2.5897	-2.6757	3.21	-2.6197	1.15
Mg	-2.6693	-2.7086	1.45	-2.7768	3.87
Na	-2.613	-2.6845	2.66	-2.645	1.21
Cl	-3.0308	-3.0944	2.06	-2.9995	-1.04
HCO3	-2.004	-1.9513	-2.70	-1.9661	-1.93
SO4	-3.4908	-3.535	1.25	-3.4828	-0.23
pH	7.4			7.3872	-0.17
ion str	0.0158			0.0146	-8.22
e Bal	0.00038			-0.00122	131.17
Thor	0.045427			0.046272	1.83
T alk	0.009908			0.009968	0.61
T Carb	0.010723	R^2=.997		R^2=.988	
WELL C4	1/23/86	A4-D4 MIX			
Ca	-2.6522	-2.6558	0.14	-2.7967	5.17
Mg	-2.6652	-3.0078	11.39	-2.8813	7.50
Na	-2.6854	-2.4975	-7.52	-2.509	-7.03
K	-5.2116	-5.4778	4.86	-5.4778	4.86
Cl	-3.0884	-3.2078	3.72	-3.2702	5.56
HCO3	-1.9978	-1.9001	-5.14	-1.9296	-3.53
SO4	-3.4839	-3.4122	-2.10	-3.3907	-2.75
pH	6.96			7.0856	1.77
ion str	0.015			0.0128	-17.19
e Bal	-0.00067			-0.0024	71.48
Thor	0.052006			0.00495	950.65
T alk	0.01005			0.00994	-1.16
T Carb		R^2=.976		R^2=.981	

Molality of Standard		Computed Molality	% Dif	After Equilib.	% Dif
NEB		MIX I1+I7			
Ca	-2.579	-2.6389	2.27	-2.6032	0.93
Mg	-3.2362	-3.2783	1.28	-3.4117	5.14
Na	-2.9884	-2.9958	0.25	-2.8062	-6.49
K	-4.0237	-4.7169	14.70	-4.7169	14.70
Cl	-3.1692	-3.1463	-0.73	-2.8973	-9.38
HCO3	-2.2775	-2.1898	-4.00	-2.3636	3.64
SO4	-3.0046	-3.2459	7.43	-3.0538	1.61
pH	7.3			7.4427	1.92
ion str	0.01			0.0101	0.99
e Bal	-0.00092			0.000289	419.79
Thor	0.029683			0.023746	-25.00
T alk	0.005278			0.004021	-31.26
T Carb	0.005806				
		R^2=.961		R^2=.896	

VITA

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Candidate for the Degree of

Doctor of Philosophy

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