GROUND-WATER QUALITY VARIANCE AT AN INSTANT OF TIME IN A SHALLOW UNCONFINED AQUIFER IN NORTH CENTRAL OKLAHOMA

Ву

JAMES F. WARD

Bachelor of Science

Southwest Missouri State University

Springfield, Missouri

1980

Submitted to the Faculty of the Graduate College of the Oklahoma State University in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE July, 1993

OKLAHOMA STATE UNIVERSITY

GROUND-WATER QUALITY VARIANCE AT AN INSTANT OF TIME IN A SHALLOW UNCONFINED AQUIFER IN NORTH CENTRAL OKLAHOMA

Thesis Approved:

hesis Ad

Dean of the Graduate College

PREFACE

The variance of ground-water quality at an instant in time was studied over two long pumping periods in May, 1992. The site, located in Stillwater, Oklahoma, consists of 41 monitoring wells that lie within a suburban area of about 11,000 square feet. The unconfined aquifer was sampled from a cluster of wells, of which three of the wells were pumped and sampled continuously.

The water was analyzed both in the field, and in the laboratory. The results of the analyses were compared to samples of water representing casing storage, and samples recovered after the wells had been purged. Since water sampling is one of the more important aspects of a hydrogeological study, the investigator is always in search of the sample that is most representative of the aquifer. If that sample can be recovered without purging the well, then time and money can be saved.

Separate from, but in conjunction with the ground-water variance research, was an attempt to detect the pesticide 2,4-D in the ground water. New immunoassay technology for the detection of herbicides in water and soil has produced a fast and inexpensive procedure for the determination of pesticide contamination. This procedure is capable of

iii

detecting the presence of pesticides in concentrations as small as 0.5 parts per billion.

.

TABLE OF CONTENTS

Chapte	r
--------	---

I.	INTRODUCTION
	Description of the Problem
II.	GENERAL FEATURES OF THE AREA
	Topography and Climate7Soil Description10Geology12Surface-Water Hydrology12Ground-Water Hydrology13Aquifer Properties13Well Construction13Recharge14
III.	SAMPLING AND ANALYTICAL METHODOLOGY FOR PESTICIDE DETERMINATION
	Sampling and Analytical Methodology 18 Field Parameters 20 Pesticide Application
IV.	SAMPLING AND ANALYTICAL ANALYSIS OF GROUND WATER
	Sampling Methodology

Chapter																		Page
				Bro	mide	•	•	•	•	•	•	•	•	•	•	•	•	50
				Nit	rate	•	•	•	•	•	•	•	•	•	•	•	•	50
				Sul	fate	•	•	•	•	•	•	•	•	•	•	•	•	53
				Dis	cuss:	ion	1.	•	•	•	•	•	•		•	•	•	55
			May	31,	1992	Sa	mp	le	E	Per	cic	bd	•	•	•	٠	•	55
				Flu	oride	Э.	٠	•	•	•	•	•	•	•	٠	•	•	55
				Chl	oride	Э.	•	•	•	•	•	•	•	•	•	•		58
				Bro	mide	•	•	•	•	•	•	•	•	•	•	•	•	58
				Nit	rate	•	٠	•	•	•	•	•	•	•	•	•	•	61
				Sul	fate	•	•	•	•	•	•	•	•	•	•	•	•	63
				Dis	cuss:	ion	ι.	•	•	•	•	•	•	•	•	•	•	63
								_										
v.	CONC	LUSION	S AN	D IM	PLIC	ATI	ON	S	AN	D	SU	JGG	JES	STI	IOI	1S		
	FOR	FURTHE	R SI	UDY.	• •	•	•	•	•	•	•	•	٠	•	•	•	•	66
		0						- - -	•									
		Conci	usic	ns o	n Pes	361	Cl	ae	_ P.	10V	ren	ler.	ιĻ	•	•	•	•	66
		Conci	usic	ns o	n wat	er	Ω.	ua	11	.су	r v	ar	12	anc	ce	•	•	67
		Impli	cați	ons.	• •	•.	:	•	. .	•	•	•	•	•	•	•	•	69
		Sugge	stic	ns I	or Fi	irt	ne	r	St	uc	ly	•	•	•	•	٠	•	70
	-																	
REFERENC.	ES	• • •	• •	• •	• •	•	•	•	•	•	•	•	•	•	•	•	•	/1
APPENDIX	- RA	W DATA	FOR	ALL	WELI	S					•						•	74

LIST OF TABLES

Table	:	Page
I.	1992 Rainfall at the Site	9
II.	Water Quality at the Site	26
III.	EnviroGuard Test Results For 2,4-D	28

.

.

•

.

LIST OF FIGURES

Figu	re	Page
1.	Site Location	8
2.	Soil Horizons	10
3.	Well Cluster Locations	15
4.	Screen Intervals	16
5.	Location of "D" Wells	19
6.	Levels of Detection	22
7.	Binding of Antibodies	23
8.	Field Sampled Temperature May 26, 1992	35
9.	Field Sampled pH May 26, 1992	36
10.	Field Sampled Specific Conductance May 26, 1992	37
11.	Field Sampled Bicarbonate May 26, 1992	38
12.	Field Sampled Temperature May 31, 1992	39
13.	Field Sampled pH May 31, 1992	40
14.	Field Sampled Specific Conductance May 31, 1992	41
15.	Field Sampled Bicarbonate May 31, 1992	42
16.	Water Levels May 26, 1992	46
17.	Fluoride May 26, 1992	47
18.	Chloride May 26, 1992	49
19.	Bromide May 26, 1992	51
20.	Nitrate May 26, 1992	52
21.	Sulfate May 26, 1992	54

viii

Figur	re	Page
22.	Water Levels May 31, 1992	. 56
23.	Fluoride May 31, 1992	. 57
24.	Chloride May 31, 1992	. 59
25.	Bromide May 31, 1992	. 60
26.	Nitrate May 31, 1992	. 62
27.	Sulfate May 31, 1992	. 64

· ·

.

CHAPTER I

INTRODUCTION

Description of the Problem

The application of pesticides occurs regularly in suburban areas across the country. This may be done by lawncare professionals, or by homeowners trying to rid their yard of unsightly weeds and other pests. Once the pesticide has been applied, it seems to be "out of sight, out of mind", unless the weeds reappear. What happens to the pesticide once it has been applied? Does it just kill the weeds and biodegrade, is it bound to the soil never to be seen again, or does it infiltrate through the unsaturated zone to a shallow aquifer? If it infiltrates, is the concentration high enough to be a threat to human health and the environment?

It has been suggested that the chemical quality of ground water in unconfined aquifers varies through time. It has been suggested that the chemical quality will differ depending on whether or not the well has been purged prior to sample collection. In conjunction with the pesticide research noted above, this investigation also attempted to determine if there is variability in the properties of

. 1

ground-water samples collected from the same aquifer, at different depths, and at the same time.

Purpose and Scope

The purpose of this report is to determine the effect, if any, of the application of a pesticide on a shallow unconfined aquifer. This will be accomplished with the use on an immunoassay test kit, which is capable of detecting pesticides in soil and water. The immunoassay technology allows for inexpensive, rapid, and portable analysis, which may eliminate the need for complete laboratory work-ups on negative samples (Vanderlaan and others, 1991). The pesticide applied to the site is 2,4-Dichlorophenoxyacetic acid (2,4-D).

This study also includes an evaluation of the temporal variability of water samples in an aquifer. Several authors have suggested that it is imperative to purge a well three or four well volumes before collecting a sample. Water samples were collected from a well cluster, which is screened in selected intervals, as well as the entire saturated thickness. Samples also were collected from casing storage prior to purging, and after removing three well volumes, or after being pumped dry and allowed to recover. Finally, samples were collected hourly while the well was continuously pumped. The water samples were tested in the field for pH, temperature, specific conductance, and bicarbonate. The samples were then analyzed with an ion chromatograph. Specifically, the concentration, in parts per million (ppm), of fluoride, chloride, bromide, nitrate and sulfate were determined.

The reliability of water samples is one of the most important factors in environmental sampling and cannot be overlooked. This study makes no attempt to simulate a situation where hazardous constituents are present in the ground-water system. Rather an attempt was made to determine whether or not valid geochemical data can be recovered from casing storage, and if so, how well these data compare with those recovered through time.

Theoretically the water present in the well bore after a well has been continuously pumped, will be identical to that in the aquifer. If the water recovered from casing storage is equivalent to that of the aquifer, then the necessity of purging is open to question.

Previous Work at the Site

Work began at this site when Hagen (1985) investigated water-level fluctuations and variations in ground-water quality during recharge events. Hagen observed that macropores were a controlling factor on these events.

Hoyle (1987) noted short-term variations in groundwater quality could be due to a combination of human activities and geochemical processes. Ross (1988) was the first to monitor the water quality in the unsaturated zone. He installed eight suction lysimeters, and four monitoring wells, and documented the susceptibility of the unsaturated zone to short-term variations in water quality.

Froneberger (1989) monitored the response of the aquifer to precipitation. He noted that when the watertable was elevated, and soil moisture was high, a small volume of water could cause a significant rise in the watertable.

Melby (1989) conducted a study to determine hydraulic conductivity values for the fine-grained alluvium aquifer present at the site.

Nelson (1989) studied the cause and effect of watertable fluctuations at the site.

General Discussion of 2,4-D

The herbicide 2,4-D generally is used to control broadleaf weeds in turf or pasture areas (Colby and others, 1989), and is usually applied as a spray. 2,4-D is considered to be a selective herbicide that is used to control one type of plant, and cause little or no damage to others (EPA, 1989). According to the Herbicide Handbook (1989), the chemical is taken up by roots within about six hours after application and resists leaching. The Handbook of Environmental Degradation Rates (1991), states that the half-life of 2,4-D in soil is from 10 to 50 days, and in water from 20 days to six months. The chemical has a high adsorption rate in soils (Colby and others, 1989) and, therefore, tends to not be very mobile. The lack of mobility is not always the case and site conditions may dictate whether or not the herbicide enters the ground water. The EPA (1989) states that soil texture, the presence of organic material, the depth to ground water, and the failure to apply the herbicide in appropriate quantities, are a few of the factors that can contribute to ground-water contamination.

Acknowledgements

I would like to express my thanks to my major advisor, Dr. Wayne A. Pettyjohn, for his support and encouragement throughout my research and during graduate school. He has set a standard of excellence that I will strive to reach throughout my career.

I would also like to thank Dr. Arthur W. Hounslow for help in this research effort, and his suggestions along the way. The geochemical background, which he has given me, continues to pay dividends.

I am also proud to have been involved with the Department of Agronomy. Dr. Brian J. Carter opened my eyes to the difference between soil and dirt, and the impact of the unsaturated zone on ground water. I appreciate the fact

that he was willing to lend his support and guidance to the completion of my research.

Additional thanks are due to Phil Ward, of the Department of Agronomy. This research could not have been finished were it not for his unselfish assistance in the laboratory.

I would also like to thank all the fellow yard workers whose research has preceded mine. There is no finer laboratory to study hydrogeology in than the one located in the suburbs of Stillwater.

Finally, I would like to thank my wife, Devona, for her unfailing support and encouragement. She is the force that helped me to uncover my lifes work, without her none of this would have been possible, and for that I am eternally grateful.

CHAPTER II

GENERAL FEATURES OF THE AREA

Topography and Climate

The study area is on the flood plain of Boomer Creek, which lies approximately 600 feet west of the site (Figure 1). The site is relatively flat, with a total relief of less than a foot. Just east of the site are outcrops of shale, which form low rolling hills with a local relief of approximately 100 feet. The legal description of the site is the NW/4 of Section 11, Township 19 North, Range 2 East, Payne County, Oklahoma. It lies within the city limits of Stillwater.

During the six months preceding the investigation total rainfall at the site was 17.86 inches. Total annual precipitation ranges between 32 and 34 inches (Pettyjohn and others, 1986), most of which falls between April and September. Precipitation at the site was 7.55 inches in November 1991, 2.13 inches in December, 3.26 inches in January 1992, 0.88 inches in February, 1.14 inches in March, and 2.90 inches in April, 1992 (Table 1). Rain events were sporadic and were followed by several days of dry conditions. November, December, and January were wet

SITE LOCATION MAP



AFTER SOIL CONSERVATION SERVICE 1986

Figure 1. Site Location	Arrow	Marks	Field	Site.
-------------------------	-------	-------	-------	-------

Table I

Month	Rainfall (inches)
January	3.26
February	0.88
March	1.14
April	2.90
Мау	2.08

1992 RAINFALL AT THE SITE

months, and it rained only three times between February and March.

The site is hot in the summer and cool in the winter, with an average air temperature of 39 degrees Fahrenheit in the winter, and an average summer temperature of 80 degrees Fahrenheit (SCS, Payne Co. Survey, 1987).

Soil Description

The study area is dominated by the Ashport Silt Loam, a deposit that is typical of a nearly flat, low level flood plain along large and small tributaries. The soils are deep and well drained, and possess moderate permeability. The Ashport Series is formed in recent alluvial sediments, which are fine-silty, mixed, thermic Fluventic Haplustolls (SCS, Payne Co. Survey, 1987). Ross (1988) described in detail the soil horizons he identified at the site. He also described the color and structure, and determined bulk density of the upper five feet of the soil. Ross identified 25 different horizons within the Ashport Silt Loam (Figure Included in this section are two buried soils, one at 2). four feet, and another at 27.5 feet. The upper buried horizon has been radiocarbon dated at 1,300 years before present, and the lower horizon has been dated at 10,600 years (+/- 170 years). Based on these dates, Hoyle (1989) determined that the rate of deposition was approximately 0.0031 feet per year, or 325 years per foot of accumulation.



Figure 2. Soil Horizons

Geology

Bedrock in the area is dominated by interbedded sandstone, siltstone, and shale. These Upper Pennsylvanian and Lower Permian rocks generally dip to the west at 40 to 50 feet/mile (Shelton and others, 1985). The Quaternary alluvium filled a valley, which is cut into the Upper Pennsylvanian Doyle Shale, a member of the Oscar Group. The Doyle contains 170 feet of interbedded red shale and sandstone, with shale the dominant type (Shelton and others, 1985). The shale is visible where it crops out just east of the site along the Atchison, Topeka and Sante Fe railroad tracks.

The alluvium is predominately a red-brown silt and clay, which is approximately 35 feet thick, that was deposited over an eight foot thick gravel lag deposit. Underlying the alluvium is a weathered shale that is part of the Garber-Wellington Formation, a fluvial deposit. These deposits are characterized by alternating layers of red shale, siltstone, and sandstone, although locally the dominant lithology is shale.

Surface-Water Hydrology

The relatively flat surface of the floodplain encourages very little surface runoff. The average runoff is approximately 4.5 inches annually (Pettyjohn and others, 1986). As noted above, the site is relatively flat, which gives rise to ponding of water during heavy rains. Boomer Creek borders the site to the west and is the major drainage for the area. Flow in the creek is sluggish due to a dam located approximately a mile upstream.

Ground-Water Hydrology

Aquifer Properties

The aquifer investigated occurs in alluvial deposits approximately 43 feet thick beneath the site, and is underlain by shale. The water table is known to fluctuate from three to nearly 13 feet below the surface, giving a saturated thickness ranging from 30 to 40 feet. Recharge of the aquifer is from precipitation, while evapotranspiration controls the level of the water table.

Tests by Hoyle (1987), and Melby (1989) yielded average hydraulic conductivities in the range of 39 to 96 gpd/ft². Considering the nature of this fine-grained aquifer these values seem large, but macropores present in the soil have made a significant impact. These same tests yielded transmissivity values in the range of 2,200 gpd/ft, and storativity values ranging from 0.01 to 0.3.

Well Construction

Forty-one monitor wells are located at the site, the

first of which was installed in 1985. Many of the wells were installed in clusters, with five locations having at least five wells of varying depth (Figure 3).

The wells consist of polyvinyl chloride (PVC) casing. Twenty-six of the wells are 2 inch diameter, one is six inches in diameter, one is four inches in diameter, six wells are 1 inch in diameter, five are a half inch in diameter, one is one and one-quarter inch, and one is threequarters of an inch in diameter. Wells at each cluster are 8.5, 9.5, 10.5, and 14 feet deep. These wells are slotted in the lower four to six inches, while a fifth well, also 14 feet deep, is slotted from seven to 14 feet (Figure 4). The slotted intervals were sand packed and topped with a bentonite slurry to fill the annular space to the surface. A concrete pad was installed at the surface and the elevation of each pad was surveyed. The wells were installed using hand auger, hollow-stem auger, and a Specifications for the individual wells Giddings Probe. are included in Appendix A.

<u>Recharge</u>

The low relief of the site tends to cause ponding of water on the surface and to increase the infiltration. Hagen (1986) studied these events in the Fall of 1985 and Spring of 1986 and determined that recharge was approximately 47 per cent of the total precipitation. Given



Figure 3. Well Cluster Locations





- -

.

.

-

the nature of the alluvium this would appear to be unusually large. Yet studies by Hagen (1986), Hoyle (1989), Froneberger (1989), and Zietlow (In Press) determined that macropores, which are present in the soil, create verticle pathways for infiltration. Zietlow (In Press) calculated the movement of water from the surface to the aquifer at 15 feet/hour following a three inch rain that fell within one hour. This type of permeability tends to be enhanced during the dry, hot summers. This research was conducted during a period when the macropore permeability was not at maximum, yet the pathways of migration were still open and the rate was high.

CHAPTER III

SAMPLING AND ANALYTICAL METHODOLOGY FOR PESTICIDE DETERMINATION

Sampling and Analytical Methodology

Samples of the ground water were taken prior to application of the commercial chemical product Weedone, containing 2,4-Dichlorophenoxyacetic acid (2,4-D). The site received 3.26 inches of rain in January 1992, and a total of 0.88 inches of precipitation fell during February. The samples were collected from well D-1, 10.8 feet deep, located in the southeast corner of the site (Figure 5), from March 3, until March 13, 1992. A peristaltic pump was chosen for this study due to the depth of the wells and the convenience of sample recovery. Due to the shallow depth of the well, samples were taken after the well was pumped dry and allowed to recover, as opposed to bailing three well volumes prior to sampling. The process of well purging is discussed in detail in Chapter IV.



Figure 5. Location of "D" Wells

Field Parameters

Temperature, specific conductance (micromohs/cm), and pH were measured in the field during sample collection, or soon thereafter in the on-site laboratory. The samples were analyzed according to procedures suggested by EPA report #625/6-90/0166 (1991). Measurements were made with a handheld digital thermometer and pH meter. Specific conductance was measured with a temperature compensating conductivity meter. The pH and conductivity meters were calibrated regularly with standard solutions to maintain quality control. Samples were refrigerated and maintained in dark glass containers for later pesticide analysis.

The pesticide analysis was performed with the Millipore EnviroGard test kit. These kits are an inexpensive and highly reliable method of determining the presence of pesticide residue in water or soil. The kits utilize an immunoassay technology, which has been in use in the medical field for years. The tests are easily run and offer results that are comparable to gas chromatography and mass spectrometry in less than two hours (Bushway and others, 1988). The detection levels vary for different pesticides but in the case of 2,4-D residues and some other phenoxy herbicides, the detection level may vary from .05 to 1000 parts per billion (ppb) as shown in Figure 6. The kits are used for a quantitative test for 2,4-D. The versatility of this system allows for use both in the field and the laboratory. Results can be noted by a visible change in color, or they may be monitored more exactly with a spectrophotometer, which compares a negative control to the water sample. The basic principle is that the color is inversely proportional to the dosage, the lighter the color compared to the control, the greater the concentration exceeds the Least Detectable Dose (LDD).

The basis of the test is the use of antibodies that bind the 2,4-D residue and a 2,4-D enzyme conjugate (Figure 7). The pesticide in the sample and the conjugate compete for the binding sites on the inside of the coated test tube. The mixture is allowed to incubate for 10 minutes after which the test tube is filled to overflowing with distilled water, decanted and as much water as possible shaken out. This is done three additional times, being sure as much water as possible is removed each time. Clear solutions of substrate and chromogen are then added to the tube and swirled for a few seconds.

This procedure will convert the sample into a compound that will cause the chromogen to turn blue. Since there are the same number of antibodies sites available on each tube, and each tube receives the same number of conjugate molecules, a sample containing a low concentration of 2,4-D residue allows more conjugate molecules to be bound to the antibody. If the sample contains a small concentration of 2,4-D, it will turn dark blue, while a high concentration

COMPOUND

LDD (ppb) *	
-------------	--

2,4-D	0.5
2,4-Methyl ester	2.5
2,4,5-T	5.0
Dichlorprop	0.5**
2,4-D Isopropyl ester	12.0
МСРА	10.0
2,4,5-TP (Silvex)	70.0

*LDD is the least detectable dose as determined from spectrophotometric interpretation of results ** estimate

Figure 6. Levels of Detection



Ο

О−е

́)−Е

 A sample containing 2,4-D (0) is added to a test tube, followed by 2, 4-D-enzyme conjugate (0-E). The 2,4-D-enzyme conjugate competes with the 2,4-D for the same antibody binding site.

2. After this mixture is incubated for 10 minutes, any unbound molecules are washed away.

- 3. Clear solutions of substrate (S) and chromogen (C) are then added to the test tube. In the presence of bound 2,4-D-enzyme conjugate the substrate is converted to a compound which causes the chromogen to turn blue (B).

One enzyme molecule can convert more than one substrate molecule. The substrate molecules then convert chromogen molecules to blue.

Figure 7. Binding of Antibodies (After Millipore, 1991)

will give rise to a lighter blue color. That is, color is inversely proportional to concentration.

Pesticide Application

The pesticide containing 2,4-D, Weedone, was applied to the surface of the site about noon on Saturday, February 29, 1992, by a local lawn care professional. The pesticide was applied with a pressure sprayer at a rate of 1.35 ounces per 1000 square feet. The site covers approximately 11,400 square feet and approximately 15.4 ounces of pesticide was applied, or 0.00135 ounces per square foot of yard. Once applied it is recommended that the area not receive water for a minimum of 24 hours. In order to maintain the integrity of the effort, rainfall was the transport mechanism, rather than application of water by means of a sprinkler.

Precipitation began at 2300 hours on Tuesday, March 3, and continued until slightly past noon on Wednesday, March 4. A total of 1.06 inches of rain fell during this event. Water levels were monitored throughout the test, samples were collected, and field parameters measured. The samples were collected from 0430 hours, Wednesday, until 2230 hours on Friday, March 13. Table 2 is a listing of the physical parameters measured, plus the time at which each sample was collected. Each water sample consisted of one liter of water that was collected after the well had been pumped dry and allowed to recover. The sample was then refrigerated in the laboratory. The analysis would have been quick and easy to do in the field, but to maximize efficiency, all samples were collected and stored.

Laboratory Analysis

The EnviroGuard Test Kit allows for the visible detection of pesticides based on color. This can be done by visual inspection, or with a spectrophotometer. If a sample is visibly lighter in color, then one can assume that it is in excess of the LDD. If, on the other hand, more precision is needed to detect any difference, the samples should be analyzed by both methods.

The results of the visual and the photometric analysis are presented in Table 3. Since there appeared to be no difference in the samples under visual inspection, the spectrophotometer method was used to detect any residue of the pesticide. This method requires that the spectrophotometer first be calibrated with a sample of deionized water to establish a baseline for the analysis. Once the baseline has been established the negative control is then measured and recorded. The process is then repeated with the other water samples and the optical difference (OD) is recorded. If the OD is greater than 0.05, then the sample contains 2,4-D (or one of the other phenoxy herbicides) equal to or greater than the LDD.

TABLE II

WATER QUALITY AT THE TIME OF SAMPLING

DATE	TIME	CONDUCTIV ITY	TEMP C	Hq	WATER LEVEL
3-4-92	0430				6.5
	0530				6.6
	0630				6.4
	0730				7.46
	0845				7.12
	1000	1160	11.0		7.31
	1115	1180	11.6		7.4
	1215	1200	11.2		7.25
	1330	1100	12.2	7.20	6.86
	1430	780	12.6	7.12	6.94
	1600	900	12.3	7.11	6.82
	1700	890	11.6	7.06	6.95
	1800	900	11.3	7.09	6.87
	1900	940	11.4	7.08	7.01
	2000	940	11.1	7.13	7.00
	2100	940	10.8	7.02	7.00
	2300	940	10.7	7.08	7.3
3-5-92	0330	950	10.2	7.19	7.65
	0600	960	9.5	7.20	7.5
	0930	990	10.7	7.22	6.55
	1045	939	11.8	7.27	6.83
	1315	920	12.4	7.15	6.45
	1615	860	12.0	7.20	6.45
	1830	840	11.6	7.22	6.48
	2145	840	10.3	7.07	7.55
3-6-92	0345	795	9.7	7.27	7.7
	0900	840	10.6	7.22	6.45

Table	II (Cont.)
-------	------	-------	---

DATE	TIME	CONDUCTIV ITY	TEMP C	рН	WATER LEVEL
	1130	870	12.3	7.22	6.6
	1745	940	11.7	7.07	6.4
	2130	-	10.4	7.19	6.4
3-7-92	0830	1060	10.8	7.12	6.46
	1515	1080	14.0	7.04	6.4
	2015	1060	11.3	7.17	6.4
3-8-92	0930	1060	11.7	7.07	6.38
	1730	1040	12.1	7.17	6.5
3-9-92	1000	1140	11.5	7.12	6.4
3-10-92	0930	1110	7.9	7.05	6.54
3-11-92	0930	1040	8.8	6.95	6.45
3-12-92	1015	899	8.8	7.04	6.49
3-13-92	1030	1100	11.1	6.89	6.49
DATE	TIME	VISUAL	OD DIFFERENCE	SPEC. 20	
---------	---------	--------	------------------	-------------	
3-6-92	CONTROL	NEG		0.138	
3-1-92	BG	NEG	0.028	0.11	
3-2-92	BG	NEG	0.004 >	0.142	
3-3-92	BG	NEG	0.02	0.118	
3-4-92	1630	NEG	0.001	0.137	
	1730	NEG	0.028	0.11	
	1830	NEG	0.01	0.128	
	1930	NEG	-	0.138	
	2045	NEG	0.028	0.11	
	2200	NEG	0.012	0.126	
3-4-92	2415	NEG	0.017	0.121	
	0230	NEG	0.001 >	0.139	
	0400	NEG	0.019	0.119	
	0500	NEG	0.012	0.126	
	0600	NEG	0.003	0.135	
3-10-92	CONTROL			.078	
3-4-92	1900	NEG	-	.078	
	2000	NEG	0.023	.055	
	2100	NEG	0.11 >	0.188	
	2300	NEG	0.01	0.068	
3-5-92	0330	NEG	0.032 >	0.11	
	CONTROL			0.087	
	0600	NEG	0.053 >	0.14	
	0930	NEG	0.067 >	0.154	
	1045	NEG	0.007 >	0.094	
	1315	NEG	0.024 >	0.111	
	1615	NEG	0.032	0.055	
	CONTROL			0.094	

ENVIROGUARD TEST RESULTS FOR 2,4-D

DATE	TIME	VISUAL	OD DIFFERENCE	SPEC. 20
	1830	NEG	0.021 >	0.115
	2145	NEG	0.019 >	0.113
3-6-92	0345	NEG	0.005	0.089
	0900	NEG	0.023	0.071
	1130	NEG	0.039	0.055
	1745	NEG	0.013 >	0.107
	2130	POS ???	0.056	0.038
	CONTROL			0.128
3-7-92	0830	NEG	0.014 >	0.142
	1515	NEG	0.013	0.115
	2015	NEG	0.016	0.112
3-8-92	0930	NEG	0.01 >	0.138
	1730	NEG	0.038	0.090
3-9-92	1000	NEG	0.017 >	0.145
3-10-92	0930	NEG	0.021 >	0.149
3-11-92	0930	NEG	0.001 >	0.129
3-12-92	1015	NEG	0.063 >	0.191
3-13-92	1030	NEG	0.052 >	0.180

Table III (Cont.)

> = VALUES BELOW LDD

Conclusions

The spectrophotometer analysis indicated that all but one sample were less than the detection limit. The sample collected at 9:30, on March 6 had an optical difference of 0.056. A sample taken less than four hours earlier had a difference of - 0.013, and the sample collected 11 hours later recorded a value of - 0.014. This implies that the pesticide migrated through eight feet of the unsaturated zone, to the well, in approximately 65 hours (0.012 feet per hour). Previous work at the site has shown that the macropores in the soil allow for the verticle migration of constituents at a rate of up to 15 feet per hour following an intense (3 inches) but short (one hour) rainfall event (Zeitlow, 1991). This rate should be considered the maximum. Assuming less than optimal conditions, this still appears to be extremely slow. In the study conducted by Zeitlow (1991) she found that bromide and chloride appeared and disappeared suddenly. It is possible that 2,4-D could react in a similar fashion. Considering the breakover point of optical difference is at 0.05 it seems to be more likely that the reading was due to possible contamination either while being collected, or during the analysis. If a positive reading were actually to be recorded after 65 hours it seems highly likely that the reading taken 11 hours later would still have in excess of the LDD.

Since the samples collected exhibited a negative

response it was necessary to check the test kits. The herbicide was applied to soil and saturated with water. A sample of the water was recovered and analyzed by the same process described above. The water sample had a visual color difference (lighter in color), and had an optical difference of 0.06, indicating that the water sample was contaminated with 2,4-D above the LDD. The kits would have detected the herbicide had it been present.

CHAPTER IV

SAMPLING AND ANALYTICAL ANALYSIS OF GROUND WATER

Sampling Methodology

Sampling of the aquifer began with a sample collected from the casing storage of each well bore. The wells sampled were the A-3, A-4, and A-5 wells (Figure 3). This was followed by a sample collected after the well had been purged three well volumes, or pumped dry, which ever was the least. When pumped dry the well was allowed to recover before a sample was collected.

There are several sampling devices that could have been used, but since the aquifer was continuously pumped and sampled, a peristaltic pump was chosen. The wells were continuously pumped, at a rate of 200 ml/minute, and pH, temperature, specific conductance, and bicarbonate were monitored. The samples were considered to be derived from the aquifer since at least three well volumes were removed (Gibb and others, 1985). The pump was adapted with three pumping heads so that three separate wells in a cluster could be continuously pumped. This allowed water samples to be collected from each well at the same time. Samples were

collected on May 26, 1992, a relatively dry period of time, and on May 31, 1992, during a steady rainfall.

Field Results

May 26, 1992 Sample Period

The results of the May 26 field analysis, are shown in Figures 8 through 11. It is common practice to pump a well prior to sample collection until the indicator parameters have stabilized within +/- 10% for two consecutive well volumes (Gibb and others, 1985). It should be noted that nearly all of the physical parameters measured at the site fell within this range. Temperature ranged from a low of 13.9° to a high of 15.2°, with a median of 14.4 degrees Celsius. The pH plotted on a nearly straight line with all values between 7.19 and 7.33, with a mean of 7.26. Specific conductance, which appeared to vary more than the other parameters, ranged from 915 to 1015, with a mean of 977 micromohs/cm. Bicarbonate (expressed as calcium carbonate) concentrations ranged from 489 to 548 mg/l, with a mean of 506. Figures 8 through 11 indicate that these parameters, on any two successive samples, fell within an acceptable range for sample collection. It also should be noted that the values for casing storage and purged wells are within this range except for specific conductance in well A-4. The values for casing storage and purged samples varied by

10.6%, and 10.2% respectively when compared to the mean value for each of the wells.

May 31, 1992 Sample Period

The results representing the rain event on May 31 are very similar to those previously described (Figures 12-15). The temperature varied between 14.6° and 15.2°, with a mean of 15.0 degrees Celsius, a difference of less than 4% during the sampling period. The highest pH recorded was 6.92 and the lowest was 6.72, while the mean was 6.8, or less than a 3% variation through time. The specific conductance remained vary stable throughout sampling from 895 to 930 micromohs/cm, a difference of less than 4%. Bicarbonate values ranged between 492.5 and 527.5, with a mean of 504 mg/1, for a variance of less than 7%. During this sampling period all of the samples collected were within the acceptable range for water sampling.



CS= CASING STORAGE, PG=PURGED, MED=MEDIAN

Figure 8. Field Sampled Temperature May 26, 1992

ա 5



Figure 9. Field Sampled pH May 26, 1992

FIELD SAMPLED SPECIFIC CONDUCTANCE VALUES MAY 26,1992



Figure 10. Field Sampled Specific Conductance May 26, 1992



Figure 11. Field Sampled Bicarbonate May 26, 1992

ယ 8





Figure 12. Field Sampled Temperature May 31, 1992

FIELD SAMPLED pH VALUES

MAY 31, 1992 DURING RAIN



Figure 13. Field Sampled pH May 31, 1992

FIELD SAMPLED SPECIFIC CONDUCTANCE VALUES MAY 31, 1992 DURING RAIN



Figure 14. Field Sampled Specific Conductance May 31, 1992

FIELD SAMPLED HCO3 AS CaCO3

MAY 31, 1992 DURING RAIN



Figure 15. Field Sampled Bicarbonate May 31, 1992

Analytical Methodology

Water was pumped into 1 liter decontaminated glass jars. Samples were analyzed for temperature, pH, specific conductance, and bicarbonate. The conductivity and the pH meters were calibrated in the field, as previously described. Bicarbonate was determined by a potentiometric titration with a Hach digital titrator to a 4.5 pH color end point with a 2N solution of HCl acid. The number of digits required to reach the end point were then converted to bicarbonate concentration.

The water was filtered through a Gelman 0.2 micrometer membrane filter into 60 ml (2 ounce), polyethylene containers, filled full with no air bubbles, and stored at or below four degrees Celsius until the field analysis was complete. Samples were handled according to the protocol suggested by EPA Report No. 600/4-79-020 (1983).

Major anions were determined with a Dionex series 2000i/SP liquid ion chromatograph. The procedures for determination of fluoride, chloride, bromide, nitrate, and sulfate are outlined in the EPA Test Method 300.0 (Pfaff, and others, 1991).

Communications with the U.S. Army Corps of Engineers Southwest Division Laboratory have indicated that the anions in the ground water remain stable for a sufficient period of time to yield reliable results. It is believed that the samples will maintain their integrity for six months or more

(Hartsfield, 1993). Ross (1988) studied the degradation of anions over time and determined that samples varied on the order of 0.1 ppm, which represented a difference of less than 1 percent.

The precision and accuracy of the ion chromatograph is no better than the method detection limit (MDL) of the tests performed. This limit is defined as the minimum concentration of a substance that can be measured and reported with a 99% confidence that the values reported are above zero. The anions in question have a MDL as follows: fluoride=0.01 ppm, chloride=0.02 ppm, bromide=0.01 ppm, nitrate=0.002 ppm, and sulfate=0.02 ppm.

Standard solutions made for the calibration of the ion chromatograph were based on previous water samples collected from the aquifer. The standard used was two ppm fluoride, 25 ppm chloride, 10 ppm bromide, 25 ppm nitrate, and 75 ppm sulfate. The samples were allowed to reach ambient air temperature, as required, before the analysis began. The chromatograph was recalibrated after every 20 samples to insure the integrity of the analysis program.

Analytical Results

The listing of analytical results and graphical presentations of the ion chromatograph are presented in the Appendix. The analyses indicate that the ground-water chemistry was very similar from May 26, to May 31, 1992. Large percentage increases were detected in fluoride, . bromide, and nitrate. These increases may be due to the fact that these anions were measured in the smallest quantities and small differences in concentration account for larger differences in percentage. Variance for chloride and sulfate was much smaller, yet it should be remembered that they are present in larger concentrations.

May 26, 1992 Sample Period

The samples collected from the aquifer on May 26 were analyzed as previously described. To determine whether casing storage or purged water was more representative of the in situ ground water, samples collected during pumping were compared to the samples collected from casing storage, and the purged well sample. Well A-3, 10.3 feet deep, with a water level 7.60 feet below land surface, was pumped dry prior to sampling, as was Well A-4. Figure 16 is a plot of water levels during the test. Three well volumes, 11.7 gallons, were removed from Well A-5 before it was sampled.

<u>Fluoride</u>. Figure 17 is a plot of the all fluoride values determined with the ion chromatograph. The figure contains data from the three wells sampled, along with the values for casing storage (cs), purged water (pg), and the median value of fluoride during the pumping of the well.



Figure 16. Water Levels May 26, 1992



Figure 17. Fluoride May 26, 1992

The median pumping values for Fluoride, over 8.5 hours, ranged from 0.4 to 0.6 ppm, with a maximum value of 1.2 ppm and a minimum of 0.2 ppm. A comparison of the values recorded during the pumping of the wells to casing storage, indicates that the wells varied from 0.02 ppm to 0.5 ppm. These same data compared to the values for the purged water varied from 0.03 to 0.2 ppm. The values determined during pumping for wells A-3 and A-4 were closer to the purged water than to the casing storage samples, while the samples for A-5 were closer to the casing storage value.

There was a fluoride increase in the A-4 and A-5 wells of approximately 0.4 ppm that coincides with a decrease in the A-3 well of approximately 0.3 ppm. This occurred between 6:00 PM and 9:00 PM, and was followed at 11:00 PM with an increase in the A-3 well, with subsequent decreases in the A-4 and A-5 wells. These changes coincide with a total of 174 gallons of water removed from the aquifer. During this time the water level declined 0.42 feet in A-3, 1.74 inches in A-4, and 0.26 inches in A-5.

<u>Chloride</u>. The data for chloride are presented in Figure 18. The median values for the three wells range between 20 and 25 ppm, while the minimum value was 21 ppm and the maximum was 31. The pumped water when compared to the casing storage samples varied from no change to a difference of only 1.0 ppm, and when compared to the purged

COMPARISON OF CHLORIDE VALUES (PPM)

WELL A-3, A-4 & A-5

MAY 26, 1992

35 CONCENTRATION IN PPM 30 25 - A-3 20 + A-4 15 ** A-5 10 5 0 ČS PG .5 1.5 2.5 3.5 4.5 5.5 6.5 7.5 8.5 MED TIME (HOURS OF PUMPING) CS=CASING STORAGE, PG=PURGED, O=ND, MED=MEDIAN

Figure 18. Chloride May 26, 1992

water varied from no change to 0.7 ppm. The samples recovered from the purging process of all three wells were closer to the values obtained through continuous pumping.

An increase of 6 ppm in chloride was noted at 4:00 PM in A-3, after which the values remained nearly constant. The A-4 and A-5 wells did not produce this effect until four hours later, when they increased 11 and 9 ppm, respectively. After the increase, values plotted on nearly a straight line.

Bromide. The water analyses for bromide are shown in Figure 19. The mean values range from 0.7 to 1.6 ppm, with a minimum value of not detectible (ND), to a maximum of 2.0 ppm. The casing storage and purged values were identical for the A-4 and A-5 wells, so there was no variance. The average value varied by only 0.14 ppm in A-3 when the pumping water was compared to the casing storage sample. A-3 varied by only 0.33 ppm when the pumping water analyses were compared to the purged sample.

Bromide in the water from A-3 tended to decrease with time while A-4 and A-5 tended to remain constant. There were minor departures for all wells, yet they did not appear to be related.

<u>Nitrate</u>. Nitrate values are shown in Figure 20. The median values ranged between 1.5 and 3.0 ppm, the minimum value was 1.3 ppm and the maximum was 3.9 ppm. A-3 casing



Figure 19. Bromide May 26, 1992



Figure 20. Nitrate May 26, 1992

storage and purged values were the same. The average value for A-4 varied by 0.5 ppm compared to casing storage, while the purged water sample varied by 0.3 ppm on average. Continuous pumping samples from A-5 had an average variance from the casing storage value of 0.34 ppm, while the purged sample varied by an average of 0.14 ppm. Although the purged water sample was more indicative of the "aquifer water", there really was not much overall difference. All three wells had an increase in nitrate through time. A-3 did show a sharp increase in nitrate concentration at 9:00 P.M., from 1.9 to 3.3 ppm, but this was not reflected in the other wells.

<u>Sulfate</u>. Figure 21 is a plot of the sulfate values for the three wells. The median values determined were between 23 and 26 ppm. The minimum reading was 22 ppm while the maximum value was 28 ppm. A-3 was the only well to show any variance through time. The average variance from casing storage was 0.8 ppm, while the average variance from the purged water sample was 1.2 ppm. The casing storage and purged water samples for the A-4 and A-5 wells were the same.

The wells maintained a linear trend throughout the pumping period, with only occasional increases noted. The large increase in the A-3 well occurred 2 hours before the end of the aquifer test and might have impacted the A-4 and A-5 wells had the aquifer test continued any longer.

COMPARISON OF SULFATE VALUES (PPM)

MAY 26, 1992

WELL A-3, A-4 & A-5

30 Мдд 25 CONCENTRATION IN 20 - A-3 15 +A-4** A-5 10 5 0 CS PG .5 1.5 2.5 3.5 4.5 5.5 6.5 7.5 8.5 MED TIME (HOURS OF PUMPING) CS=CASING STORAGE, PG=PURGED, 0=ND, MED=MEDIAN

Figure 21. Sulfate May 31, 1992

Discussion. The samples collected on May 26 tend to support the theory that monitoring wells need to be purged prior to ground-water sampling. Three wells were sampled, and five different anions analyzed. The purged water sample compared more closely to the aquifer water on six occasions, and casing storage compared closer three times, but six of the samples showed effectively no difference at all.

May 31, 1992 Sample Period

The wells were sampled in the same manner as described for May 26. Figure 22 is a graph of the water levels during the sampling period.

Fluoride. The comparison of fluoride values during the rain event on the May 31 is shown in Figure 23. The median values for fluoride ranged from 0.6 to 1.0 ppm. The minimum concentration was 0.3 and the maximum was 1.2 ppm. The comparison of values recorded during the pumping of the wells to casing storage indicated less variation in A-3, 0.09 ppm as compared to 0.21 ppm. A-4 and A-5 were better approximated by the sample that was taken after the wells were purged. The A-4 purged water sample had an average variation of 0.1 ppm, while the casing storage sample varied by an average of 0.6 ppm. A-5 had similar results. The purged sample varied by an average of 0.14 ppm, and the casing storage sample varied by an average of 0.4 ppm.

A-4 and A-5 saw an increase in the concentration of

WATER LEVELS MAY 31, 1992



Figure 22. Water Levels May 31, 1992



Figure 23. Fluoride May 31, 1992

fluoride after 1:00 PM, after eight gallons of water had been pumped, A-3 had a similar increase one hour later. Following this increase, the A-3 and A-5 wells decreased and A-4 remained constant. It is apparent that the fluoride concentration is linked to the shallow screened interval in A-3, an interval that is also open in A-5.

Chloride. A comparison of chloride values is shown in Figure 24. The median values for chloride ranged between 20 and 23 ppm. The minimum value was 21 ppm and the maximum was 49 ppm (probable laboratory error). Ignoring this point the maximum concentration was 27 ppm. A-4 values for casing storage and purged water samples were identical. The purged water sample in A-3 is closer to the water sampled during pumping, with an average variation of 0.3 ppm, compared to 0.5 ppm (excluding the 49 ppm) for the casing storage. The variation was larger in A-5, where the purged water varied by an average of 1.3 ppm, and the casing storage by 2.7 ppm.

The values for the three wells remained fairly constant throughout the pumping process. The chloride concentration tended to increase in A-5 during the first three hours, and later values were nearly identical. A-4 increased for at least one hour, and then was constant. A-3 had only minor increases in chloride throughout the pumping period.

<u>Bromide</u>. A comparison of bromide values is shown in Figure 25. The median concentrations of bromide varied from

COMPARISON OF CHLORIDE VALUES (PPM)

MAY 31, 1992 WELL A-3, A-4 & A-5



Figure 24. Chloride May 31, 1992

COMPARISON OF BROMIDE VALUES (PPM)

MAY 31, 1992 WELL A-3, A-4 & A-5



Figure 25. Bromide May 31, 1992

0.6 to 1.2 ppm, which are also the minimum and maximum values recorded during the pumping period. The casing storage values varied less during the pumping of the aquifer. A-3 varied from the casing storage by 0.07 ppm, and the purged water varied by an average of 0.13 ppm. A-4 exhibited no variation during the pumping (Figure 24) with a nearly straight line through all points. The casing storage sample collected from A-5 varied on average by 0.7 ppm, while the purged sample varied by 0.8 ppm.

The concentration in A-3 decreased with the time of pumping. A-4 did not vary through time, and A-5 varied by about 0.1 ppm during the pumping period. The concentrations of chloride appear to vary independently of each other in this instance.

Nitrate. The nitrate values are shown in Figure 26. The median values for nitrate vary from 2 to nearly 4 ppm during the pumping period. The minimum concentration was 1.9 ppm, and the maximum was 3.7 ppm. Overall, the purged water varied less than the casing storage during the pumping of the aquifer. In well A-3 the casing storage varied by an average of 0.3 ppm, and the purged water varied by 0.01 ppm. The casing storage in A-4 varied by 0.2 ppm, and the purged water varied by only 0.1 ppm. Well A-5 varied from casing storage by 4.6 ppm, and the purged water varied by only 0.07 ppm. Nitrate concentrations remained fairly constant throughout the pumping of the aquifer.

COMPARISON OF NITRATE VALUES (PPM) MAY 31, 1992 WELL A-3, A-4 & A-5



Figure 26. Nitrate May 31, 1992

The values for the shallow well, A-3, remain lower than the other wells throughout, while A-4 plots just above A-3, and A-5 plots just above the other two.

<u>Sulfate</u>. Figure 27 is a plot of the sulfate values for the three wells. The median values are between 24 and 28 ppm. The average casing storage values in A-4 and A-5 are closer to the pumping values, and the purged water sample is closer in A-3. The comparison of casing storage to the pumped water did not vary through time in A-3. In A-4 the casing storage varied by an average of 0.3 ppm, and the purged water varied by 1.3 ppm. The casing storage value in A-5 varied by 1.14 ppm from the pumped water, and the purged water varied by 2.14 ppm.

The sulfate concentrations followed a similar pattern. A-3 displayed no variation during pumping, and the values for A-4, and A-5 were consistently lower. The concentrations in A-4 and A-5 varied only slightly during the pumping of the wells. The values for A-5 remained at or near 27 ppm throughout the pumping period.

Discussion. The waters sampled during the rain event

on the May 31, were consistent throughout the pumping period, with the exception of fluoride, which was erratic. Chloride, bromide, nitrate, and sulfate values were uniform from the beginning until the end. The median values were nearly identical to the initial readings. Chloride,
COMPARISON OF SULFATE VALUES (PPM) MAY 31, 1992 WELL A-3, A-4 & A-5 30 CONCENTRATION IN PPM 25 20 --- A-3 15 +A-4**₩** A-5 10 5 0└ CS PG .5 1.5 2.5 3.5 4.5 5.5 TIME (HOURS OF PUMPING) 6.5 MED CS=CASING STORAGE, PG=PURGED, 0=ND, MED=MEDIAN

Figure 27. Sulfate May 31, 1992

nitrate, and sulfate values all plot within an order of magnitude of each other during the pumping period.

The influence of the precipitation appears to have had a stabilizing effect on the results during the pumping of the aquifer. The macropores enhanced the soil properties allowing precipitation to infiltrate rapidly.

The ion chromatograph was used to analyze for five anions, and the water samples came from three wells. This allowed a comparison of casing storage, and purged water, to the aquifer through time. There were 15 opportunities for one analysis to be compared to another. The samples from casing storage were closer to the pumping values in five samples, the purged water was closer in nine, they were the same in one. This would suggest that previous authors have been correct when they suggested that a sample collected after purging a well is more representative than a sample collected from casing storage. It must be noted that the analyses were all very similar, and the values determined for casing storage and purged water would have led an investigator to similar conclusions.

CHAPTER V

CONCLUSIONS AND IMPLICATIONS AND SUGGESTIONS FOR FURTHER STUDY

Conclusions on Pesticide Movement

The herbicide investigated in this research was 2,4-Dichlorophenoxyacetic acid, or 2,4-D as it is more commonly known. It was expected that the permeable nature of the soil and structure found at this site would permit the herbicide to reach the shallow unconfined aquifer, despite the general lack of mobility of 2,4-D.

This research indicates that 2,4-D may not have been transported into the shallow aquifer, at least during the study interval. There was one positive reading taken during the sampling of the aquifer, but the author believes that if this were truly a positive response to the herbicide there would have been an increase detected, either before or after the positive response, which would have supported the presence of 2,4-D. Through time, other researchers at this site have documented an injection phenomena where increases in anions would occur over a period of months. These increases when graphically represented appear as if an

injection, or chemical shot had occurred. It has been suggested that possibly this could have occurred here. That is possible, but it appears more likely that a false positive reading occurred, and no 2,4-D made its way into the aquifer.

Conclusions on Water-Quality Variance

This study suggests that field and laboratory values of ground-water samples tend to vary but little at any instant in time. This means that samples collected from this unconfined aquifer tend to yield the same results whether they are collected after the purging of the well, or from the casing storage. The results initially appear to support the accepted standard of purging a well three to four well volumes before sampling, yet this research indicates that the casing storage samples were within a range to yield comparable results to the samples collected after purging of the wells.

The ability to sample discrete intervals in a aquifer allows the researcher to uncover some of the misconceptions of ground-water sampling. Hagen (1986) noted that hard and fast rules are not appropriate in all sampling situations. The guidelines that one uses when sampling an unconfined aquifer may not be the same as those appropriate for sampling a confined aquifer. Hagen also noted a special case, the cluster well, where it is possible to recover

discrete samples from within an aquifer. The length and placement of the screen tends to dictate the quantity of water contributed to the sample, and this will affect the quality of the water recovered. Aquifers are neither homogeneous nor isotropic throughout. This fact, coupled with the length and placement of the screen, also can affect the quality of the water sample.

The A-3 screened interval (9.9-10.1 feet) is near the center of the zone screened in A-5 (7.0-14.0 feet), while A-4 (13.3-13.6 feet) is screened in the basal part of the same interval. This means that A-3 and A-4 provide water from an interval of 0.2-0.3 feet, while the A-5 samples an interval of 7 feet. Hagen determined that most of his samples more closely resembled the interval sampled by the deepest Those results were confirmed during this research screen. also. The values obtained from A-4 and A-5 were very similar, while the values for A-3 were not. The variance in A-3 may be due to screen location (the top of the saturated interval), or it may be sampling a less permeable portion of the aquifer. When possible, thin (less than 20 feet thick) unconfined aquifers should be screened through the entire saturated thickness to allow all permeable zones to contribute to the water sample. This could be a problem if the saturated zone is too thick. There would be a potential to mask the ground-water quality, either for better or worse, since the most permeable zones would supply the

majority of the water.

The analyses of the ground water during May 31 show that verticle movement through the macropores in the soil can created a more constant quality during sampling. The trends were noticeably linear, with the exception of fluoride, and there was very little variation of the anions through time.

Implications

There still are no hard and fast rules to follow when sampling ground water. This research has indicated that in a shallow unconfined aquifer, representative water samples can be obtained from the casing storage, yet the safest approach, probably, is to purge before sampling. The research has shown that water samples will vary with the amount of water purged (Hagen, 1986). Most water sampling is occurring with the assistance of state and federal regulators. To insure quality control of the ground-water sample, it is imperative to take every precaution available.

There is only one major implication of this study and the others that have occurred at this site, and that is to develop a consistent protocol for sampling. Consistency is the key to ground-water sampling. Whether the well is purged three or four well volumes, or whether the sample is collected from the casing storage may make very little difference in the long run, if the same procedure is followed each time.

Just as lithology and hydrologic properties of an aquifers vary throughout their areal extent and thickness so will ground water at any instant in time. While water particles travel to the well-bore, no two molecules will follow the same path, and therefore they can never be expected to be the same.

Suggestions for Further Study

The use of immunoassay systems to detect pesticides in soil and water is becoming more common. Research should continue to focus attention on this quick and efficient testing system as improvements are made.

Since the purging volume calculated for ground water sampling take into account only the amount of water contained in the casing, there needs to be an effort to determine what effect the purging has on the water in the filter pack. This water would also be impacted by the casing material. Very little research has been done to analyze this situation.

The construction of a majority of monitoring wells includes a sediment sump. What is the effect of this sump on the samples collected? If sediment particles are collected in the sump, are some of the chemical constituents of the water attracted to the soil and their presence diminished or increased in the water analysis?

REFERENCES

- Acre, J.T., 1989. The Influence of Macropores on Water Movement in the Unsaturated Zone. Unpublished M.S. Thesis, Oklahoma State University.
- Barcelona, M.J., J.P. Gibb, J.A. Helfrich, and E.E.Garske, 1985. Practical Guide for Ground-water Sampling. Illinois State Water Survey, Contract Report 374, 94 p.
- Cohen, S.Z., C. Eiden, and M.N. Lorber, 1986. Monitoring Ground Water for Pesticides: Washington, D.C., American Chemical Society Symposium Series 315, p.170-196.
- Clark, D.W., 1990. Pesticides in Soils and Ground Water in Selected Irrigated Agricultural Areas Near Havre, Ronan, and Huntly, Montana. U.S.Geol. Survey Water-Resources Investigations Report 90-4023, 34 p.
- Driscoll, F.G., 1986. Groundwater and Wells. Johnson Division, St. Paul, Minnesota, 1089 p.
- Freeze, R.A., and J.A. Cherry, 1979. Groundwater. Prentice-Hall, Englewood Cliffs, New Jersey, 604 p.
- Froneberger, D.F., 1989. Influence of Prevailing
 Hydrogeologic Conditions on Variations in Shallow
 Ground-Water Quality. Unpublished M.S. Thesis,
 Oklahoma State University.
- Hagen, D.J., 1986. Spatial and Temporal Variability of Ground-water Quality in a Shallow Aquifer in Northcentral Oklahoma. Unpublished M.S. Thesis, Oklahoma State University.

Hartsfield, Y., 1993. Personal Communication.

- Heath, R.C., 1983. Basic Ground-water Hydrology. U.S. Geological Survey Water-supply Paper 2220, 84 p.
- Hem, J.D., 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey Water-supply Paper 2254, 263 p.

- Hoyle, B.L., 1987. Suburban Hydrogeology and Ground-water Geochemistry of the Ashport Silt Loam, Payne County, Oklahoma, Unpublished M.S. Thesis, Oklahoma State University.
- Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M., and Michalenko, E.M., 1991. Handbook of Environmental Degradation Rates. Lewis Publishing, 725 p.
- Melby, J.T., 1989. A Comparative Study of Hydraulic Conductivity Determinations for a Fine-grained Alluvium Aquifer. Unpublished M.S. Thesis, Oklahoma State University.
- National Council on Agricultural Science and Technology, 1985. Pesticides in Agriculture and Ground Water Quality: Washington, D.C., p. 38-62.
- Nelson, M.J., 1989. Cause and Effect of Water-Table Fluctuations in a Shallow Aquifer System. Unpublished M.S. Thesis, Oklahoma State University.
- Parsons, D.W., and J.M. Witt, 1988. Pesticides in Ground Water in the U.S.A.: Corvallis, Oregon State University Extension Service, 18 p.
- Pettyjohn, W.A., 1976. Monitoring cyclic fluctuations in ground-water quality. Ground Water, v. 14, pp 472-480.
- Pettyjohn, W.A., H. White, and S. Dunn, 1983. Water Atlas of Oklahoma. University Center for Water Research, Oklahoma State University, 72 p.
- Ross, R.R., 1988. Temporal and Verticle Variability of the Soil- and Ground-water Geochemistry of the Ashport Silt Loam, Payne County, Oklahoma. Unpublished M.S. Thesis, Oklahoma State University.
- Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Crosby, and J.S. Fryberger, 1981. Manual of Ground-water Quality Sampling Procedures. NWWA/EPA Series, 93p.
- Shelton, J.W., J.S. Foss, A.J. Garden, and J.L. Franks, 1985. Geology and Mineral Resources of Payne County, Oklahoma. Oklahoma Geological Survey Bulletin 137, 85 p.
- Soil Conservation Service, 1972. Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. U.S. Department of Agriculture, 63 p.

- Soil Conservation Service, 1987. Soil Survey of Payne County, Oklahoma. U.S. Department of Agriculture, 268 p.
- U.S. Environmental Protection Agency, 1986. RCRA Groundwater Monitoring Technical Enforcement Guidance Document (TEGD): OSWER-9950.1.
- U.S. Environmental Protection Agency, 1991. The Determination of Inorganic Anions in Water by Ion Chromatography-Method 300.0.
- U.S. Environmental Protection Agency Region VIII, 1989. Private Pesticide Applicators Training Manual.
- U.S. Geological Survey, 1979. Topographic Map of Stillwater North Quadrangle, Oklahoma, 7.5 Minute Series.
- Vanderlaan, M., L.H. Stanker, B.E. Watkins, and D.W. Roberts, 1991. Immunoassays for Trace Chemical Analysis Monitoring Toxic Chemical in Humans, Food, and the Environment. American Chemical Society, 374, p.

Zietlow, P., 1991. Personal Communication.

APPENDIX

RAW DATA FOR ALL WELLS

DATE	TIME	CONDUCTIV ITY	TEMP C	рН	WATER LEVEL
3-4-92	0430				6.5
	0530				6.6
	0630				6.4
	0730				7.46
	0845				7.12
	1000	1160	11.0		7.31
	1115	1180	11.6		7.4
	1215	1200	11.2		7.25
	1330	1100	12.2	7.20	6.86
	1430	780	12.6	7.12	6.94
	1600	900	12.3	7.11	6.82
	1700	890	11.6	7.06	6.95
	1800	900	11.3	7.09	6.87
	1900	940	11.4	7.08	7.01
	2000	940	11.1	7.13	7.00
	2100	940	10.8	7.02	7.00
	2300	940	10.7	7.08	7.3
3-5-92	0330	950	10.2	7.19	7.65
	0600	960	9.5	7.20	7.5
	0930	990	10.7	7.22	6.55
	1045	939	11.8	7.27	6.83
	1315	920	12.4	7.15	6.45
	1615	860	12.0	7.20	6.45
	1830	840	11.6	7.22	6.48
	2145	840	10.3	7.07	7.55
3-6-92	0345	795	9.7	7.27	7.7
	0900	840	10.6	7.22	6.45
	1130	870	12.3	7.22	6.6

Water Quality Data Measured At The Time Of Sampling For Pesticide Analysis

DATE	TIME	CONDUCTIV ITY	TEMP C	рH	WATER LEVEL
	1745	940	11.7	7.07	6.4
	2130	-	10.4	7.19	6.4
3-7-92	0830	1060	10.8	7.12	6.46
	1515	1080	14.0	7.04	6.4
	2015	1060	11.3	7.17	6.4
3-8-92	0930	1060	11.7	7.07	6.38
	1730	1040	12.1	7.17	6.5
3-9-92	1000	1140	11.5	7.12	6.4
3-10-92	0930	1110	7.9	7.05	6.54
3-11-92	0930	1040	8.8	6.95	6.45
3-12-92	1015	899	8.8	7.04	6.49
3-13-92	1030	1100	11.1	6.89	6.49

•

	FLUORIDE	CHLORIDE	BROMIDE	NITRATE	SULFATE
A1	ND-ND	40.134- 39.49	ND-0.932	5.755- 4.389	33.582- 33.256
A 2	0.275-ND	38.257- 19.825	1.17- 0.815	3.362- 2.697	34.576- 26.031
A3	0.963- 0.296	24.088- 23.439	1.675- 1.806	1.123- 1.111	23.744- 22.043
A 4	0.964- 0.523	19.526- 19.697	0.856- 0.854	2.43- 2.548	25.713- 25.66
A 5	0.568- 0.716	21.837- 23.165	0.702- 0.733	2.819-3.0	26.046- 26.286

COMPARISO	N OF	CASING	STORA	GE V	ALUES	vs
PURGED	VALU	ES (PPM	I) MAY	26,	1992	

GROUNDWATER	ANALYSIS 1	FOR	PUMPING	WELLS	(PPM)	MAY	26,	1992
(PUMPING START	TED AT 1430	0)						

		FLUORIDE	CHLORIDE	BROMIDE	NITRATE	SULFATE
1500	A3	0.323	23.287	1.691	1.266	22.266
	A 4	0.302	20.163	-	2.368	25.295
	A 5	0.539	21.072	0.748	2.859	25.78
1600	A3	0.387	28.547	1.665	1.611	22.932
	A 4	0.54	20.456	0.781	2.74	26.313
	A 5	0.51	22.015	0.691	2.992	26.261
1700	A3	0.286	23.013	1.627	1.619	23.062
	A 4	1.008	20.091	0.755	2.67	25.65
	A 5	0.473	22.024	0.717	2.97	26.045
1800	A3	0.292	22.519	1.252	1.803	22.998
	A 4	0.569	20.379	0.726	2.95	25.986
	A 5	0.782	22.521	0.651	3.374	27.066
1900	A3	0.571	22.121	2.023	1.977	23.262
	A 4	0.994	20.192	0.716	2.765	25.894
	A 5	0.544	21.596	0.642	3.098	25.769
2000	A3	0.304	21.792	1.176	1.881	22.987
	A 4	1.024	30.982	0.709	2.85	27.535
	A 5	1.04	31.119	0.705	2.865	27.573
2100	A3	0.485	23.444	0.927	3.308	26.568
	A 4	0.549	21.041	0.704	2.969	26.276
	A 5	0.821	22.028	0.951	3.276	26.543
2200	A3	0.565	21.02	1.257	1.871	22.403
	A 4	0.846	20.561	0.774	2.8	25.948
	A 5	0.698	21.643	0.725	3.265	26.08
2300	A3	1.036	21.406	1.243	1.986	23.259
	A4	[.] 0.294	20.639	0.963	2.947	26.368
	A 5	0.318	22.106	0.681	3.358	27.016

	FLUORIDE	CHLORIDE	BROMIDE	NITRATE	SULFATE
A 1	0.614-ND	42.949- 42.047	1.114- 1.122	3.91-4.01	35.115- 34.519
A 2	ND-ND	36.322- 36.932	1.354- 1.190	2.721- 2.944	31.255- 31.678
A 3	0.993- 0.716	26.464- 23.393	1.10- 1.329	2.315- 1.962	25.959- 23.787
A 4	ND-0.547	20.682- 21.122	0.573- 0.697	2.76- 2.892	27.236- 27.989
A 5	1.028- 0.542	21.097- 25.426	ND-1.539	8.002- 3.452	27.911- 28.533

COMPARISON OF CASING STORAGE VALUES VS PURGED VALUES (PPM) MAY 31, 1992

-

		FLUORIDE	CHLORIDE	BROMIDE	NITRATE	SULFATE
1100	A3	0.751	23.036	1.264	1.845	23.56
	A 4	1.006	49.892	0.672	2.869	26.759
	A 5	0.597	22.937	0.614	3.412	26.846
1200	A 3	0.864	22.587	1.238	1.908	23.624
	A 4	0.586	23.566	0.693	2.943	26.433
	A 5	0.597	23.532	0.677	2.927	26.307
1300	A 3	1.03	22.311	1.194	1.919	23.598
	A 4	0.34	21.012	0.744	3.07	26.576
	A 5	0.596	27.487	0.60	3.39	26.826
1400	A3	1.008	23.666	1.164	2.01	23.524
	A 4	0.635	20.969	0.672	3.07	26.373
	A 5	0.868	22.545	0.65	3.4	26.522
1500	A3	1.22	22.663	1.144	2.04	23.67
	A 4	0.611	20.684	0.660	2.92	25.807
	A 5	0.523	22.52	0.569	3.67	26.994
1600	A 3	0.525	22.106	1.105	2.103	23.531
	A 4	0.514	21.116	0.706	3.06	26.65
	A 5	0.68	22.506	0.579	3.643	26.934
1700	A3	1.044	21.774	1.107	2.074	23.782
	A4	0.718	21.131	0.662	3.114	26.738
	A 5	0.552	22.567	0.823	3.57	26.98

GROUNDWATER ANALYSIS FOR PUMPING WELLS (PPM) MAY 31, 1992 (PUMPING STARTED AT 0920)

WELL SPECIFICATIONS

WELL & TD	SCREENED INT.	DIAMETER (inches)	ELEV. (ft)
WELL & TD A1 8.5 A2 9.2 A3 10.3 A4 13.8 A5 14.0 B1 6.6 B2 9.3 B3 11.0 B4 13.2 B5 13.4 B6 11.3 B7 13.9 B8 18.7 B9 21.2 B10 25.7 B11 40.3 C1 8.3 C2 9.2 C3 10.6 C4 14.6 C5 14.0 D1 8.2 D2 9.3 D3 10.8 D4 14.2 D5 14.0 E1 8.7 E2 9.7 E3 10.5 E4 14.1 E5 14.0 F1 40.0 F2 40.0 G1 10.3 G2 14.0	SCREENED INT. 8.1 - 8.2 8.7 - 8.9 9.9 - 10.1 13.3 - 13.6 7.0 - 14.0 6.1 - 6.4 8.8 - 9.1 10.5 - 10.8 12.7 - 13.0 4.4 - 13.2 11.0 - 11.2 13.6 - 13.8 18.4 - 18.6 20.9 - 21.1 25.4 - 25.6 38.4 - 40.0 7.9 - 8.1 8.9 - 9.1 9.9 - 10.4 14.2 - 14.4 7.0 - 14.0 8.0 - 8.2 9.0 - 9.2 9.9 - 10.4 13.6 - 13.9 7.0 - 14.0 8.3 - 8.5 9.3 - 9.5 10.1 - 10.3 13.6 - 13.9 7.0 - 14.0 8.3 - 8.5 9.3 - 9.5 10.1 - 10.3 13.6 - 13.9 7.0 - 14.0 10.0 - 40.0 10.0 - 40.0 9.7 - 10.1 13.5 - 13.8 9.6 - 10.0 13.4 - 13.7	DIAMETER (inches) 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0	ELEV. (ft) 885.97 885.97 885.96 885.94 886.00 886.01 886.01 886.03 886.04 885.99 886.10 885.92 885.96 885.94 885.94 885.94 885.94 885.94 885.94 885.94 885.73 885.73 885.73 885.71 885.71 885.71 885.74 885.82 885.82 885.82 885.82 885.82 885.82 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.80 885.00 886.03 885.80 885.8
II 11.0 I2 14.5 I3 14.9 OU1 14.0	$14.0 - 14.3 \\ 10.0 - 14.4 \\ 13.6 - 14.0$	1.0 2.0 2.0	886.01 885.99

.

VITA -

James F. Ward

Candidate for the Degree of

Master of Science

Thesis: GROUND-WATER QUALITY VARIANCE AT AN INSTANT OF TIME IN A SHALLOW UNCONFINED AQUIFER IN NORTH CENTRAL OKLAHOMA

Major Field: Geology

Biographical:

- Personal Data: Born in Oakland, California, December 8, 1952, the son of John D. and Gertrude B. Ward. Married to Devona R. Ward on October 20, 1979. Father to Austin J. Ward, born February 28, 1983, and Alyssa P. Ward, born September 12, 1984.
- Education: Graduated from Marshfield High School, Marshfield, Missouri, in May, 1971; received Bachelor of Science Degree in Geology from Southwest Missouri State University in August, 1980; completed the requirements for the Master of Science degree at Oklahoma State University in July, 1993.
- Professional Experience: Professional Geologist with Dyco Petroleum Corporation, Tulsa, Oklahoma, October, 1980 to June, 1991; Teaching Assistant, Summer Hydrogeology Program, Oklahoma State University, June, 1992; Professional Hydrogeologist, U.S. Army Corps of Engineers, June, 1992 to present.