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*Western Michigan University*

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INTERACTION OF SPECIFIC CONTAMINANTS  
IN PULP AND PAPER EFFLUENTS/  
LEACHATES WITH THE SOIL

Steven G. Ziolkowski

A Thesis submitted  
in partial fulfillment of  
the course requirements for  
The Bachelor of Science Degree

Western Michigan University

Kalamazoo, Michigan

April, 1982

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Also many thanks go to Mr. Ray Wagner and Mr. Budd Goldsmith from Simpson Paper Company. Their cooperation and assistance was deeply appreciated.

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I would also like to thank Dr. Ferguson from the Physics Department for analyzing my soil samples on the PIXE instrument.

My appreciation goes to Dr. Harrison of the Geology Department too. His insight and knowledge of the soils and minerals located around Kalamazoo helped me to understand my data in a clearer manner.

And finally, I would like to thank my wife, Jamie, who typed this paper and gave me her support throughout this entire project which helped make things go much easier for me.

## ABSTRACT

This thesis deals with the interaction of specific contaminants in pulp and paper effluents and how they leach into the soil. The mill included in my study applies its effluent to special irrigation fields on a daily basis. The mill produces some specialty paper which involves the use of heavy metals in its papermaking process and as a result some of the metals are applied on the irrigation field. By taking soil samples from the irrigation fields and analyzing them for heavy metals, I hope to come up with some conclusions for the behavior of vertical migration of heavy metals in the soil. By performing other tests such as soil pH and sieve analysis, I think a better understanding of the characteristics of the soil will be established.

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## LITERATURE REVIEW

The study of specific contaminants in pulp and paper effluents has been an area of interest to environmental engineers for the past several centuries. By analyzing effluents from a mill we are able to determine exactly what materials we can afford to release into the environment and what materials we can not. Once a large collection of data has been established, and conclusions drawn, then and only then can we begin to look for ways of applying the effluent to the surrounding environment. One way that has been practiced for centuries is the use of land application. This type of treatment makes use of the plants, the soil surface and the soil matrix.

It has been known that the idea of using land treatment systems in the Western civilization began as long ago as ancient Athens.<sup>1</sup> A particular wastewater irrigation system in Bunzlau, Germany was said to have been in operation for more than 300 years after it was constructed in 1559.<sup>2</sup> For the most part, land-treatment systems didn't really take effect until the second half of the nineteenth century in Europe. Due to high level pollution problems occurring in many rivers the only way they could dispose of the untreated wastewater was to apply it directly to the land. This so called "sewage farming" was practiced by transporting the untreated wastewaters into the agricultural areas for irrigation and disposal. In the 1870's this method of "sewage farming" was recognized in England as an acceptable way of treating their wastewaters.<sup>3</sup> However, as these urban areas began to expand, more and more advanced treatment technology became available and therefore many of the older treatment systems were dropped due to the need to develop the land.

Land treatment systems in the United States began as far back as the 1870's as did Europe.<sup>4</sup> The U.S. used the sewage farming idea as a first step towards water pollution control. By the first half of the twentieth

century these systems were being replaced by in-plant treatment systems or by one of the following: 1) managed farms where the treated wastewaters were used for crop production, 2) landscape irrigation sites, or 3) ground water recharge sites. It should be pointed out that these newer land-treatment systems appear to exist mainly in the West where the resource value of wastewater was at an added advantage.<sup>5</sup>

There are three major processes which can be used for land treatment of effluents from a mill, the first is irrigation, then rapid infiltration, and finally overland flow. The particular mill which I will be studying uses the irrigation type of process, so for this reason we'll look at irrigation in more depth.

Irrigation is really the most predominant land application type of process used today. This method simply involves the application of the effluent directly to the land for treatment and for meeting the growth need of the plants. The applied effluent is treated by physical, chemical and biological means as it leaches down into the soil. The effluent can be applied to the crops or vegetation (including forestland) by one of two ways, sprinklers or by surface techniques used to avoid possible surface discharge of nutrients.<sup>6</sup> The mill included in my study uses the sprinkler systems to apply their effluents during the warm months and overland during the cold winter months.

Plants play an important role in a land treatment system. The main purpose of plants are to take up nitrogen and phosphorous from the applied effluent, maintain and increase water intake rates and soil permability, reduce erosion, and serve as a medium for microorganisms. The types of plants grown in these irrigated fields depends on some important factors. First of all the nitrogen removal capability of the plant is important,

the water need and tolerances are critical, it's sensitivity to specific contaminants in the effluent, public health regulations, and lastly plants management considerations. The types of plants (crops) used in the fields consist of three classes, 1) forage and field crops, 2) landscape vegetation, and 3) woodlands.<sup>7</sup> The crops grown by the mill I'm interested in are mainly alfalfa and timothy hay, both of these crops are grown and harvested on an annual basis. It's important to note that for forage and field crops, primary treatment prior to application is often sufficient.

#### Mill Background Information

The mill included in my study is the Simpson-Lee Paper Company in Vicksburg. This is a mill which has been applying its effluent from its paper making process to an area of approximately 60 acres near the mill. The effluent is first passed through a primary clarifier which removes about 98% of the suspended solids. The effluent from the clarifier is then pumped through lines out to the designated areas of the fields. At the present time between 2 and 3 MGD of effluent, which is 28% to 38% (on an annual basis) is applied to the 60 acres of cropland by means of a sprinkler system. This sprinkler type of set-up is used from April to November to irrigate such crops as alfalfa and timothy hay. During the winter months the mill uses an overland flow method into two lower elevation leaching areas consisting of some 50 total acres. In case of any trouble with the pressurized irrigation system the flow from the primary clarifier is diverted to an "emergency overflow area" near the paper mill which can handle up to 4 million gallons. Within the irrigation fields there are some 16 groundwater monitoring wells where tests can be run to determine if an contamination occurs in the groundwater. Some of the groundwater tests consist of COD, pH, TDS, nitrate nitrogen, and Kjeldahl nitrogen.<sup>8</sup>



Simpson Paper Company produces several types of specialty grades of paper which include photographic paper, blueprint paper, fire proof paper and artist paper. As a result of producing these specialty papers a certain amount of heavy metals are used in the paper making process. Naturally the effluent from this process will contain many of the heavy metals that went into making the paper. Approximately 3.2 percent of these largely insoluble metal pigment complexes go into the effluent and are sprayed onto the crops and land. On an annual basis we are talking about 300 to 400 pounds of metals applied over the 60 acres. The particular metals we are concerned with are lead chromates, mercury, cadmium, zinc, and selenium.<sup>9</sup> Although most of the heavy metal particles are removed in the primary clarifier, approximately 1.5 pounds of metals per day find their way out to the irrigation system and eventually onto the plants and into the soil. As a result I think it's important to do an analysis on the heavy metals in the soil to see how much has been accumulated over the years and possibly learn more about the characteristics of heavy metals and how they react in the soil.

On the following page is a breakdown of how the testing procedures will be conducted. Once the soil samples have been collected, they will be analyzed by a PIXE instrument (Particle Induced X-ray Emissions) which will determine the concentration of heavy metals in each sample. Also pH tests will be performed on each sample to give us an idea of the different pH ranges that occur in each of the testing fields. Concentrations of the heavy metals found in the groundwater was also obtained from some data made available by the mill. All of this data was collected and analyzed to see if any correlations or trends could be drawn. The results and conclusions from my data are found later in the thesis under "Discussion of Results".

### EXPERIMENTAL PROCEDURES

1. Test for the migration of heavy metals at different depths of the soil.
  - a) Designate 7 sites located throughout one of the irrigation fields as testing grounds. (See figure 1)
    - 1) Take four samples from each of the designated sites.
    - 2) Analyze samples at the surface, 6", 12" and 18" depth.
2. Do a test on heavy metals in certain areas of greater effluent application vs. area of less application.
  - a) Take 3 samples from areas of high application.
  - b) Take 3 samples from areas of low application.
3. Set aside an area of land which will serve as a control. (This land has not been sprayed with an effluent and is the same type of soil found in the irrigation fields.)
  - a) Take 2 samples and analyze them to see what the soil mainly consists of.
  - b) Take samples at the surface, 6", 12", and 18" depth.
4. Compare soil samples collected in September 1971 to samples that I collected in February 1982 and see what kind of build up of metals have occurred over this time period. \*
5. Obtain data from the mill pertaining to the concentration of heavy metals in the groundwater so that this can be entered into an overall mass balance.
6. Do a pH test on each sample to determine what the pH range is in each of the testing fields.<sup>10</sup>
  - a) Air dry 50 grams of soil.

\* Data proved to be nonconclusive.

- b) Mix 50 ml of distilled water with each sample for one hour.
- c) Read the pH directly from a meter for each sample.

7. Sample preparation for the PIXE instrument

- a) Oven dry samples for 24 hours.
- b) Compress samples (2500 psi) into small pellets.
- c) Insert pellets into plastic holders.
- d) Place plastic holder into PIXE instrument.

FIGURE 1

(Irrigation fields and testing sites)

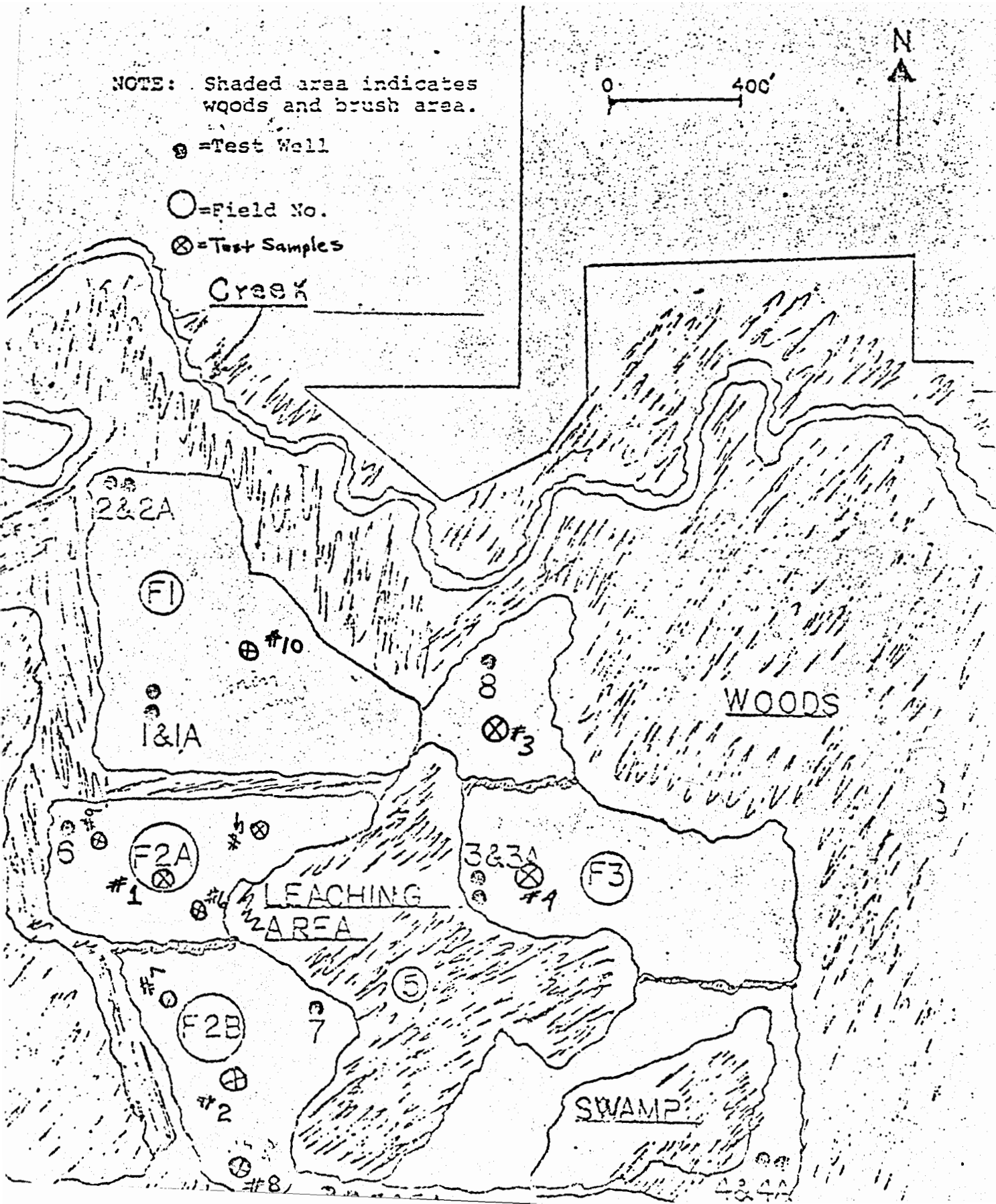


TABLE 1  
PIXE ANALYSIS  
(AVERAGE VALUES)  
CONTROL FIELD (SITES 1 AND 2)

DEPTH	ELEMENT	ppm	% unc *	DEPTH	ELEMENT	ppm	% unc
SURFACE	K	4001.45	25	6"	K	3774.6	25
	Ca	1687.6	25		Ca	1482.95	25
	Ti	1685.4	20		Ti	1562.4	20
	Cr	545.3	23		Cr	575.25	23
		669.0	25		Mn	890.55	25
	Fe	11159.35	15		Fe	10686.2	15
	Cu	6.75	28		Cu	9.05	23
	Zn	52.8	15		Zn	50.15	16
	Ga	7.2	31		Ga	8.9	29
		28.0	34		Pb	23.75	37
	Rb	77.4	15		Br	4.75	44
	Sr	112.65	15		Rb	74.9	15
	Y	19.25	29		Sr	108.1	15
	Zr	373.8	15		Y	24.95	26
	Br	2.7	63		Zr	338.3	15

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
12"	K	4583.05	25	18" **	K	3680.3	25
	Ca	2146.5	25		Ca	2171.5	25
	Ti	1802.9	20		Ti	1671.6	20
	Cr	1007.15	22		Cr	810.9	21
	Mn	476.35	25		Mn	434.6	25
	Fe	22928.4	15		Fe	15830.1	15
	Cu	15.55	19		Cu	11.6	20
	Zn	60.7	15		Zn	49.5	15
	Ga	9.55	29		Ga	9.5	28
	Pb	36.8	31		Pb	60.5	28
	Br	2.9	70		Br	5.4	42
	Rb	115.3	15		Rb	88.8	15
	Sr	103.4	15		Sr	93.4	16
	Y	10.05	58		Y	14.4	35
	Zr	199.4	15		Zr	242.7	15

\* PERCENT UNCERTAINTY

\*\* ONLY ONE 18" SAMPLE TAKEN FROM CONTROL FIELD

TABLE 2  
PIXE AVERAGES  
FIELD 2A\* (SITES #1, #5, #6)

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc.
SURFACE	K	3973.3	25	6"	K	3670.2	25
	Ca	2952.6	25		Ca	1803.2	25
	Ti	3626.8	20		Ti	1657.2	20
	Cr	669.0	23		Cr	522.7	24
	Mn	480.7	25		Mn	659.7	25
	Fe	13036.2	15		Fe	10949.2	15
	Cu	21.2	18		Cu	9.2	23
	Zn	145.8	15		Zn	59.4	15
	Ga	8.9	29		Ga	8.5	29
	Pb	104.4	27		Pb	29.1	36
	Br	10.0	52		Br	6.6	43
	Rb	66.3	16		Rb	69.7	16
	Sr	108.6	15		Sr	104.5	15
	Y	12.4	54		Y	18.6	29
	Zr	269.2	15		Zr	309.9	15

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc.
12"***	K	3845.0	25	18"	K	3167.7	25
	Ca	1766.1	25		Ca	1528.0	25
	Ti	1553.1	20		Ti	1125.6	20
	Cr	577.5	23		Cr	590.9	23
	Mn	463.9	25		Mn	270.3	25
	Fe	11296.7	15		Fe	13226.0	15
	Cu	7.25	22		Cu	9.95	24
	Zn	47.1	15		Zn	37.7	15
	Ga	6.8	30		Ga	6.5	29
	Pb	21.8	33		Pb	23.3	42
	Br	2.8	70		Br	4.8	48
	Rb	62.9	15		Rb	69.1	15
	Sr	95.7	15		Sr	83.5	15
	Y	10.2	58		Y	9.6	48
	Zr	206.7	15		Zr	425.1	15

\* SITE #9 OMITTED IN FIELD 2A

\*\* OMIT SITE #5 DATA AT 12" DEPTH

TABLE 3

PIXE AVERAGES

FIELD 2B (SITES #2, #7, #8)

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
SURFACE	K	4644.2	25	6"	K	4001.5	25
	Ca	2760.6	25		Ca	1970.3	25
	Ti	3198.2	20		Ti	1722.8	20
	Cr	576.2	23		Cr	618.3	23
	Mn	551.6	25		Mn	475.5	25
	Fe	11574.1	15		Fe	11253.0	15
	Cu	12.3	20		Cu	6.8	28
	Zn	128.4	15		Zn	49.7	15
	Ga	7.8	29		Ga	7.9	29
	Pb	61.0	28		Pb	33.8	40.
	Br	7.9	37		Br	5.1	55
	Rb	59.5	15		Rb	68.3	15
	Sr	106.0	15		Sr	101.0	15
	Y	14.2	35		Y	16.0	29
Zr	253.8	15	Zr	292.1	15		
DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
12"	K	5121.0	25	18"	K	3783.0	25
	Ca	1952.0	25		Ca	1795.4	25
	Ti	1795.9	20		Ti	1413.9	20
	Cr	769.1	23		Cr	804.7	23
	Mn	494.3	25		Mn	287.3	25
	Fe	17045.3	15		Fe	17975.8	15
	Cu	8.3	26		Cu	8.4	27
	Zn	47.7	15		Zn	50.4	15
	Ga	8.5	29		Ga	11.4	29
	Pb	65.3	31		Pb	37.2	29
	Br	4.9	54		Br	4.8	44
	Rb	88.0	15		Rb	86.0	15
	Sr	104.1	15		Sr	90.7	15
	Y	12.7	37		Y	6.6	61
Zr	300.0	15	Zr	188.5	15		

TABLE 4  
PIXE AVERAGES  
FIELD #3 (SITES #3, #4)

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
SURFACE	K	4765.6	25	6"	K	4786.6	25
	Ca	2385.2	25		Ca	1934.6	25
	Ti	2251.1	20		Ti	2181.9	20
	Cr	643.6	23		Cr	497.4	23
	Mn	617.3	25		Mn	693.9	25
	Fe	13311.4	15		Fe	12268.2	15
	Cu	17.15	18		Cu	9.3	22
	Zn	69.9	15		Zn	55.6	15
	Ga	13.1	29		Ga	8.7	29
	Pb	44.7	27		Pb	26.0	36
	Br	7.2	40		Br	3.4	57
	Rb	76.5	15		Rb	72.3	15
	Sr	101.6	15		Sr	95.2	15
	Y	18.1	36		Y	20.1	28
	Zr	346.8	15		Zr	343.6	15

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
12"	K	4426.0	25	18"	K	3513.6	25
	Ca	1838.9	25		Ca	1700.3	25
	Ti	1851.8	20		Ti	1548.8	20
	Cr	1090.1	23		Cr	1040.6	23
	Mn	299.8	25		Mn	289.7	25
	Fe	22528.3	15		Fe	23338.5	15
	Cu	15.2	20		Cu	16.0	19
	Zn	58.4	15		Zn	57.7	15
	Ga	8.6	29		Ga	9.9	29
	Pb	49.9	29		Pb	42.7	30
	Br	5.3	44		Br	4.8	45
	Rb	111.2	15		Rb	92.0	15
	Sr	91.6	15		Sr	94.5	15
	Y	12.1	49		Y	13.4	48
	Zr	251.2	15		Zr	256.4	15



TABLE 5  
PIXE ANALYSIS  
FIELD 1\* (SITE #10)

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
SURFACE	K	4371.1	25	6"	K	3945.1	25
	Ca	2135.9	25		Ca	1784.9	25
	Ti	1868.1	20		Ti	1826.0	20
	Cr	479.3	24		Cr	505.9	23
	Mn	664.3	25		Mn	795.4	25
	Fe	10737.3	15		Fe	11008.2	15
	Cu	2.5	63		Cu	5.1	33
	Zn	40.8	16		Zn	50.8	15
	Ga	3.8	41		Ga	7.8	30
	Pb	14.0	51		Pb	17.7	43
	Br	2.0	81		Br	5.1	42
	Rb	66.0	16		Rb	70.3	16
	Sr	95.1	15		Sr	91.6	16
	Y	18.1	29		Y	12.0	37
	Zr	362.1	15		Zr	270.9	15

DEPTH	ELEMENT	ppm	% unc	DEPTH	ELEMENT	ppm	% unc
12"	K	4635.5	25	18"	K	3864.7	25
	Ca	1922.3	25		Ca	1508.7	25
	Ti	1915.2	20		Ti	1553.7	20
	Cr	514.8	23		Cr	814.8	21
	Mn	796.5	25		Mn	267.2	25
	Fe	12330.5	15		Fe	16450.2	15
	Cu	8.4	29		Cu	10.7	21
	Zn	53.7	15		Zn	46.0	16
	Ga	9.4	28		Ga	10.9	28
	Pb	13.4	59		Pb	21.8	39
	Br	2.5	68		Rb	87.1	15
	Rb	81.3	15		Sr	104.9	15
	Sr	105.0	15		Y	10.5	42
	Y	12.4	37		Zr	208.9	15
	Zr	330.5	15				

\* ONLY ONE SAMPLE OBTAINED FROM FIELD 1.

IRRIGATION FIELDS — CONTROL SITES  
(Amount of metals applied)

DEPTH	ELEMENT	FIELD 2A ppm	FIELD 2B ppm	FIELD 3 ppm	FIELD 1 ppm
SURFACE	K	— *	643	764	370
	Ca	1265	1073	698	448
	Ti	1941	1513	566	183
	Cr	124	31	98	—
	Mn	—	—	—	—
	Fe	1877	415	2152	—
	Cu	15	6	10	—
	Zn	93	76	17	—
	Ga	2	1	6	—
	Pb	76	33	17	—
	Br	7	5	5	—
	Rb	—	—	—	—
	Sr	—	—	—	—
	Y	—	—	—	—
	Zr	—	—	—	—

DEPTH	ELEMENT	FIELD 2A ppm	FIELD 2B ppm	FIELD 3 ppm	FIELD 1 ppm
6"	K	—	227	1012	171
	Ca	320	487	452	302
	Ti	95	161	620	264
	Cr	—	43	—	—
	Mn	—	—	—	—
	Fe	263	567	1582	322
	Cu	1	—	1	—
	Zn	9	—	6	1
	Ga	—	—	—	—
	Pb	5	10	2	—
	Br	2	1	—	1
	Rb	—	—	—	—
	Sr	—	—	—	—
	Y	—	—	—	—
	Zr	—	—	5.3	—

\* Control concentration was higher than irrigation field concentration.

DEPTH	ELEMENT	FIELD 2A ppm	FIELD 2B ppm	FIELD 3 ppm	FIELD 1 ppm
12"	K	CONTROL	538	— *	52
	Ca	VALUES	—	—	—
	Ti	ARE ALL	—	49	112
	Cr	HIGHER	—	83	—
	Mn	↓	18	—	320
	Fe		—	—	—
	Cu		—	—	—
	Zn		—	—	—
	Ga		—	—	—
	Pb		29	13	—
	Br		2	2	—
	Rb		—	—	—
	Sr		1	—	2
	Y		3	2	2
	Zr		101	52	131

DEPTH	ELEMENT	FIELD 2A ppm	FIELD 2B ppm	FIELD 3 ppm	FIELD 1 ppm
6"	K	CONTROL	103	—	184
	Ca	VALUES	—	—	—
	Ti	ARE ALL	—	—	—
	Cr	HIGHER	—	—	4
	Fe	↓	2146	7508	620
	Cu		—	4	—
	Zn		1	8	—
	Ga		2	1	1
	Pb		—	—	—
	Br		—	—	—
	Rb		—	3	—
	Sr		—	1	12
	Y		—	—	—
	Zr		—	14	—

\* Control concentration was higher than irrigation field concentration.

FIGURE 2 (PIXE Analysis)

CONTROL SITE 2

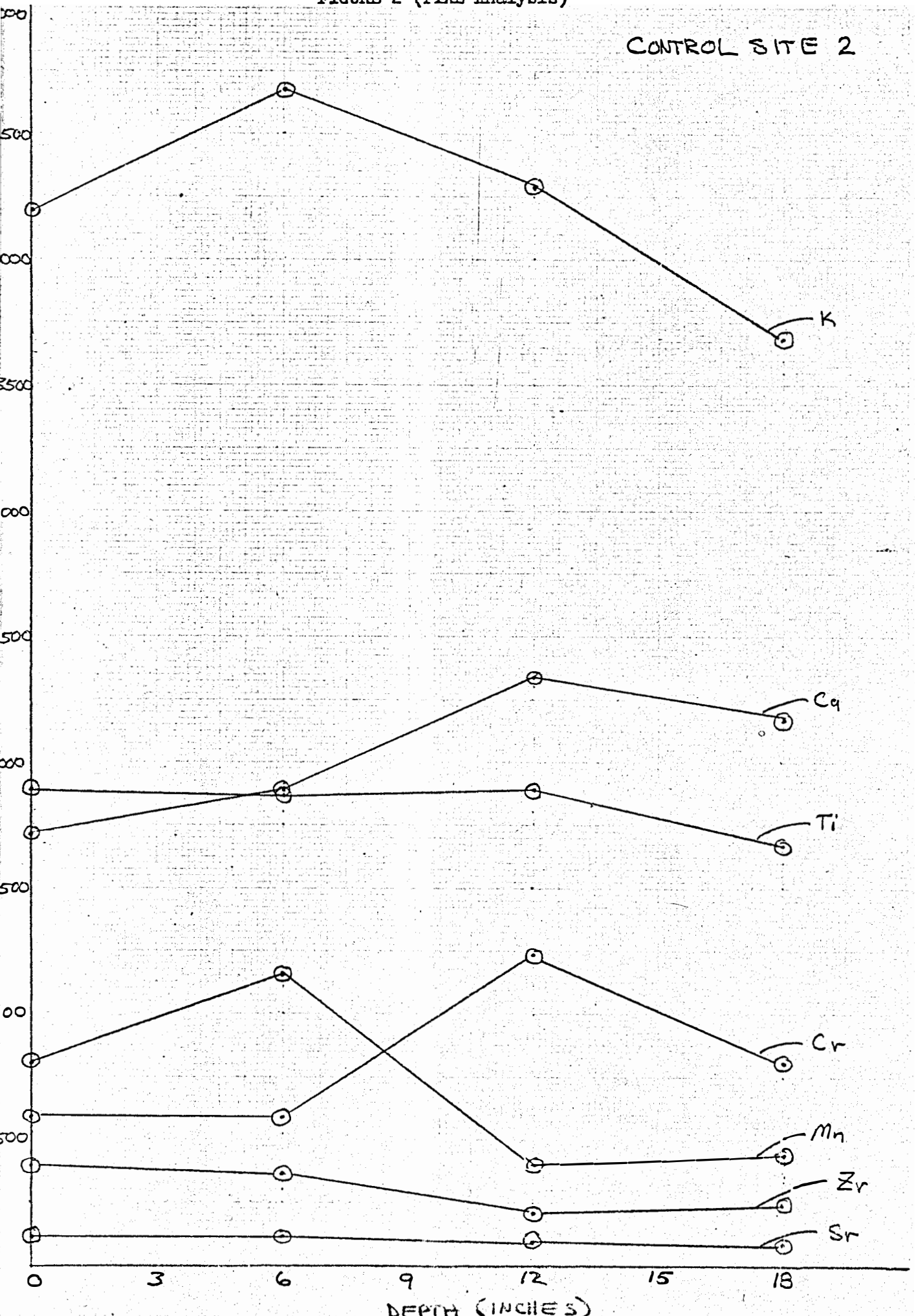


FIGURE 3

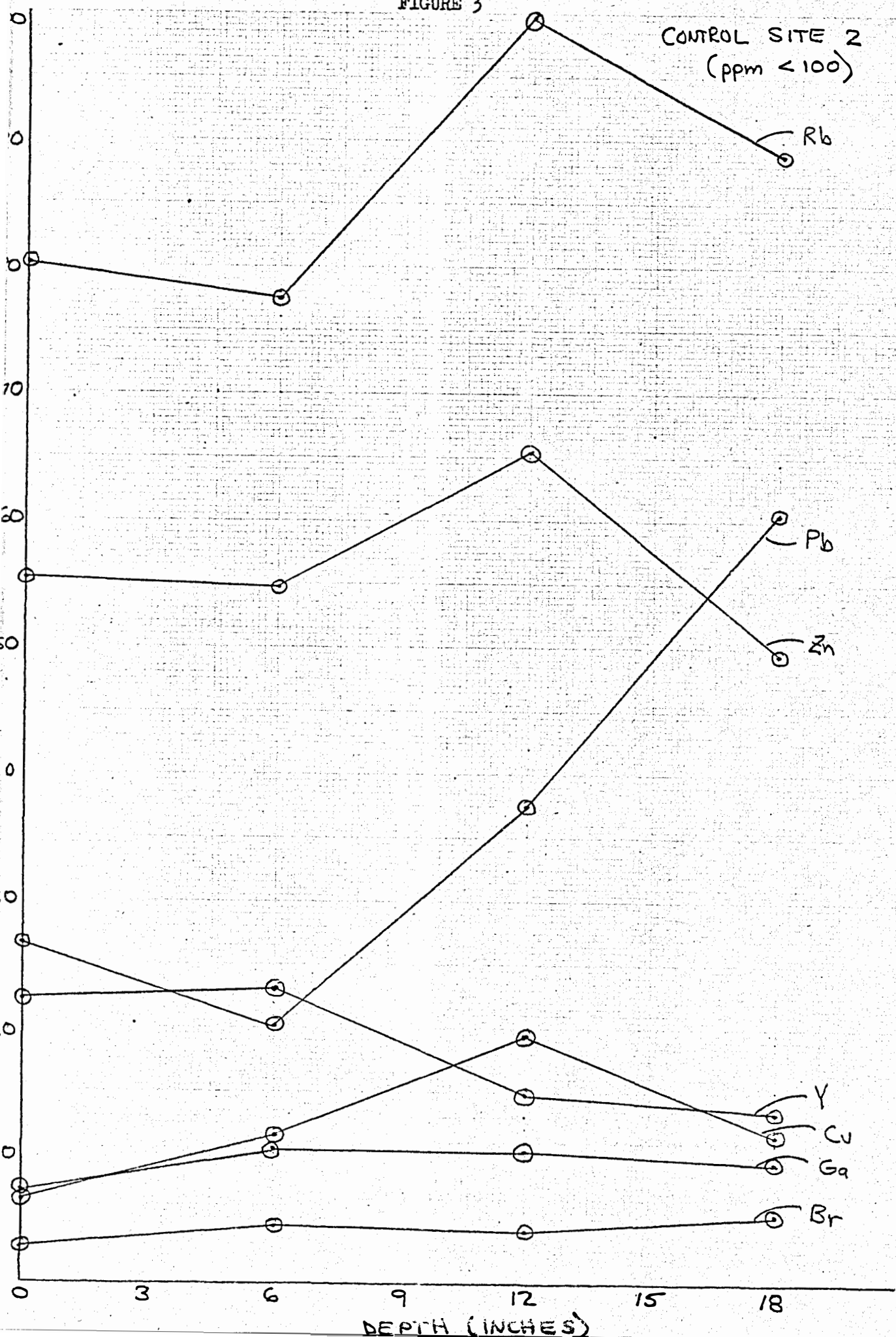


FIGURE 4

SITE 9 (FLD 2A)

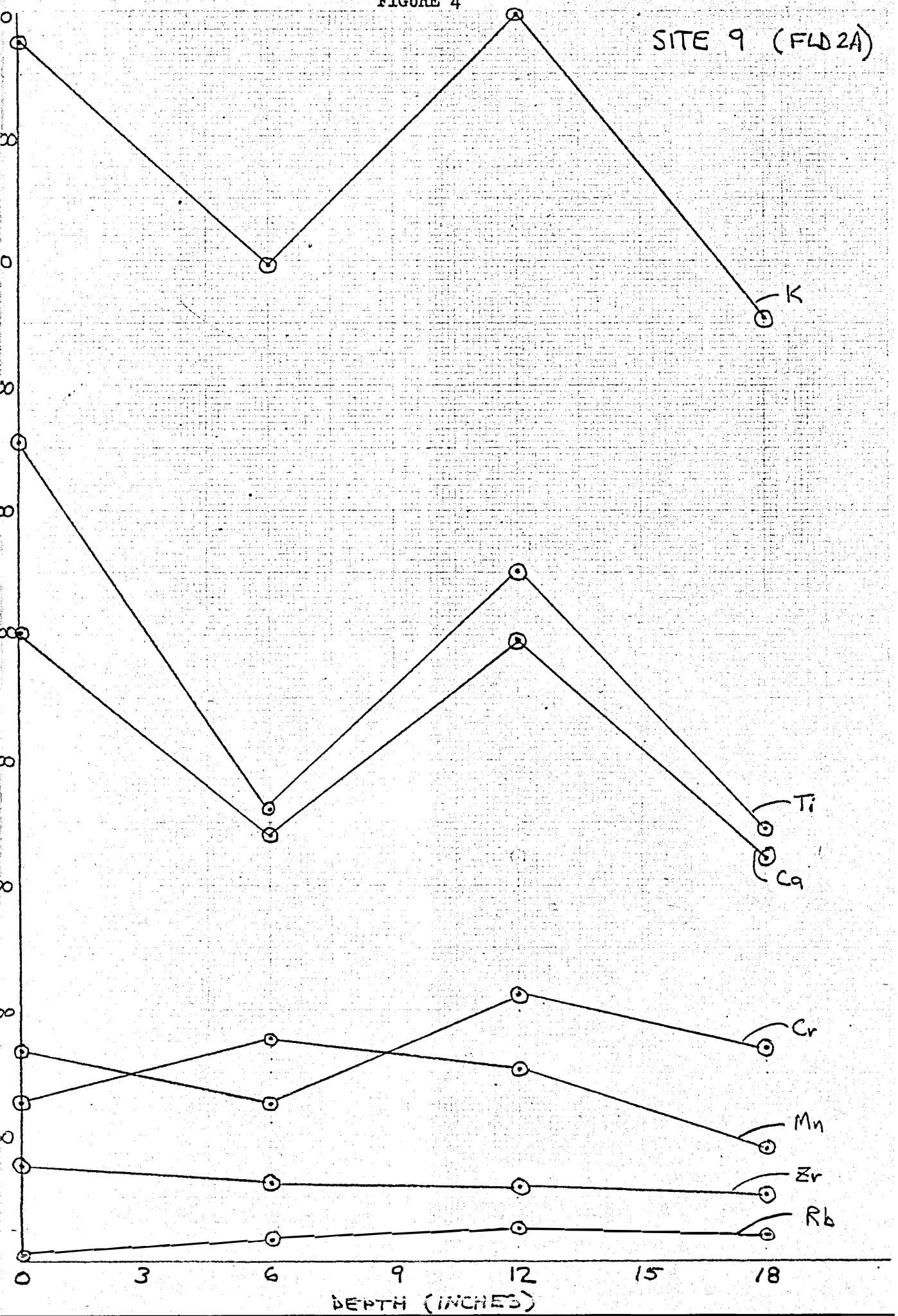
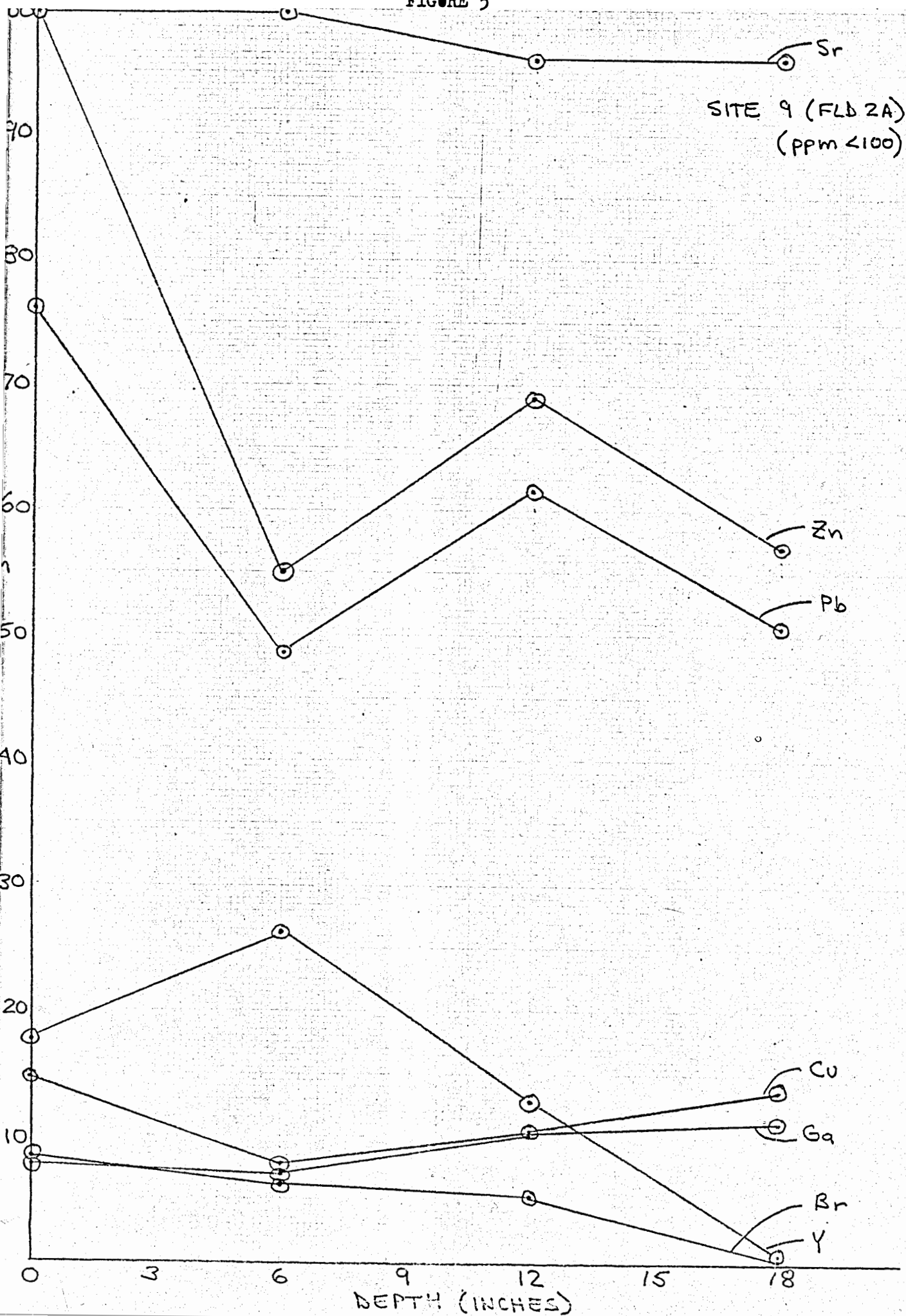


FIGURE 5



# LEAD IN SOIL

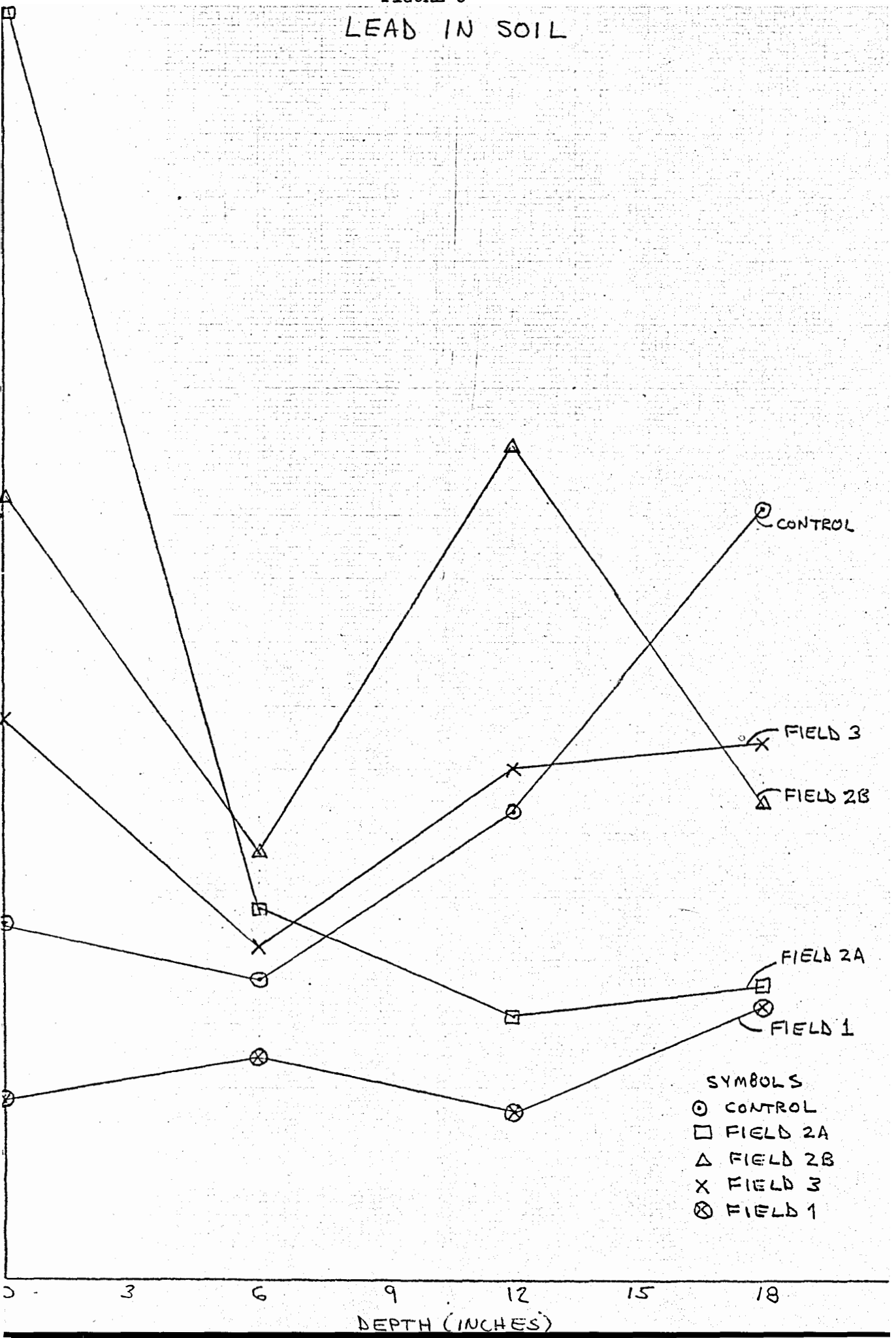




FIGURE 7

CHROMIUM IN SOIL

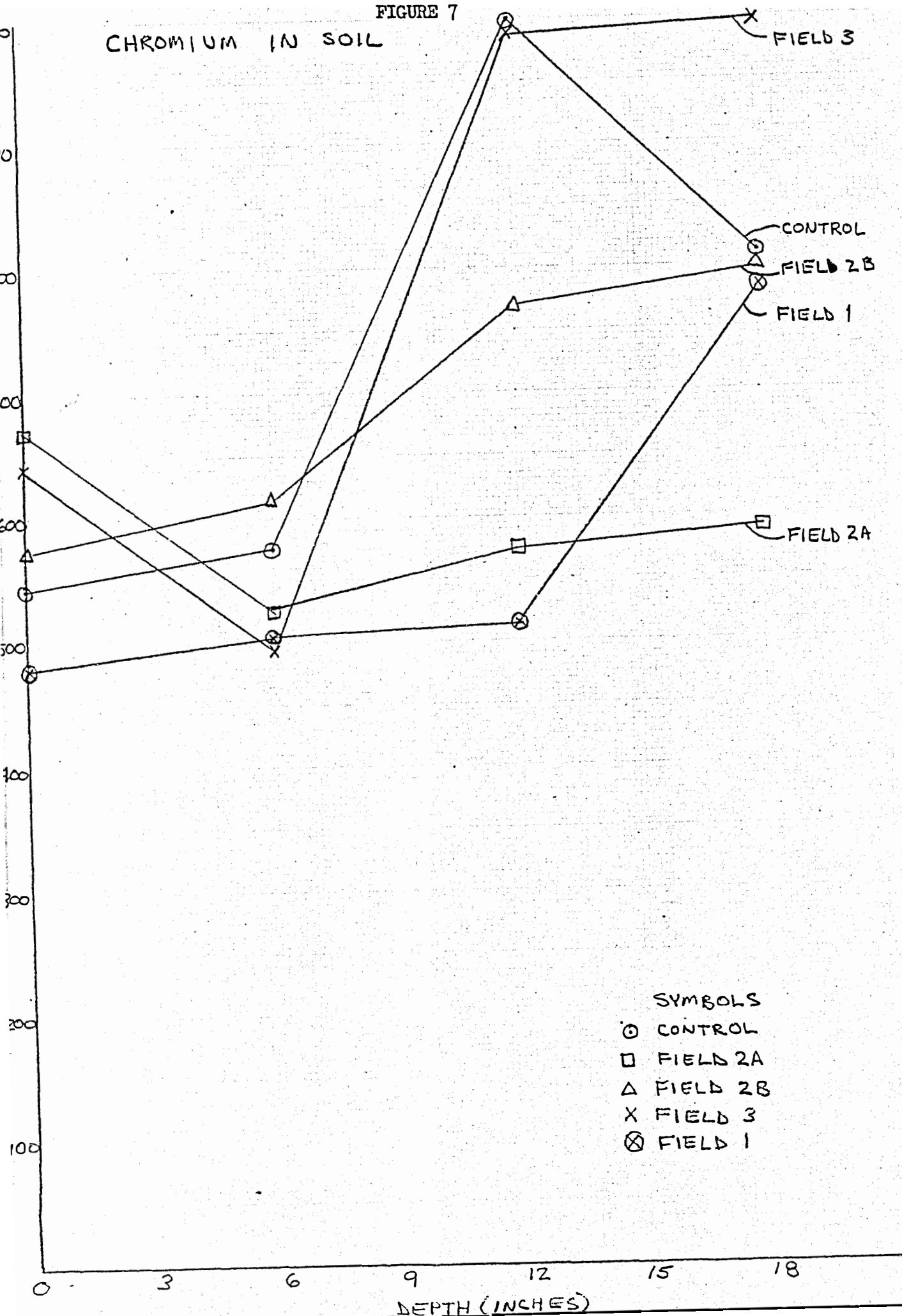
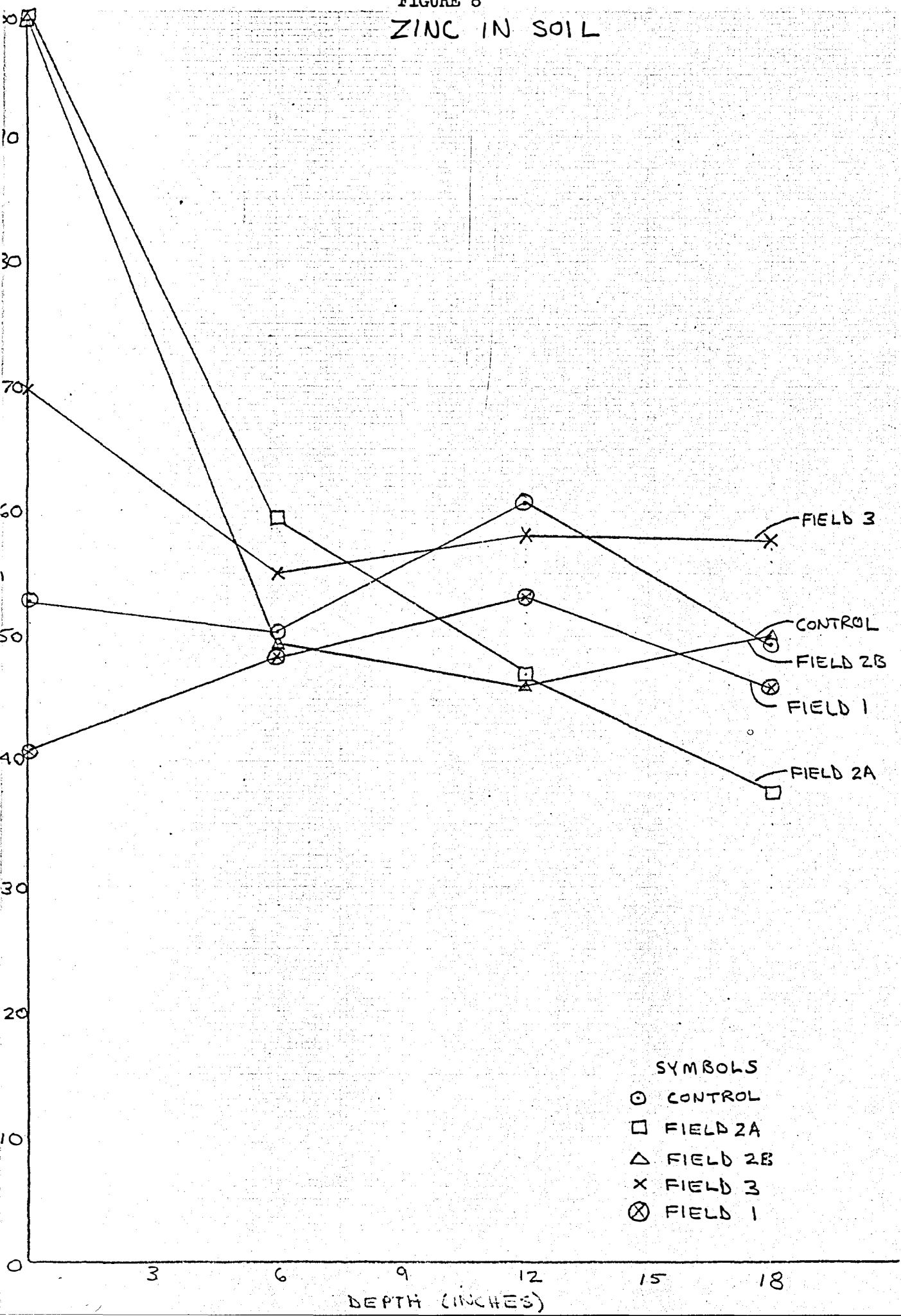


FIGURE 8

ZINC IN SOIL



# TITANIUM IN SOIL

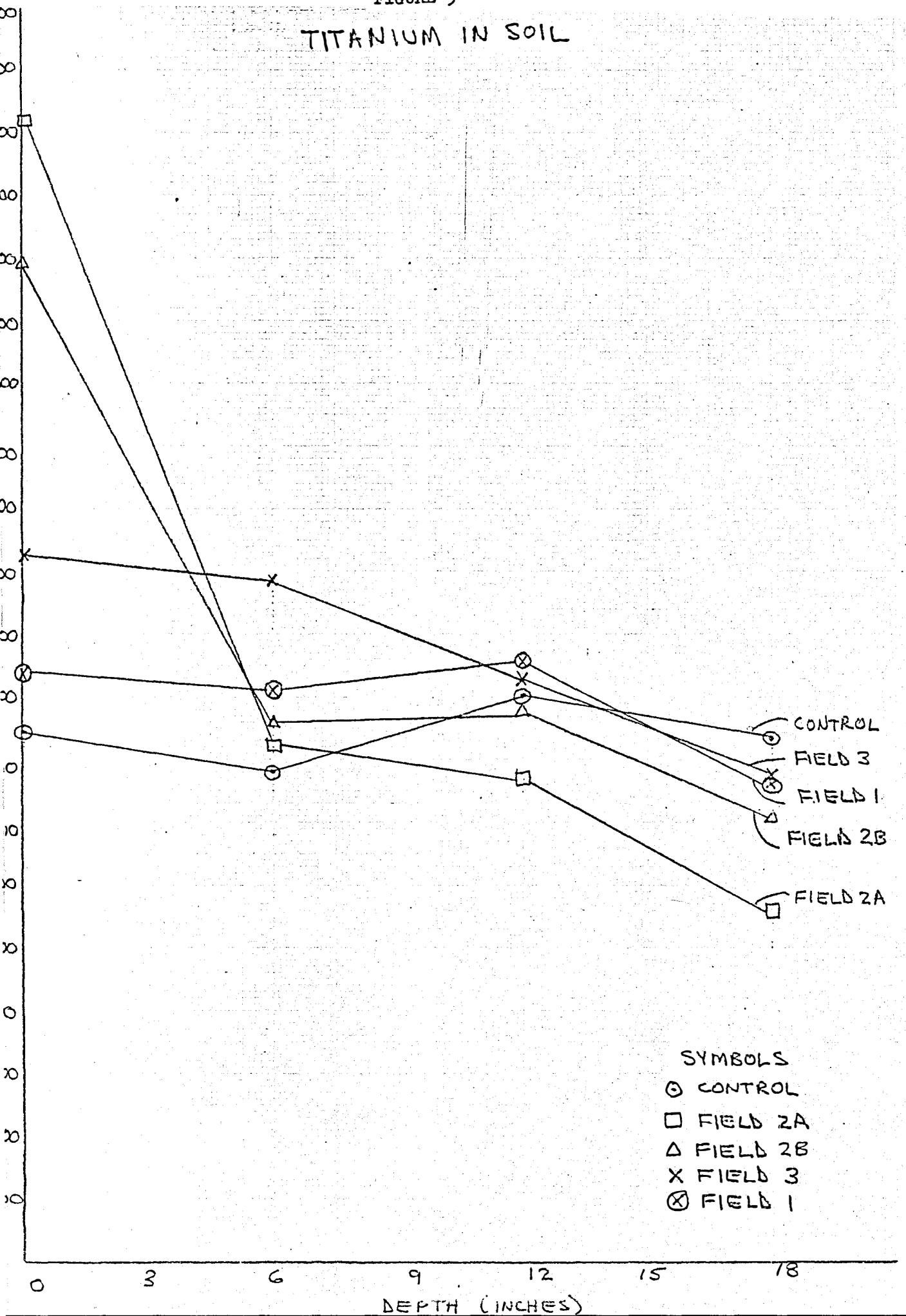


TABLE 8

## pH TESTS

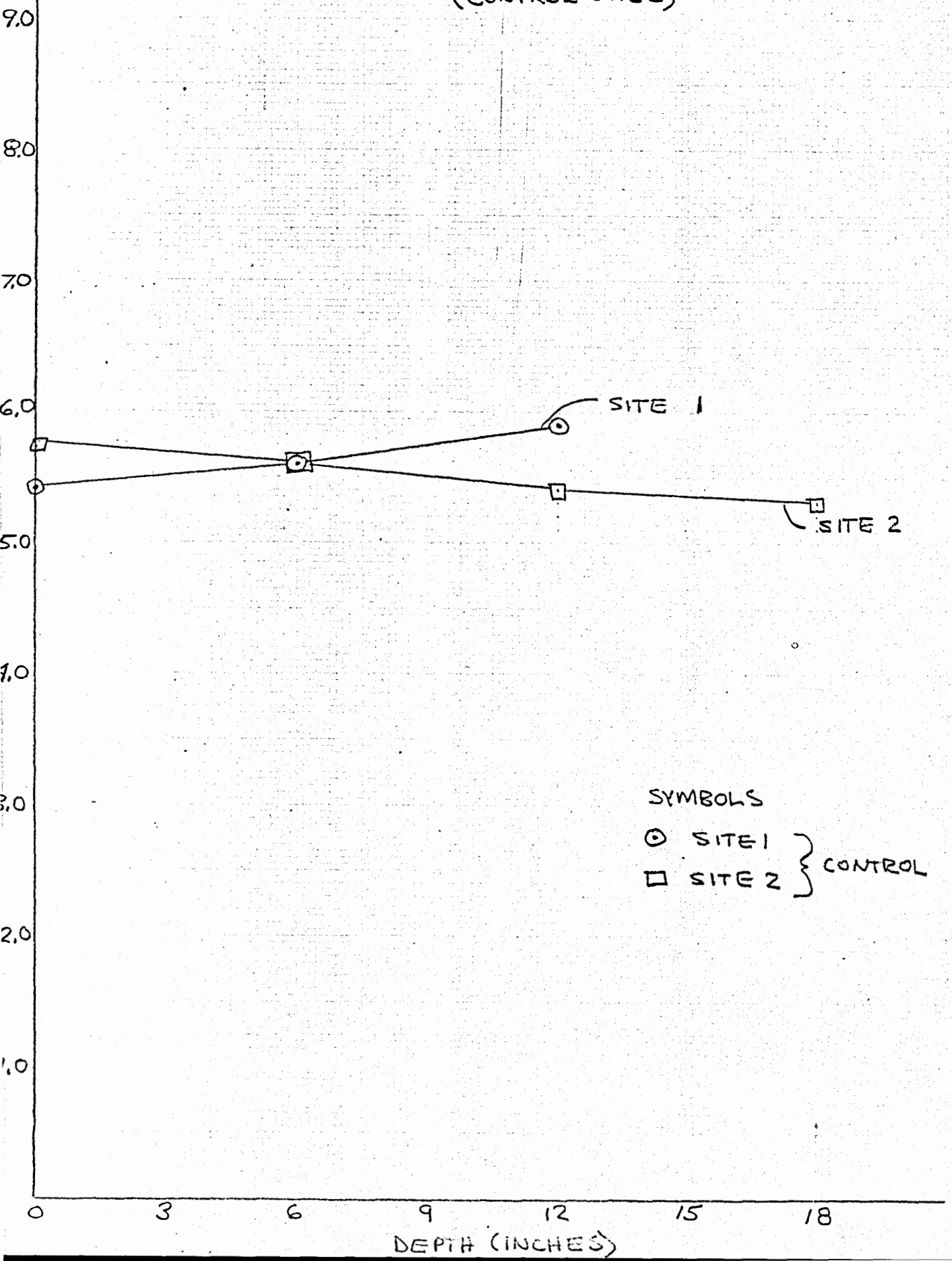
<u>SITES</u>	<u>DEPTHS</u>	<u>SOIL</u>	<u>H<sub>2</sub>O (Distilled)</u>	<u>pH READING</u>
#1 (FLD 2A)	Surface	50 grams	50 ml	5.8
	6"	"	"	6.4
	12"	"	"	6.3
	18"	"	"	5.8
#2 (FLD 2B)	Surface	"	"	6.6
	6"	"	"	6.4
	12"	"	"	6.3
	18"	"	"	6.5
#3 (FLD 3)	Surface	"	"	5.6
	6"	"	"	5.6
	12"	"	"	6.0
	18"	"	"	5.0
#4 (FLD 3)	Surface	"	"	5.6
	6"	"	"	6.1
	12"	"	"	5.5
	18"	"	"	5.2
#5 (FLD 2A)	Surface	"	"	6.6
	6"	44.8	44.8	7.2
	12"	50.0	50.0	7.0
	18"	41.3	41.3	6.7
Control Site #1	Surface	50.0	50.0	5.4
	6"	32.6	32.6	5.6
	12"	40.3	40.3	5.9
	18"		—	—
#6 (FLD 2A)	Surface	50.0	50.0	5.8
	6"	"	"	5.9
	12"	"	"	6.0
	18"	"	"	6.1
#7 (FLD 2B)	Surface	41.9	41.9	6.5
	6"	50.0	50.0	6.4
	12"	"	"	6.4
	18"	"	"	6.3

TABLE 8 (continued)

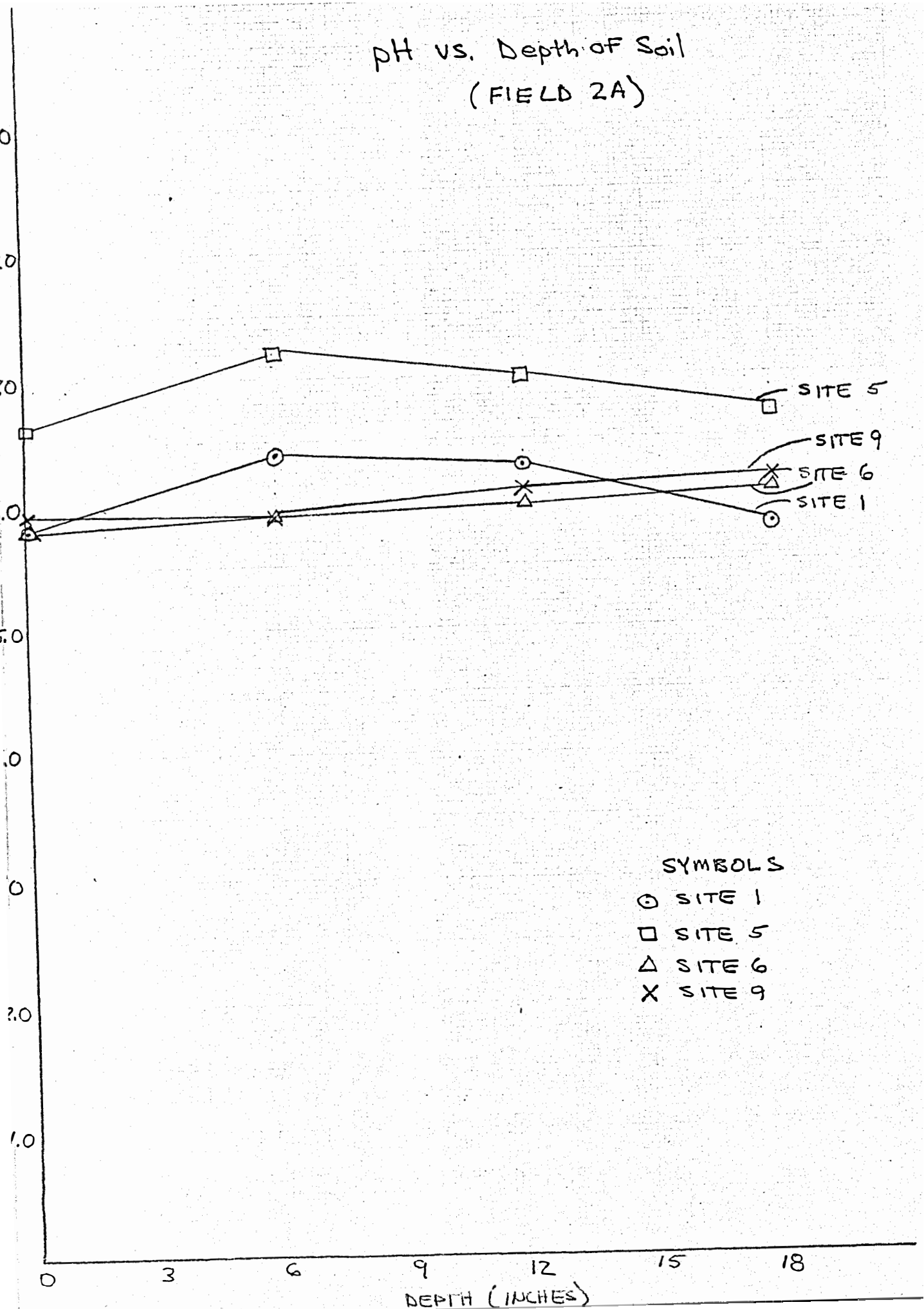
pH TESTS

<u>SITES</u>	<u>DEPTHS</u>	<u>SOIL</u>	<u>H<sub>2</sub>O (Distilled)</u>	<u>pH READING</u>
#8 (FLD 2B)	Surface	32.8 grams	32.8 ml	6.7
	6"	50.0	50.0	6.7
	12"	"	"	6.7
	18"	"	"	6.6
#9 (FLD 2A)	Surface	"	"	5.9
	6"	"	"	5.9
	12"	"	"	6.1
	18"	"	"	6.1
#10 (FLD 1)	Surface	35.8	35.8	6.6
	6"	50.0	50.0	6.4
	12"	"	"	6.0
	18"	"	"	4.8
Control Site #2	Surface	"	"	5.7
	6"	"	"	5.6
	12"	"	"	5.4
	18"	"	"	5.3

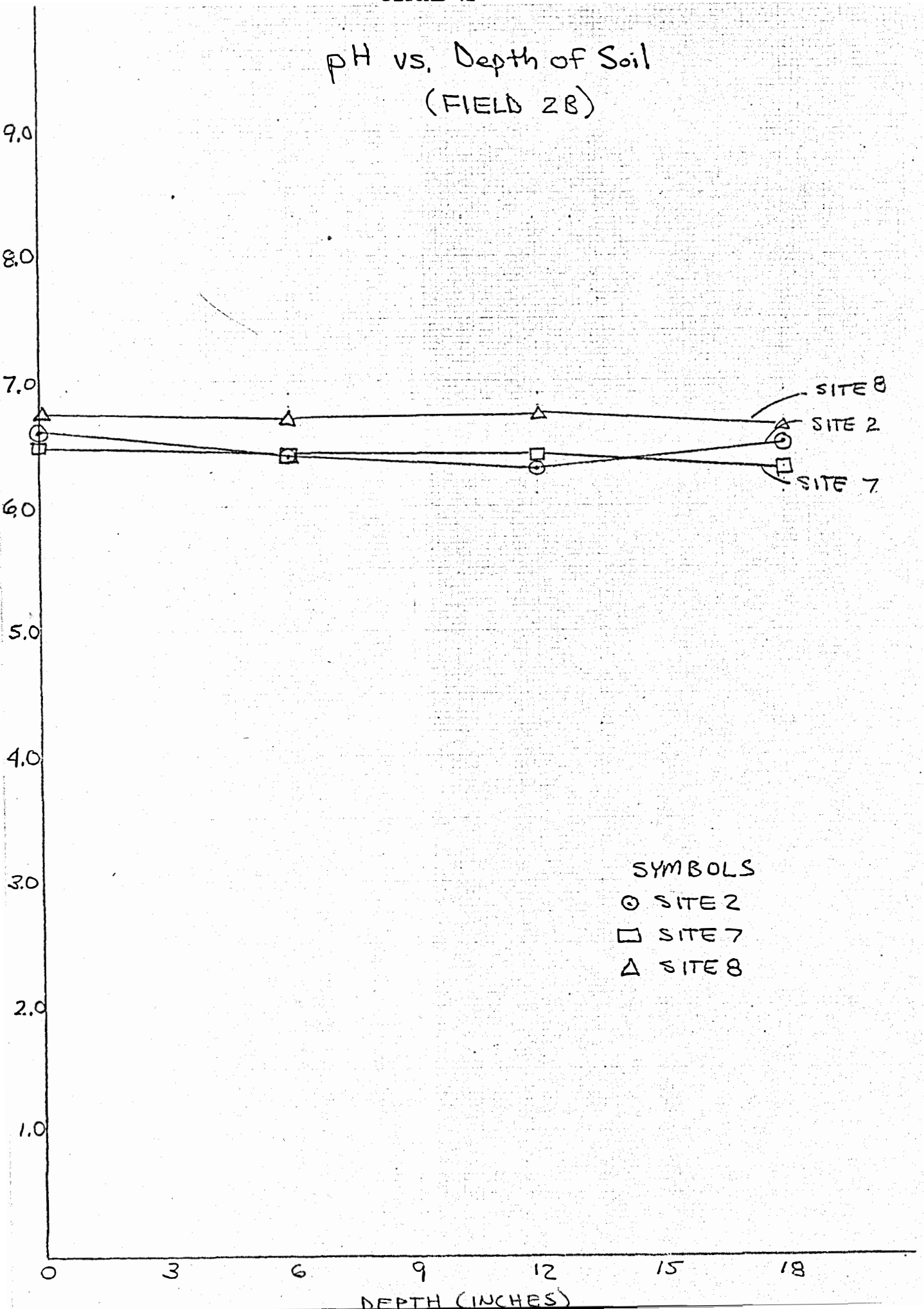
pH vs, Depth of Soil  
(CONTROL SITES)



# pH vs. Depth of Soil (FIELD 2A)

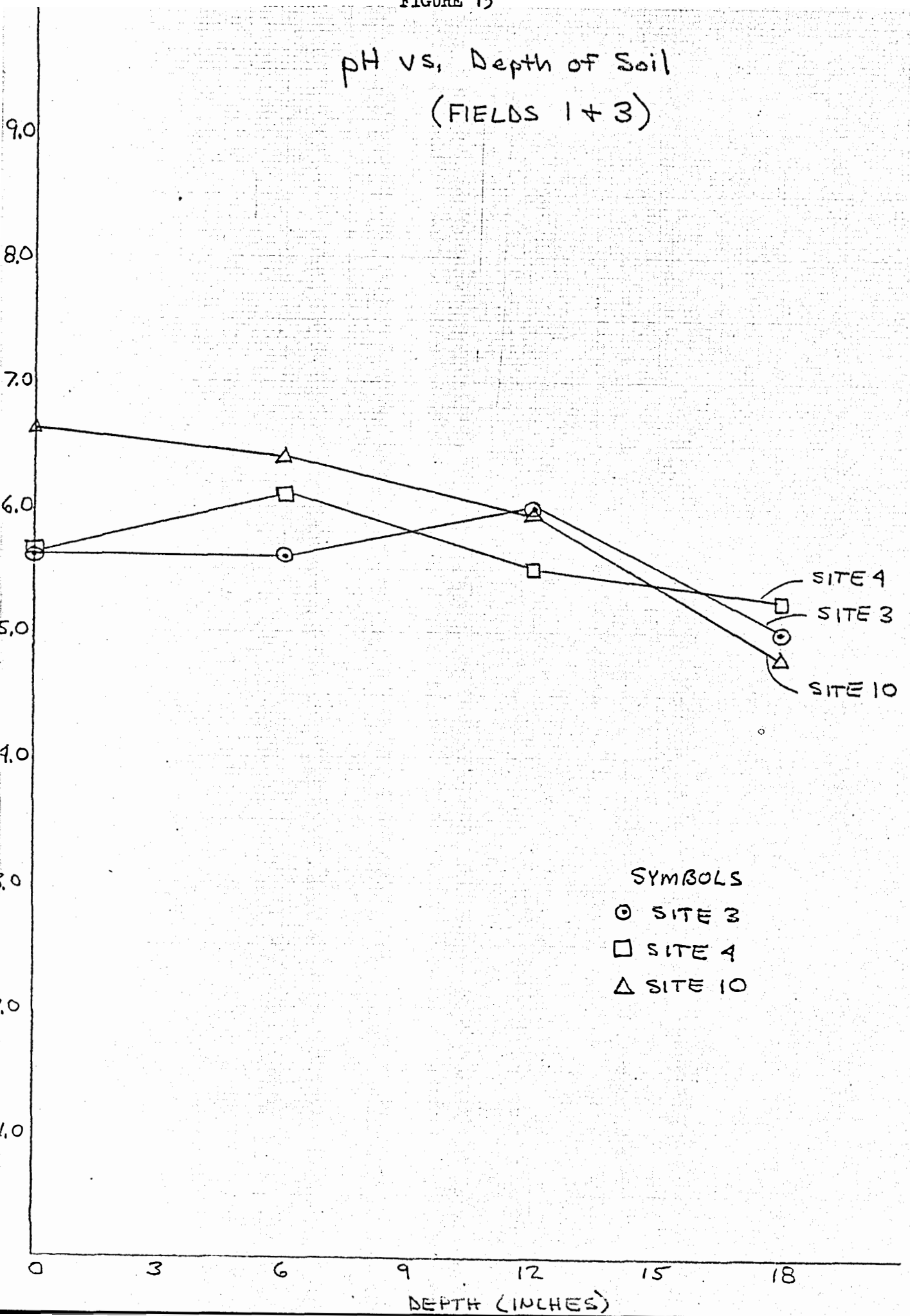


# pH vs. Depth of Soil (FIELD 2B)





pH vs. Depth of Soil  
(FIELDS 1 + 3)



SIMPSON PAPER COMPANY

VICKSBURG MILL

JULY, 1980 METALS TESTING OF WATER SAMPLES FROM MONITORING WELLS

WELLS	* Silver ppm	** Barium ppm	** Cadmium ppm	** Chromium ppm	* Copper ppm	** Iron ppm	** Potassium ppm	** Manganese ppm	** Sodium ppm	* Lead ppm	** Antimony ppm	* Selenium ppm	** Zinc ppm
No. 1	<.0002	0.1	<0.007	<0.02	0.01	0.4	1.8	0.02	31.4	<0.001	<0.2	<0.005	0.08
No. 1A	<.0002	0.2	<0.007	<0.02	0.001	3.9	2.3	0.5	59.7	<0.001	<0.2	<0.005	0.1
No. 2	<.0002	0.2	<0.007	<0.02	0.004	0.02	1.8	<0.02	45.8	<0.001	<0.2	<0.005	0.3
No. 2A	<.0002	0.1	<0.007	<0.02	<0.001	2.4	2.5	0.4	59.4	<0.001	<0.2	<0.005	0.2
No. 3A	<.0002	0.1	<0.007	<0.02	<0.001	0.08	1.8	0.1	59.4	<0.001	<0.2	<0.005	1.5
No. 6	<.0002	<0.1	<0.007	<0.02	0.002	0.02	1.4	<0.02	56.6	<0.001	<0.2	<0.005	0.1
No. 10	<.0002	<0.1	<0.007	<0.02	<0.001	0.02	0.8	<0.02	4.3	<0.001	<0.2	<0.005	0.4
No. 12	<.0002	8.3	<0.007	<0.02	<0.001	21.1	3.1	0.3	9.2	<0.001	<0.2	<0.005	0.02
No. 12A	<.0002	0.5	<0.007	<0.02	<0.001	1.2	6.3	0.1	30.3	<0.001	<0.2	<0.005	0.02
No. 13	<.0002	0.2	<0.007	<0.02	<0.001	0.08	1.6	0.03	20.0	<0.001	<0.2	<0.005	0.004
No. 13A	<.0002	0.1	<0.007	<0.02	<0.001	5.6	3.6	0.4	63.4	<0.001	<0.2	<0.005	0.004
* Graphite Furnace Technique      ** Flame Technique													

TABLE 9

## DISCUSSION OF RESULTS

By observing the graphs and analyzing the data I've collected from my soil samples; I have come up with some conclusions about my results. First I would have to say that the migration of the heavy metals down through the first eighteen inches of soil showed a very random distribution. The PIXE (Particle Induced X-ray Emissions) analysis shows that the concentration of the metals did not follow any consistent pattern going from the surface down to eighteen inches. For example, site 9, in field 2A showed a concentration of 127.6 ppm of zinc at the surface, 55.3 ppm at the six inch depth, but 69.0 ppm at the twelve inch level and then back down to 57.0 ppm at the eighteen inch mark. At this same site the lead concentrations vary from 76 ppm at the surface to 48.6 ppm, 61.6 ppm, 50.7 ppm at 6, 12, and 18 inches respectively. These types of variations at the different levels in the soil seem to point out that my theory of the heavy metals consistently decreasing as you go down through the soil was not exactly right. However, I can offer some explanation as to why the amounts of the heavy metals might fluctuate so much throughout the soil.

In the soil itself you have an area known as the leaching zone which is where some of the heavy metals may be absorbed by soil particles and by plant roots or may simply pass straight through the soil and continue downward. The next zone we observe is the accumulation zone, where the heavy metals may build up and become trapped and can result in our higher concentrations. Still if we go down farther in the soil we reach a zone which is relatively unaffected by any of the surface application of metals. This zone may be somewhere between 8 - 10 feet below the surface.

Now when looking back at my results, I would have to say that my soil samples taken at the deeper levels showed higher concentrations than the ones

at the surface. It could be that I was in the accumulation zone where the metals were at their highest amounts, thus explaining the increase in metal concentrations. Also these irrigation fields are used to grow different types of crops. Every three to four years the fields have to be plowed to aerate the soil and mix up the dead organic material on the surface of the soil. Due to this plowing the heavy metals at the surface are mixed up and carried down into the soil deeper. The depth of the plow is set at about eight inches, and as a result higher concentrations of metals are very possible at the lower depths in the soil. Since the fields are plowed every 3 to 4 years its impossible to get a direct vertical migration of the heavy metals since the mill began, because the metals are upset due to the plowing and are not in their original pattern since the beginning of the irrigation program.

Another important factor that comes into play is the size of the particles such as clay have a stronger affinity for the positive charged particles than larger particles. Clay particles already have a negative charge associated with them and therefore they would naturally be attracted to the positively charged metals flowing through the soil. As a result, it's possible that where the concentration of the metals seems higher as I went deeper into the ground it could be due to a higher amount of clay particles at that particular depth. The soil where I obtained my samples is basically a sandy loam type of soil, however, if any clay particles were present they would most likely attract the heavy metals with more consistency. A sieve analysis may have aided in particle distribution data. However it was suggested that this data would not have been of qualitative value and therefore I chose not to perform the sieve analysis test.

When observing my data from the control fields I could see that in many instances there were higher concentrations of some elements than I

expected. I couldn't understand why there was so much potassium, titanium, iron and manganese in the control field when there was no application of heavy metals from the mill. After talking to Mr. Harrison in the geology department here at Western I was made aware of the fact that there are many minerals in the soil in the Kalamazoo area that naturally contain the elements mentioned above. Some of the more common minerals are quartz ( $\text{SiO}_2$ ), Feldspar ( $\text{KAlSi}_3\text{O}_8$ ), Mica ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ), Magnetite ( $\text{Fe}_3\text{O}_4$ ), and Illmenite ( $\text{FeTiO}_3$ ). The mineral magnetite ( $\text{Fe}_3\text{O}_4$ ) has the ability to exchange it's iron cation with other cations in the soil such as titanium, manganese, and zinc. This explanation helped point out exactly where some of the metals found naturally in the soil come from.

Another factor that can effect the migration of heavy metals in the soil is the pH. I conducted some pH tests on all of my soil samples and plotted the results on graphs on page 25. The ranges of the pH were from 5.4 to 5.9 for the control field and about 5.0 to 7.0 for the other irrigation fields. These ranges are just about what is expected. If the pH levels were around 4.0, then there would be reason for concern since this acidic condition may cause the minerals to release some of the heavy metals adhering to their outer structure making them available to move around and concentrate in other areas of the environment. When growing crops it's best to have a high pH soil since this is what crops prefer, therefore, this could be the reason for the higher pH values for the irrigation fields. Typically farmers like pH values around 6.5.

I would like to point out here that the results I received from the PIXE analysis have a total amount of the particular metal in any given soil sample. To obtain a rough estimate of how much of a certain metal was applied to an area I subtracted the control sample from the sample in the

irrigation field. These were averages of the different sites I had established throughout the different fields. For example in field 2A I averaged the PIXE results for sites 1, 5, and 6 to get values for the surface, 6 inch 12 inch and 18 inch depths. For the control field I had established only two sites, therefore I used these two PIXE results and averaged them together to give a rough estimate of the metal concentrations in the control field. It should be made clear at this point that my results are in no way the exact amounts of the metals applied to the fields. In order to come up with a relatively close approximation, many more samples would have to be taken. In my experiment I had taken a total of 51 soil samples throughout the different irrigation fields and control field. I would estimate that at least 200 samples would have to be taken in order to make a good basis for establishing an average number for the metal concentrations.

All of the results from the PIXE instrument are not precise amounts. For each element analyzed there is a percent uncertainty that goes along with it. For example, potassium has 25 percent uncertainty, zinc 15%, lead 29%, copper 20%, and so on. This percent uncertainty varies for the different elements due to the instrument's ability to read the different energy levels of the elements. Some elements are easier to detect than others, therefore they have a lower percent uncertainty. There are a set of standards that the PIXE instrument is calibrated for and depending on how close the PIXE comes to these standards is another factor influencing the percent uncertainty. As a result, the concentrations recorded for my soil samples can vary as little as 2 ppm and as high as 4000 ppm depending on the particular element.

Another area to be concerned with is groundwater contamination. Although I didn't do any groundwater tests the mill did have some data available from the monitoring wells taken in July 1980. After looking at the data

(Table 9) it became apparent that the mill was not exceeding any water standards and that when compared to the amount of heavy metals trapped in the soil, the groundwater had a very small amount.

### CONCLUSIONS

Finally, I would like to summarize some of the factors involved when collecting soil samples from a given site. In any particular field, samples collected close to each other could vary largely due to some of the reasons I mentioned earlier: natural concentration of minerals, particle size distribution (clay vs. sand particles) and leaching and accumulation of the particular metal in that site. Due to the many influences that effect my results I would have to say that my method of accounting for the heavy metal application to the irrigation fields is non-conclusive. However my method of analysis is still of value to the mill since it does give the total amount of the metals in the soil. If another PIXE analysis were taken in three or four years and if noticeably higher concentrations were detected, then I think a closer look into the application of the heavy metals would definitely be necessary.



### FUTURE STUDIES

For future studies of the heavy metal application on the irrigation fields, I would have to say that an alternative method of determining the amount of heavy metals applied to the fields would be a chemical extraction of the metals from the soil particle. Soil samples would be obtained through out the irrigation fields and each one would be treated equally by some type of acid extraction to strip away any of the metals adhering to the outside of a certain mineral. Then by using an atomic absorber instrument the amount of metals stripped off can be readily detected. This type of stripping analysis does not account for any of the natural metals that are incorporated in the inside structure of the mineral. As a result, all the metals you are extracting from the samples are the ones directly applied by the spray irrigation system. Also an analysis of the leaves, stems, and roots of the plants growing in the irrigation fields is advised. Since plants do not contain the metals naturally, any amount detected through the PIXE analysis would be directly related to the heavy metal application too. By analyzing both plant samples and soil samples, we can grasp a better understanding of exactly how much heavy metals have actually been applied to the irrigation fields. If the tests do show high levels of heavy metals then it will be necessary to act as quickly as possible to avoid any permanent damage to the environment.

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