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HEAVY METALS STUDY

1979 Progress Report on the Field Leaching and Reclamation Program and the Removal of Metals from Stockpile Runoff by Peat and Tailings

Minnesota Department of Natural Resources

Division of Minerals

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HEAVY METALS STUDY

1979 Progress Report on the
Field Leaching and Reclamation Program
and the Removal of Metals from
Stockpile Runoff by Peat and Tailings

Paul Eger
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Minnesota Department of Natural Resources
Division of Minerals
1980

Acknowledgements

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EXECUTIVE SUMMARY

Objectives

The objectives of the Heavy Metal Study are to:

1. Evaluate the effect of revegetation on controlling heavy metal release from Duluth gabbro material.
2. Evaluate the effectiveness of peat and tailings to remove heavy metals from leachate solutions.

Results - Field (Objective 1)

1. A revegetated topsoil cover on the stockpile reduced the volume of runoff by 24-30%. Glacial outwash soil was too droughty to support sufficient vegetation to reduce runoff.
2. An increase in copper release was observed for the pile with the revegetated topsoil cover. This is presumably the result of the increase in organic material in the solution.
3. The lowest nickel release was observed for the pile with the revegetated topsoil cover. The pile also shows a decreasing sulfate release which suggests a decrease in the rate of oxidation of the sulfide minerals.
4. Control of acid production is critical to controlling trace metal release. As pH decreases, metal concentrations increase. pH decreases were observed in two piles in 1979, one an uncovered control pile, and a pile with a partially revegetated glacial outwash cover.

Results-Laboratory (Objective 2)

1. Peat was effective in removing trace metals from runoff with a low pH (3.8) and high trace metal concentrations (2-64 mg/l).

In column tests, trace metal concentrations were reduced by as much as 98%.

2. Peat was less effective in removing metals from the runoff with a near neutral pH (7.2) and lower trace metal concentrations (<.5 mg/l).

3. Tailings did not remove metals from the solution with low pH.

4. On the less concentrated leachate, tailings did remove some metals, but were not as effective as peat.

Work in Progress

Funding from IRRRB has been received to carry the field program to the end of the biennium. An EPA grant has been received to extend the field study to include two full scale gabbro stockpiles at Erie Mining Company's Dunka operation.

Additional laboratory work will be done to comprehensively study the effectiveness of various materials to remove trace metals from leachate solutions. This work will be funded by the U. S. Bureau of Mines and is an extension of the preliminary experiments that were conducted under the LCMR funding.

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Overview

In 1974, AMAX Exploration Inc. acquired Bear Creek's leases for properties located in T 60N R 12W, about 4 miles S.E. of Babbitt, Minnesota. Very little information existed on the potential environmental problems that might be associated with developing Minnesota's copper-nickel resources. The AMAX project became a pilot study. A comprehensive monitoring network was developed and an agreement was reached to conduct leaching tests on stockpiled materials.

In 1977, AMAX constructed six test piles (FL1-FL6) containing lean ore material. The overall composition ranges from 0.300 - 0.348% copper, 0.083 - 0.085% nickel and 0.634 - 1.414% sulfur (Table I). More detailed information on the composition and construction is given in Appendix I. In 1978, a cooperative research effort between DNR and AMAX was initiated. DNR has primary responsibility for the leaching portion of the study, while AMAX is responsible for the revegetation aspects. The objectives of the study were to

- 1) Examine the leaching characteristics of residual mine waste material.
- 2) Evaluate the effects of reclamation activities on leachate quality and quantity.
- 3) Develop a successful revegetation program for the AMAX project.

Water quality data collected at AMAX (Eger et al (1978)) as well as data generated by the Regional Copper-Nickel Study (Eger and Lapakko 1980) indicated that stockpile runoff, unless adequately controlled, could cause environmental problems. Trace metal concentrations in stockpile runoff were 10 to 10,000 times higher than natural background concentrations found in streams and lakes of the area.

TEST PILE CHARACTERIZATION

Table I

Pile	Mass (tons)	Average Composition			Treatment
		Cu	Ni	S	
1	1784	.348	.083	.634	Uncovered, control
2	1784	.348	.083	.634	Covered with topsoil, revegetated
3	1784	.348	.083	.634	Covered with glacial outwash, revegetated
4	1784	.348	.083	.634	Uncovered, control
5	2370	.300	.085	1.414	Covered with glacial outwash, revegetated
6	1723	.339	.084	.787	Uncovered, control

Revegetation is one possible method of controlling the water quality problem. A revegetated soil covering should reduce both the amount of water and oxygen reaching the rock surfaces. As the amount of water and/or oxygen is reduced the leaching rate should decrease, and the concentration of trace metals in the runoff should decrease.

Data collected during the Regional Copper-Nickel Study, demonstrated the ability of peat to remove metals from solution (Eger, Lapakko and Otterson (1980) and Ryss and Hoffman (1979)). Duluth gabbro tailings, due to their large silicate surface area, were another possible material that might remove metals from solution. Laboratory leaching experiments (Eger and Lapakko (1980)) demonstrates that the tailings released only very small quantities of trace metals to solution and tended to maintain pH in a range favorable for metal removal. Preliminary laboratory experiments were conducted to examine the metal removal capacities of both peat and tailings.

This report is organized in two chapters. The first chapter presents the results of the field program which is the study of the effect of revegetation on metal release. The second chapter presents the results of the laboratory work, which is the study of the metal removal capacity of peat and tailings.

CHAPTER 1

AMAX FIELD PROGRAM

INTRODUCTION

Historically one of the major problems associated with the mining of metal sulfide deposits has been the release of toxic trace metals through the leaching of mining wastes (Hawley, 1972; Eisenreich et al, 1976). In most documented cases of leaching problems, the leachate is acidic, often with pH values as low as 2 to 3.

Most of the field studies reported in the literature involved materials that contained a high concentration of sulfide minerals. Hawley reports that acid leachate has been associated with materials that contain 2.5 to 70 percent sulfide. The Duluth gabbro is a low grade disseminated deposit. "Model" lean ore and waste rock concentrations developed by the Regional Copper-Nickel Study (1980) range from .655 percent sulfur for lean ore to .207 for waste rock. Even though the gabbro is in general a low grade deposit, early water quality samples (1974) collected near stockpiled gabbro at Erie Mining Company's Dunka Pit, near Babbitt, MN, indicated elevated levels of trace metals. Studies conducted by the Regional Copper-Nickel Study (Eger and Lapakko, 1980) have confirmed the findings of the early samples. Metal concentrations in leachate samples are 10 to 10,000 times the natural background concentrations.

Lean ore and waste rock stockpiles, unless controlled, may pose significant environmental problems. Not only is there evidence that stockpile runoff will contain elevated metal concentrations, but the mass of material that will be stockpiled is extremely large. For its open pit prospect, AMAX has projected that stockpiles 500-600 feet high would cover 3,400 acres.

METHODS

Water quality samples and flow measurements are collected from each test pile. Complete information on methods can be found in the 1978 progress report (Eger et al 1979). Only changes made in 1979 will be discussed in this section.

Flow weighted composite samplers were installed on all piles at the end of 1978. Rustrak event recorders were connected to each pile and provide a continuous flow record.

All water quality samples collected in 1979 were flow weighted composites. One sample was collected from each pile for each rain event $\geq .3$ inches of rainfall. Base flow samples were also collected. A flow rate of 300 ml/min, was chosen as the cutoff between interflow and base flow. To avoid mixing base flow and interflow for storms that occurred at night, base flow samples were collected at the end of each working day and composited with the previous day's sample. An empty sample container was always on the pile at the end of the day, so that night storms could be sampled.

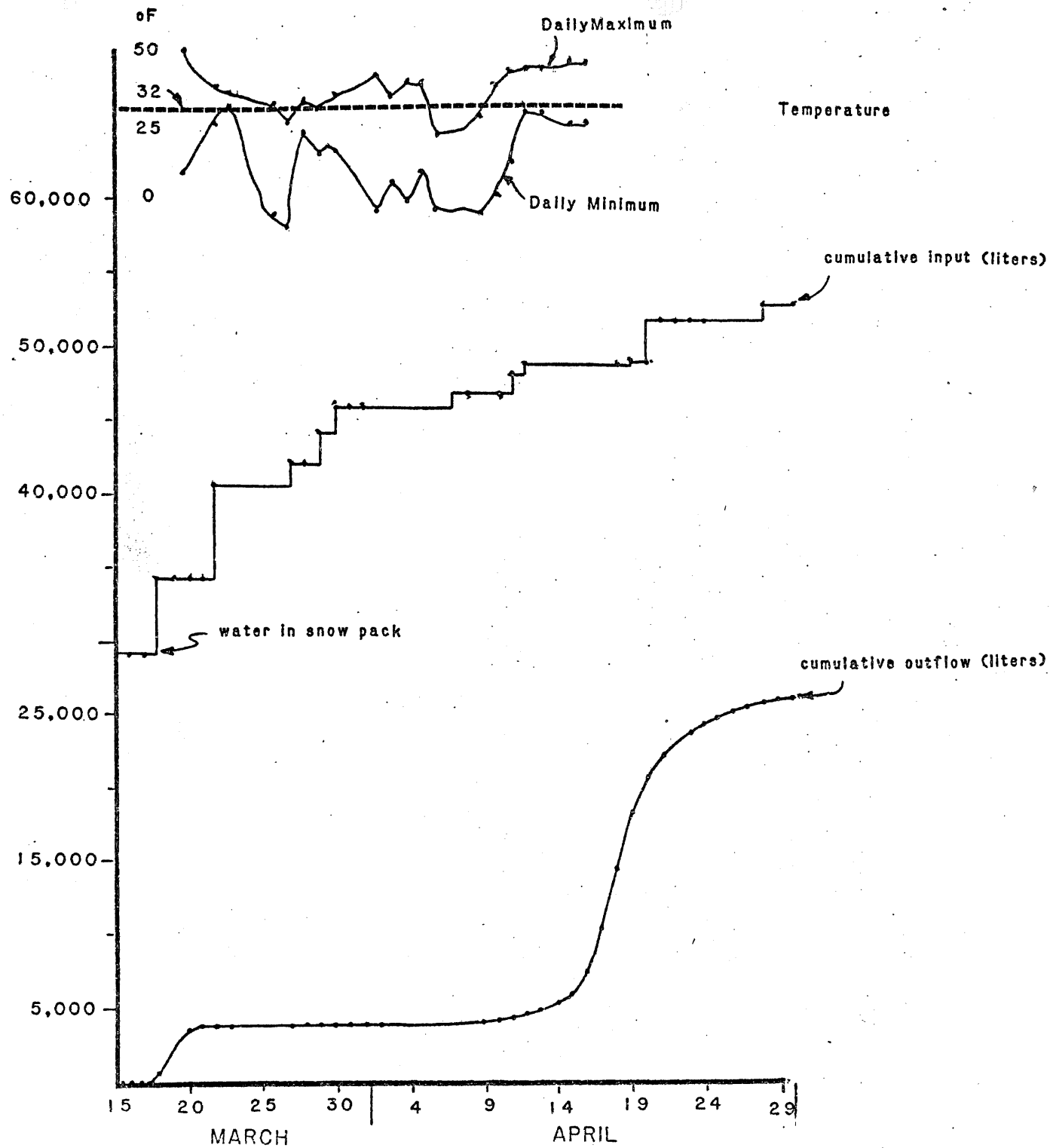
RESULTS

Flow

Daily hydrographs for 1978 and 1979 were constructed for each pile and are presented in Appendix II. Daily flows varied substantially, ranging from peak flows of 8700 l/day to no flow during extended dry periods.

1978 flow records did not begin until the middle of April, so that some of the runoff from snow melt was not recorded. In 1979, measurements of the water in the snow pack were made (Appendix III) and flow measurements began in mid-March. The first runoff occurred on March 18, the result of warm temperatures and .64 inches of rain. Temperatures dropped and runoff ceased on March 21. Temperatures remained low and additional snow accumulated. Temperatures began to increase around April 9 and most of the snow melt was released in a one week period, April 15-22. (Figure 1) Twenty nine (29) to

Figure 1. SNOW MEL: 1-9 PL1



forty five (45) percent of the total runoff occurred during this period.

(Table II)

Frequency analyses of the runoff data for 1978 and 1979 (Figures 2,3,4,5) indicated:

1- 70 to 87% of the time the daily flow is less than 500 liters/day (base flow) (Figure 2,4).

2- 60-83% of the total runoff volume occurs at flows greater than 500 liters/day (interflow) (Figures 3,5).

Overall runoff varies from 36 to 65% in 1978 and 34 to 59% in 1979.

(Table III) (Figure 6).. The 1978 data does not include spring runoff.

Water Quality

The complete set of water quality data for 1979 is presented in Appendix IV. Statistical summaries for 1978 and 1979 (Tables IV and V) and box plot summaries Appendix V indicate that trace metal concentrations are one to five orders of magnitude higher than natural background concentrations for streams of the area (Table IV). Average trace metal concentrations generally increased from 1978 to 1979, often accompanied by a decrease in pH. For example, average metal concentrations in FL 3 increased from .077 to .102 mg/l for copper and from .253 to .998 for nickel while pH decreased from 7.6 to 7.0. Average sulfate concentrations declined in piles 1,2,4,6 and increased in 3 and 5. Average sulfate concentrations for FL5 increased from 1262 to 2567 mg/l. Concentration was plotted against time and flow for both 1978 and 1979 (Appendix VI). In 1978, with the exception of piles 5 and 6, no trend of concentration with time was observed. Piles 5 and 6 exhibited a declining pH over the summer and a corresponding increase in trace metal concentrations. pH stabilized in the range of 3.8 to 4.0 for FL 5 in 1978 and dropped to 3.3 to 3.5 in 1979. In 1979, pH continued to decline in FL 6, from 7.0 to 4.5, with a corresponding increase in

TABLE II

SPRING MELT

Pile	Volume Spring Melt	Total Yearly Runoff (liters)	% of Total Runoff Due to Spring Melt
1	26,076	86,013	30.3
2	27,744	74,320	37.3
3	33,013	86,358	38.2
4	34,234	74,695	45.8
5	38,076	114,656	33.2
6	34,405	119,505	28.8

Figure 2.

FREQUENCY DISTRIBUTION FOR AMAX 1978 DATA

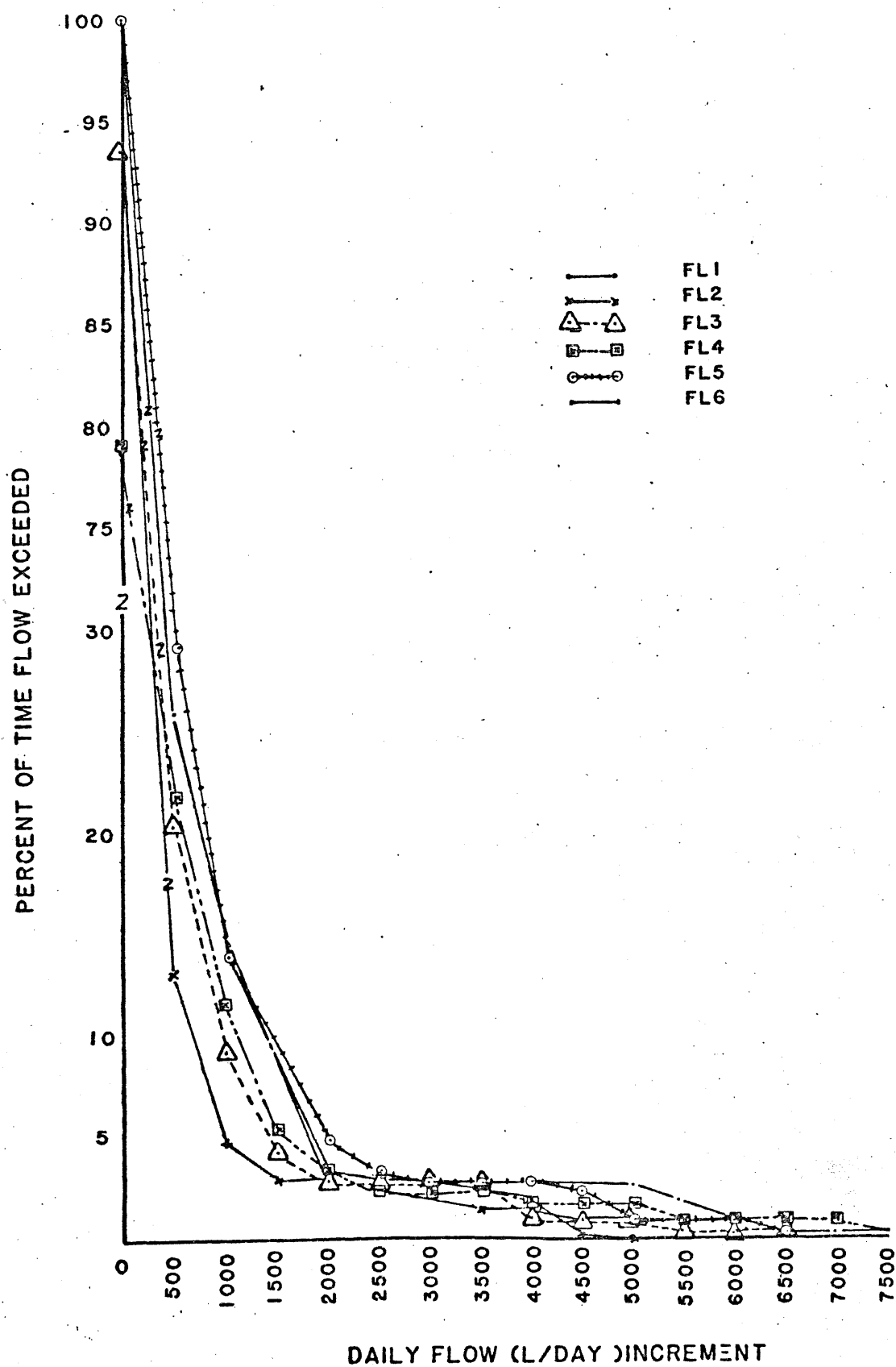


Figure 3

DISTRIBUTION OF RUNOFF 1978

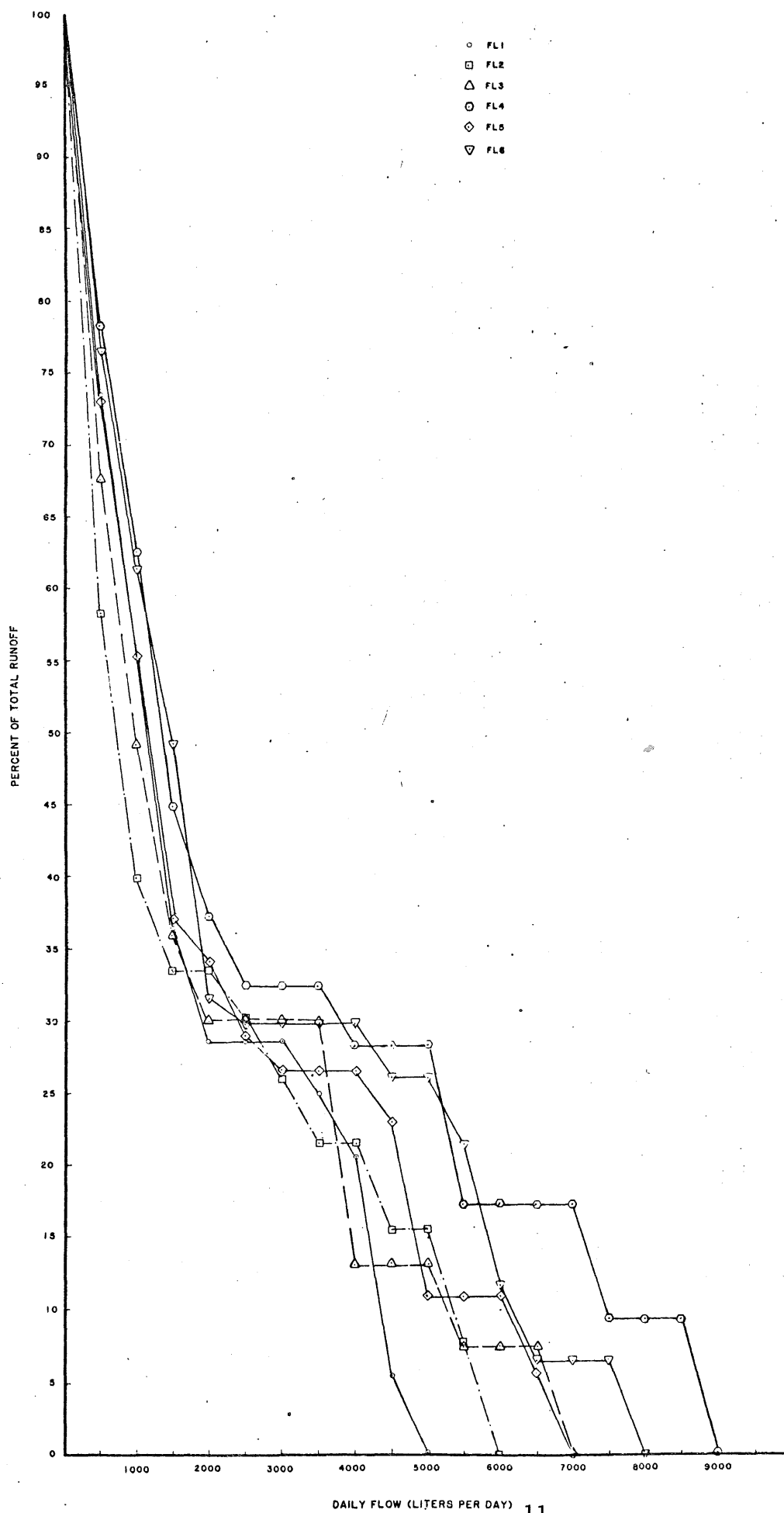


Figure 4. FREQUENCY DISTRIBUTION FOR AMAX 1979 DATA

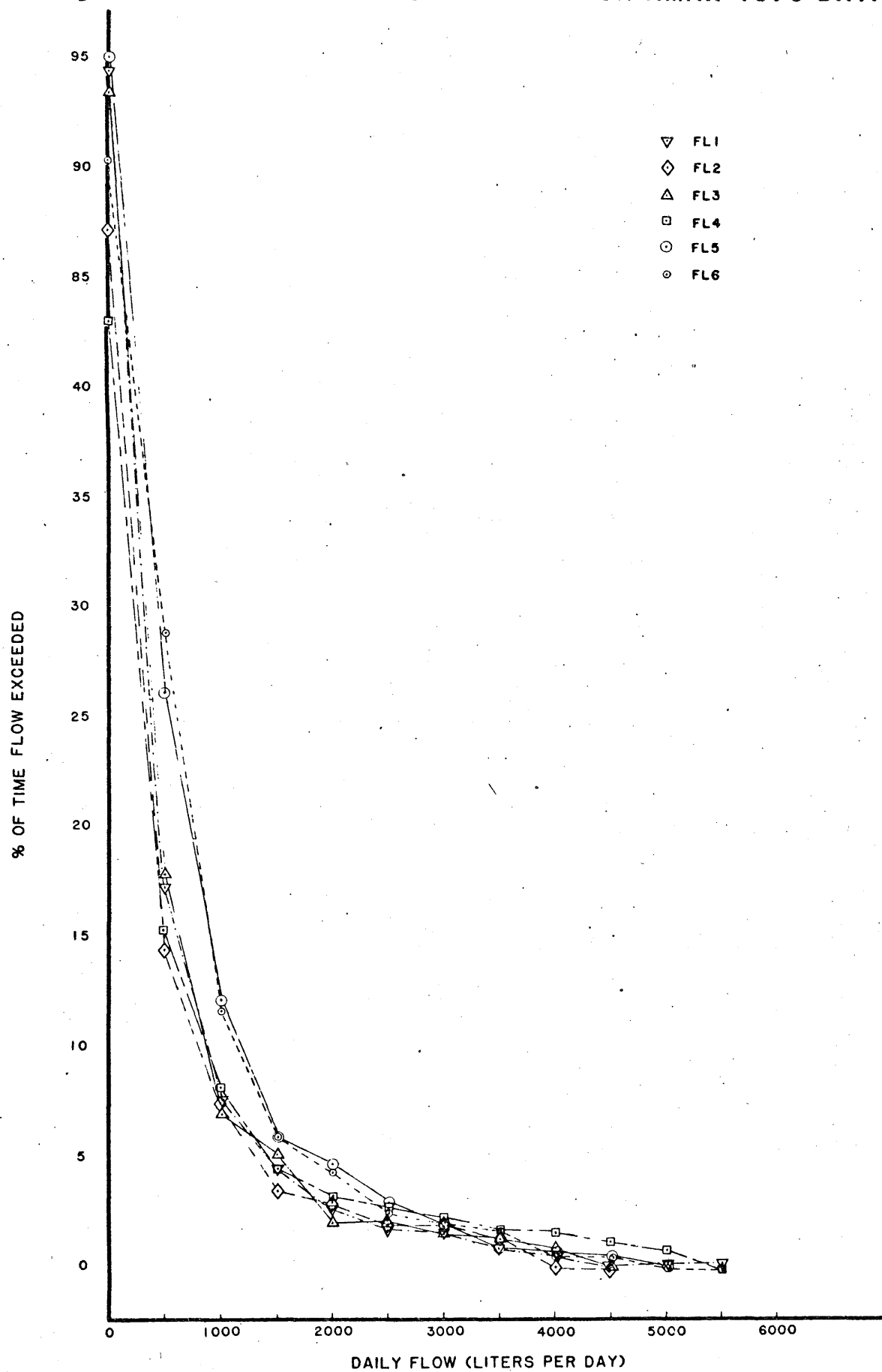
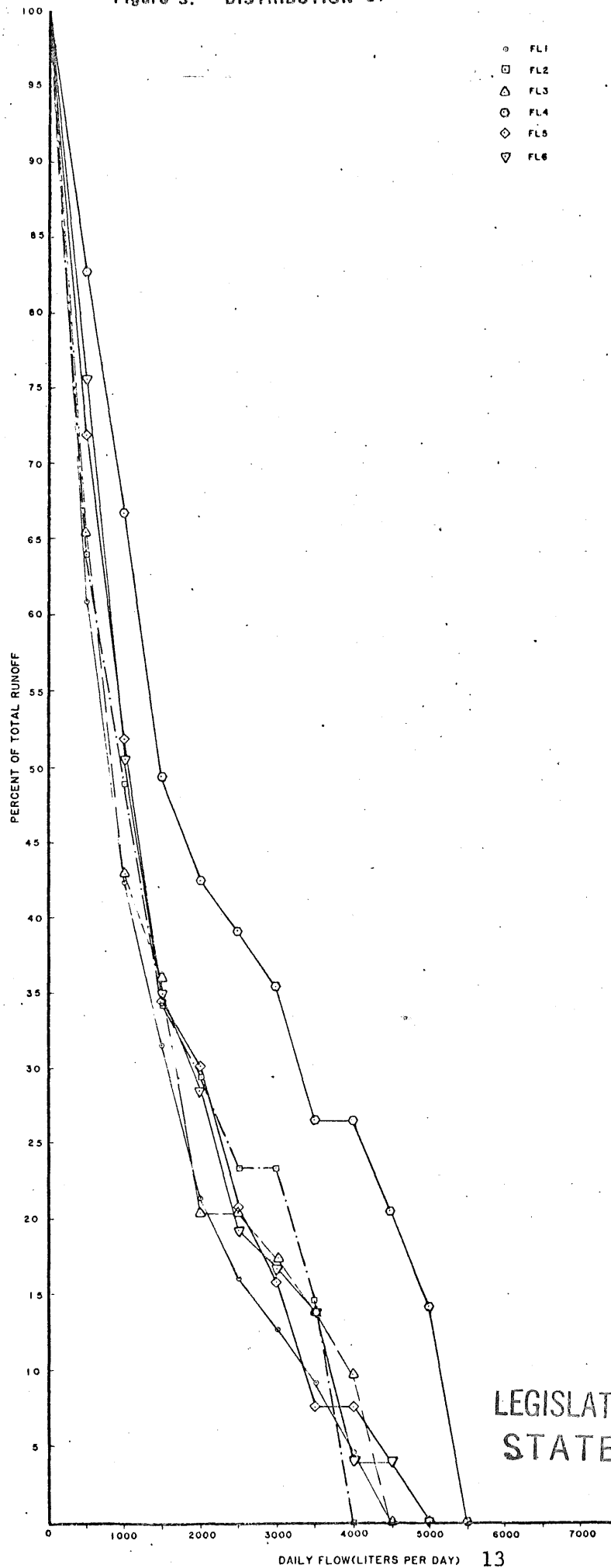


Figure 5. DISTRIBUTION OF RUNOFF 1979



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TABLE III

OVERALL RUNOFF⁺

	1	2	3	4	5	6
1978						
%	50	36	54	50	63	65
cm of water	28.2	20.5	30.6	28.2	35.6	36.6
1979						
%	45	34	45	35	51	58
cm of water	29.1	22.1	29.4	22.6	34.6	36.9

⁺Overall Runoff =
$$\frac{\text{total volume of outflow measured (l) during the sampling season}}{\text{total volume of water into the pile}} \times 100\%$$

In 1978, some of the spring runoff was not measured and no measurements of the water in the snow pack were made.

In 1979, the total outflow includes the entire season's outflow from spring melt to freeze up. The total input includes the water on the snow pack and all the rainfall that occurred during the sampling period.

Figure 6

PERCENT RUNOFF 1978 AND 1979

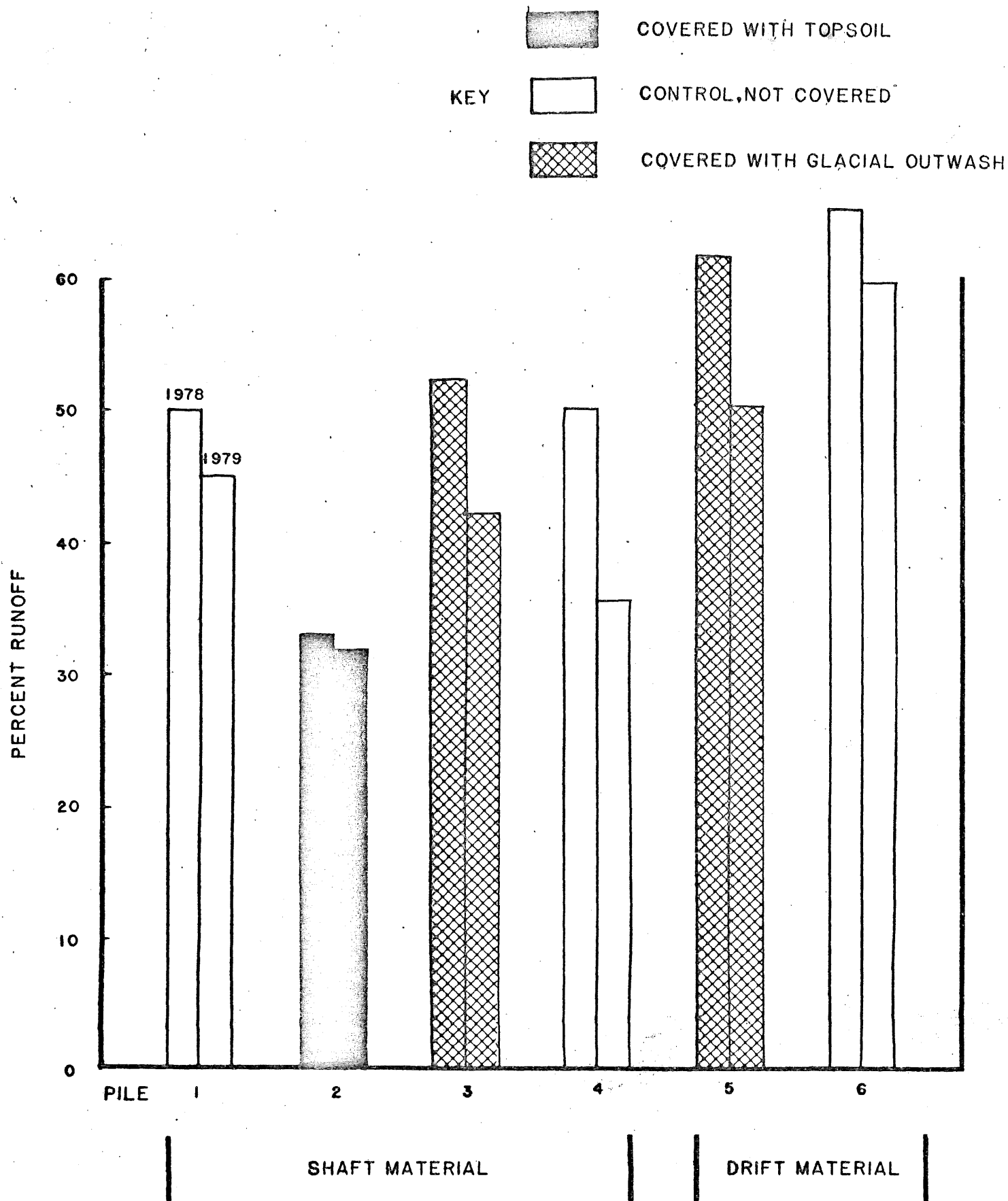


TABLE IV

1978 Water Quality Summary - Mean Values

Background Water
Quality for Streams in the area³

pH	7.7	7.6	7.6	7.5	5.6	7.4	6.8	- 7.0
Alkalinity	49.9	36.5	32.6	33.6	6.0	36.5	15.	-25.
Spe. Cond.	2160.	1920.	1190.	1720.	2550.	4690.	60.	
Calcium	275.	223.	163.	219.	341.	520.	6.	- 8.
Magnesium	22.	27.	28.	22.	37.	122.	3.	- 6.
Sodium	250.	233.	119.	160.	208.	545.	1.5	
Potassium	32.	25.	24.	40.	15.	14.		
Copper	.032	.082	.077	.023	2.55	.20	.001-	.0015
Nickel	.310	.273	.253	.237	26.9	1.37		.001
Iron	.027	.032	.087	.028	4.59	.081		.55
Manganese	.121	.181	.148	.160	4.34	1.34		
Cobalt	.022	.021	.026	.023	3.28	.170		
Zinc	.014	.056	.042	.077	1.01	.057		.001
Sulfate	1165.	912.	602.	835.	1262.	1677.	5.	-10.
Chloride	3.2	24.1	25.9	8.1	32.6	328.	3.	- 5.
Nitrate-N	4.8	18.4	8.0	1.6	54.9	180.		.01
Ammonia-N	.45	.47	.57	.64	7.0	105.		
Total-P	.10	.12	.10	.08	.10	.25		.02
Number of ² Samples	7-20	5-13	8-13	8-23	4-19	6-16		

¹ All metal values are for samples filtered through a .45 micron filter and are in mg/l² Not all parameters were analyzed on all samples, the maximum number refers to metal samples.³ Metal values are for unfiltered samples

TABLE V

1979 WATER QUALITY SUMMARY, MEAN VALUES

Parameter ¹	1	2	Pile 3	4	5	6
pH	7.3	7.3	7.0	7.0	3.5	6.0
Alkalinity	29.6	26.5	20.0	21.0	---	6.0
Sp. cond.	1511	1465	1188	1001	3043	2851
Calcium	271	205	174	159	318	317
Magnesium	25	30	36	17	144	116
Sodium	98	133	68	48	149	206
Potassium	26	24	25	29	18	7
Copper	.032	.122	.102	.215 ⁴	44.3	2.1
Nickel	.361	.354	.998	1.56 ⁴	159.3	9.3
Iron	.020	.047	.035	.073	9.2	.077
Manganese	.097	.163	.135	.259	13.7	3.44
Cobalt	.023	.026	.055	.054	12.0	.69
Zinc	.026	.059	.104	.101	5.4	.45
Sulfate	966	761	684	514	2567	1289
Chloride	4.6	18	6.5	4.5	15.5	99
Nitrate N ³	1.3		3.3	.74	11.6	82
Ammonia N ³	.15	.28	.08	.067	.7	18
DOC	7.8	13.0	6.3	3.9	6.8	7.7
Number of Samples ²	33	23-32	23-34	13-26	22-35	23-37

¹All metal values are for samples filtered through .45 micron filter and are in mg/l.

²Not all parameters were analyzed on all samples: the maximum number refers to metal samples.

³Less than 5 samples.

⁴Median values are Cu, .027 Ni, .321: three of the samples had very high trace metal content and had undue influence on the data.

trace metal concentration. pH also declined in FL 3 during 1979 reaching a minimum value of 6.3 prior to freeze up. Nickel and copper concentrations increased as the pH decreased, reaching maximum values of 2.84 mg/l and .22 mg/l respectively.

Nickel concentrations FL 1 increased during the season; from about .2 mg/l to .7 mg/l, but copper remained relatively constant at about .03 mg/l.

No general trends were observable at pile FL 2, as the concentration values fluctuated throughout the season.

FL 4 had metal release patterns that were very different from the other piles. Extremely high concentrations (Ni = 14.6, 12.3 mg/l) were found in the first two spring melt samples. Reanalysis of the samples confirmed the high nickel concentrations, but the possibility of sample contamination cannot be ruled out. After the end of a long dry period, during which FL 4 had not flowed for 33 days a large (1.19 in.) rain produced a low pH (5.75) and high metal (Ni = 4.14 mg/l Cu = .7 mg/l) concentrations.

Mass Release

The total mass release for each element and each pile was calculated by several methods for both 1978 and 1979, and estimated for 1977 (Tables VI, VII, VIII). In general, FL 5 and 6 release more mass than FL 1-4; as much as one thousand times more for copper and nickel.

The rate at which mass is released from the test pile was calculated by

$$\text{Rate of Release } \left(\frac{\text{mg}}{\text{mt day}} \right) = \frac{\text{total mass release (mg)}}{\text{stockpile size (mt)} \times \text{total sampling period (days)}}$$

Results are presented in Figures 7 through 14.

TABLE VI

TOTAL MASS RELEASE
1977

Mass Release (kg)

	1	2	3	4	5
Calcium	17.00	16.00	12.00	22.00	12.00
Magnesium	1.60	2.05	2.30	3.00	0.25
Sodium	45.00	58.8	35.00	32.00	-
Potassium	1.40	1.75	1.40	2.70	0.44
Copper	0.003	0.0036	0.0035	0.0023	0.0009
Nickel	0.024	0.026	0.028	0.035	0.078
Iron	0.0073	0.006	0.0052	0.0058	0.001
Manganese	0.0052	0.0072	0.0062	0.0081	0.014
Cobalt	0.0007	0.0012	0.0011	0.0012	0.0084
Zinc	0.0012	0.0042	0.001	0.0088	0.0008
Sulfate	69.00	90.30	93.00	100.00	41.80
Chloride	34.00	27.6	18.00	42.00	4.20
NO ₃ -N	9.80	12.20	6.50	4.40	4.98
Total P	0.02	0.42	.01	0.012	0.002

TABLE VII

TOTAL MASS RELEASE
1978

Mass Release* (kg)

	1	2	3	4	5	6
Calcium	22.8	15.6	14.79	20.2	41.1	62.65
Magnesium	1.83	1.89	2.54	2.03	4.46	14.70
Sodium	20.78	16.3	10.80	14.76	25.1	65.66
Potassium	2.66	1.75	2.18	3.69	1.81	1.69
Copper	.0027	.0058	.007	.0021	.31	.024
Nickel	.0258	.0192	.023	.0219	3.25	.165
Iron	.0022	.0022	.0079	.0026	.55	.0098
Manganese	.01	.0127	.0134	.0148	.52	.16
Cobalt	.0018	.0015	.0024	.0021	.40	.02
Zinc	.0012	.0039	.0038	.0071	.122	.0069
Sulfate	96.8	64.0	54.6	77.0	x152.	202.0
Chloride	.266	1.69	2.35	.75	3.93	39.5

*Mass calculated from (average concentration x total outflow)

TABLE VIII

TOTAL MASS RELEASE
1979

Mass Release* (kg)

	1	2	3	4	5	6
Calcium	19.37	12.11	13.43	10.50	33.10	34.39
Magnesium	1.75	1.72	2.79	1.14	14.78	12.95
Sodium	6.57	6.86	5.74	3.31	15.10	21.64
Potassium	1.83	1.46	1.89	1.81	1.79	.677
Copper	.0025	.0090	.0085	.02	4.37	.230
Nickel	.0280	.0204	.0808	.1561	16.58	1.03
Iron	.0017	.0036	.0033	.0109	1.01	.0085
Manganese	.0075	.0097	.0110	.023	1.43	.372
Cobalt	.0019	.0015	.0045	.0046	1.28	.079
Zinc	.0023	.0036	.0085	.0075	0.54	.046
Sulfate	63.26	38.25	51.5	33.79	245.9	130.66
Chloride	.302	1.14	0.52	.3110	1.39	10.96

*Mass calculated by Method II (Appendix VII)

Figure 7 RATE OF RELEASE OF CALCIUM

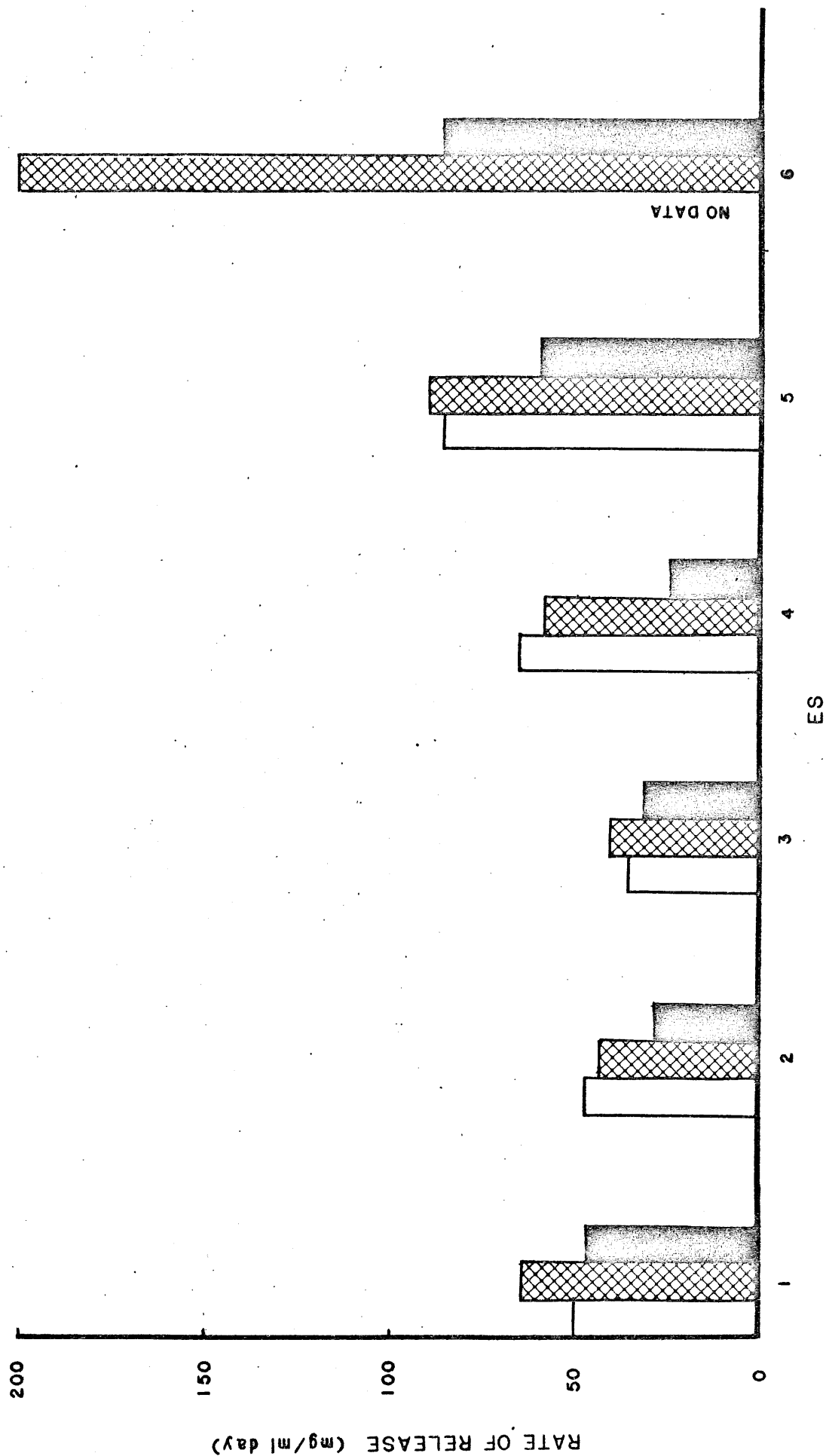
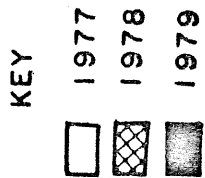


Figure 8 **RATE OF RELEASE OF MAGNESIUM**

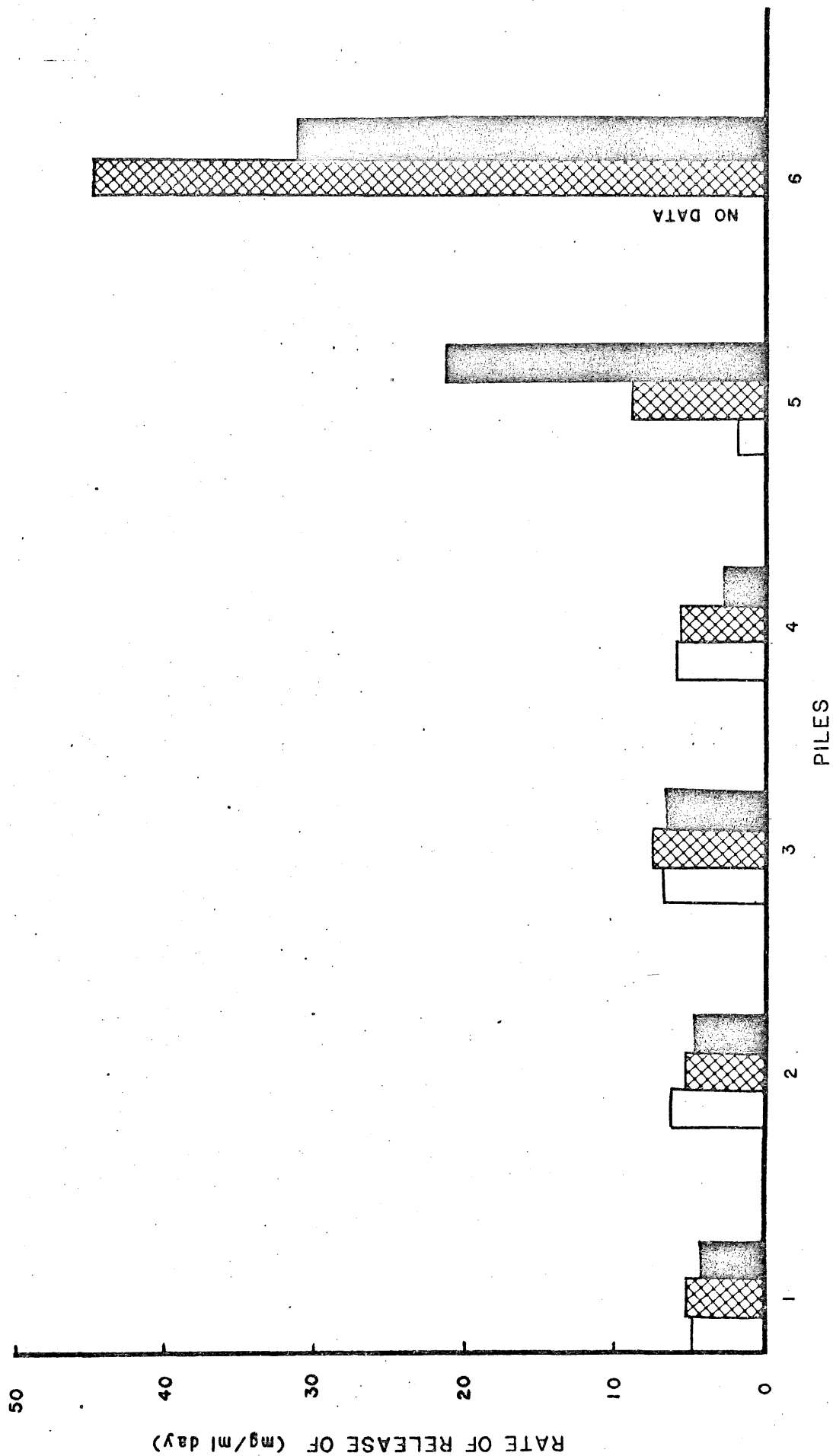
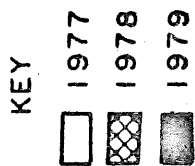


Figure 9 **RATE OF RELEASE OF SODIUM**

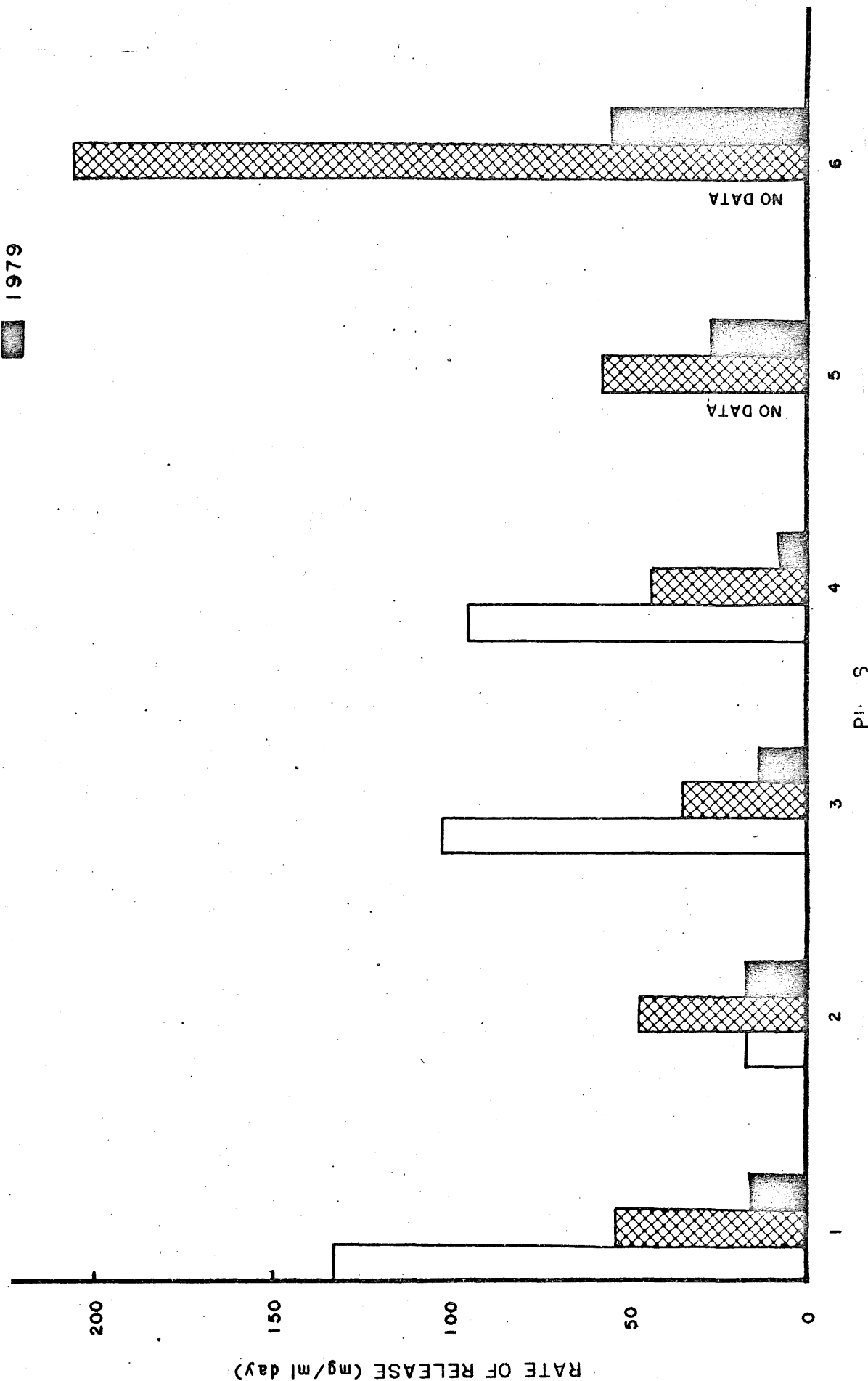
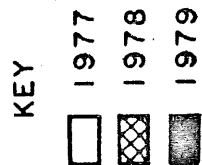


Figure 10 RATE OF RELEASE OF SULFATE

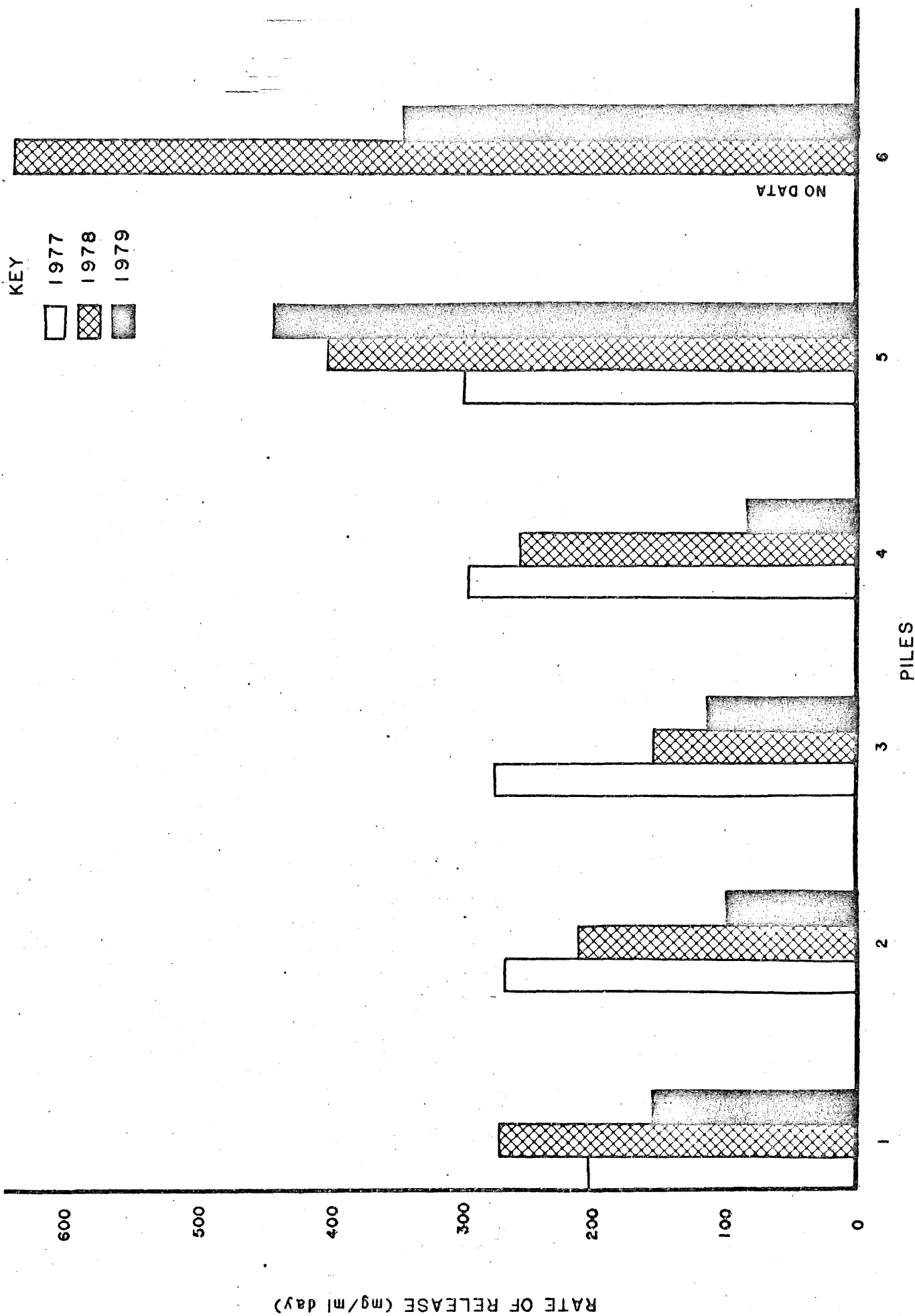


Figure 11

RATE OF RELEASE OF NICKEL

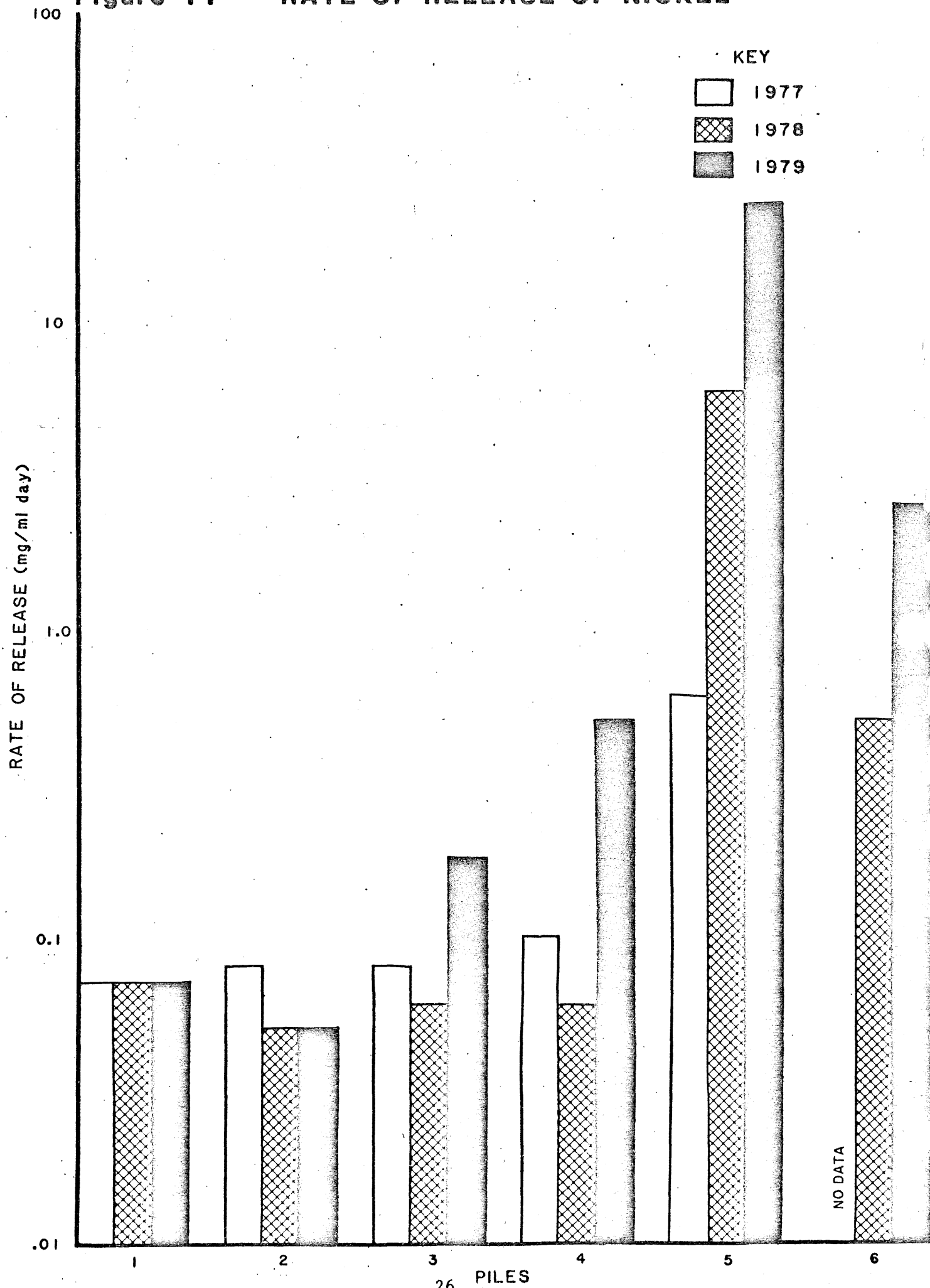


Figure 12

RATE OF RELEASE OF COPPER

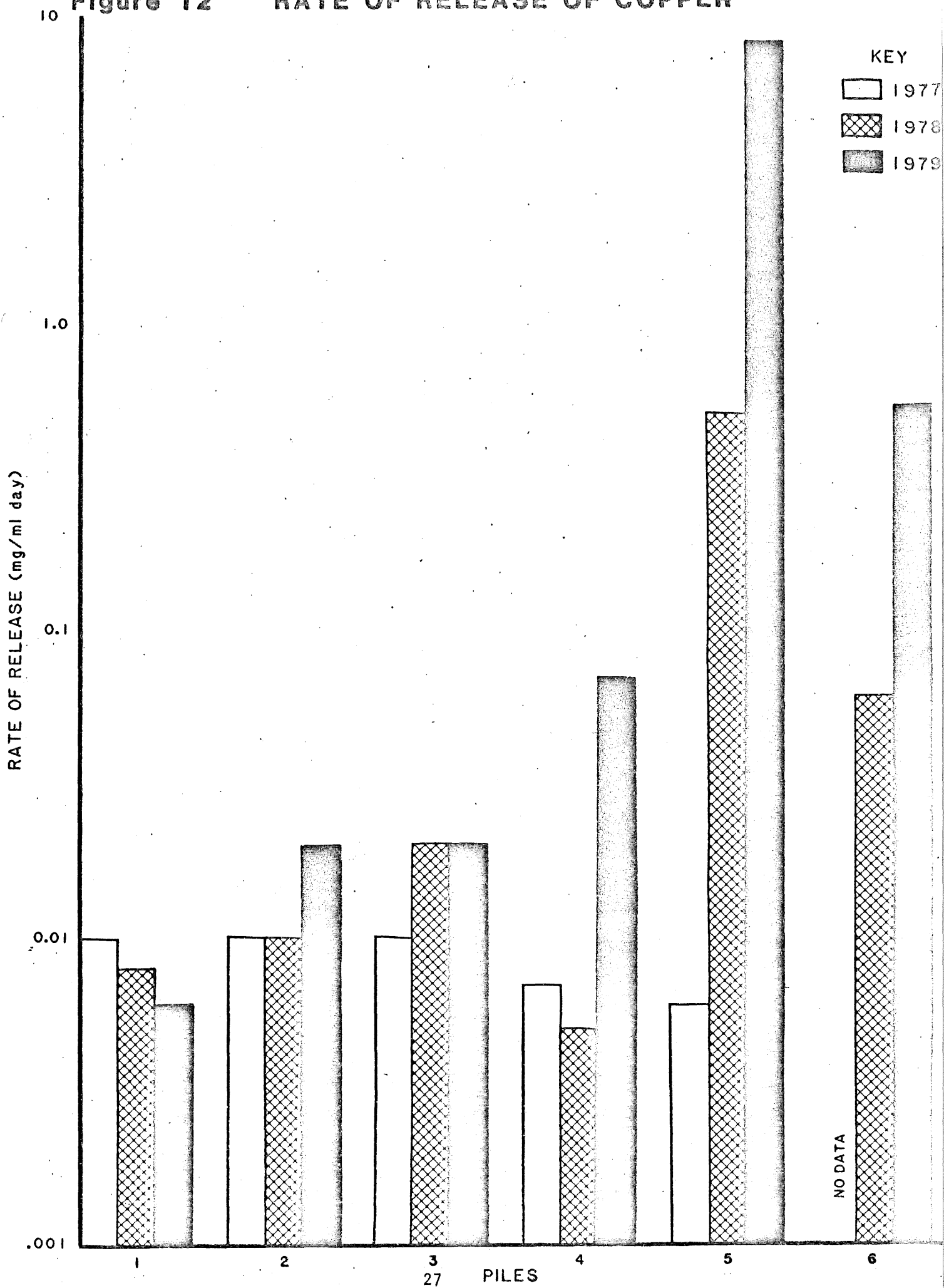


Figure 13

RATE OF RELEASE OF ZINC

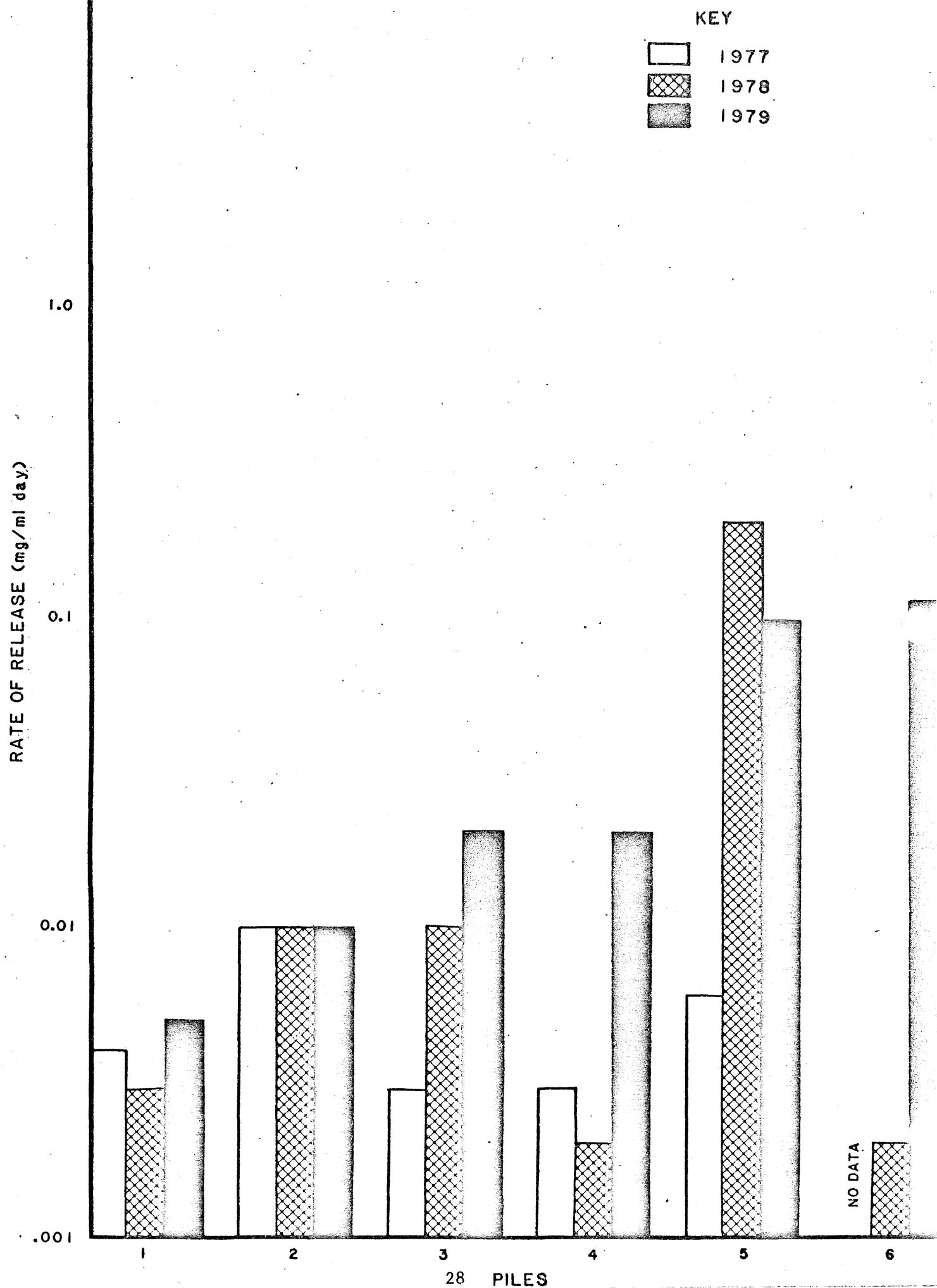
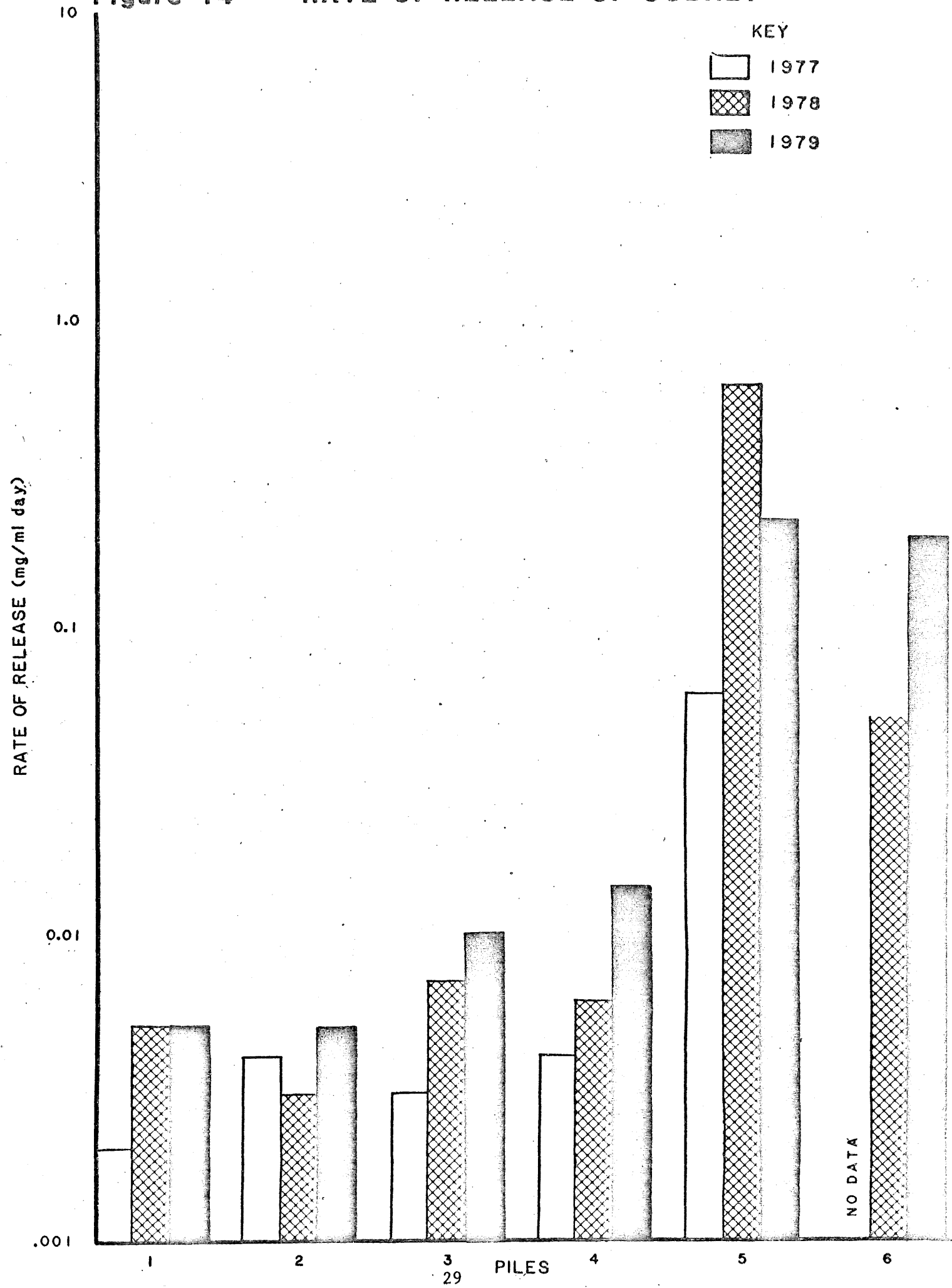


Figure 14

RATE OF RELEASE OF COBALT



DISCUSSION

Flow

Overall runoff percentages decreased from 1978 to 1979 (Figure 6).

The largest decrease occurred in pile 4, with runoff percentage decreasing from 50 to 35 percent. FL4 exhibits less base flow than the other test piles (Appendix II) and there were 153 days (59%) without flow. It is possible that a hole has developed in the hypalon liner, which permits water to escape. The hourly hydrographs from individual rain storms are being examined to determine if this hypothesis is valid.

The overall decrease in percent runoff can be attributed to the difference in rain patterns. (Figure 15) In 1978 there were a total of six storms where the rainfall exceeded 1.2 in., while there were none in 1979. In July and August of 1978, large flows (peak flows > 4200 liters/day) resulted from five rain storms greater than 1.1 in. In 1979 rain storms were smaller and so summer runoff peaks were also smaller. (Figure 15, Table IX).

The monthly runoff results are shown in Figures 16 and 17. In 1978 rainfall exceeded evaporation in both July and August; rainfall for each month was greater than 5 inches. In 1979, July and August were much drier (< 3 inches per month) and evaporation exceeded precipitation.

In 1978, a 28% reduction in runoff was obtained with the revegetated topsoil cover but no reduction was obtained with the revegetated glacial outwash cover (Figure 6). Biomass measurements (Table X) indicate that there was four times more biomass on the topsoil pile than on the outwash soil.

Assuming a transpiration ratio of 600kg of water per one kg dry weight organic matter produced (Wisler and Brater, 1959) a reduction of 55,000 liters of water is predicted for the topsoil. The actual observed reduction was 26,000 liters, or about one-half of the predicted value.

Figure 15

STORM SIZE COMPARISON (IN INCHES)

1978 AND 1979

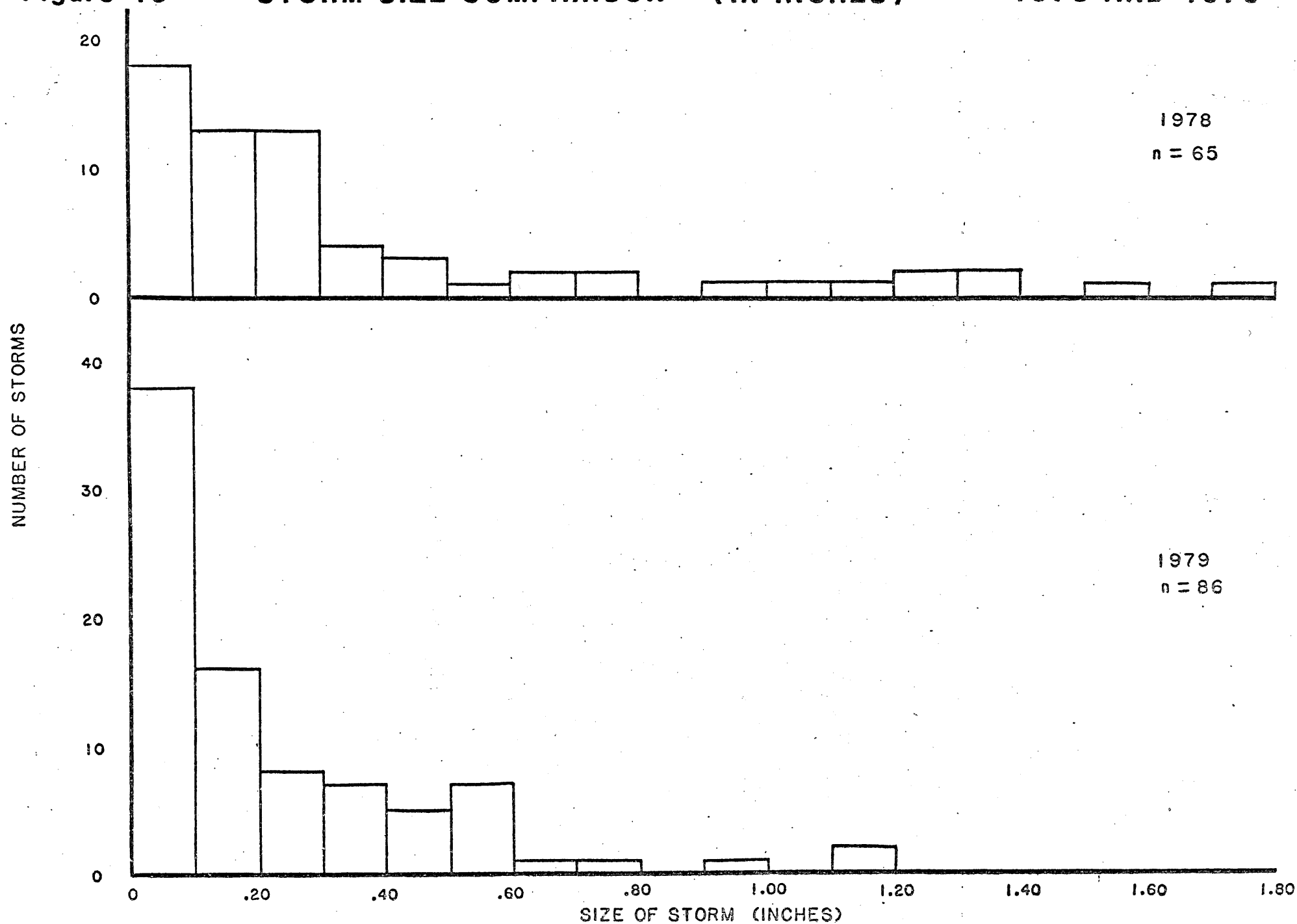


TABLE IX

PEAK FLOWS

Year	Number of days when flow exceeded 5000 l/day	Maximum Peak Flow liters/day	Pile
1978	15	8694	4
1979	2	5332	4

Figure 16

MONTHLY RUNOFF PERCENTAGES AMAX TEST PILES, 1978

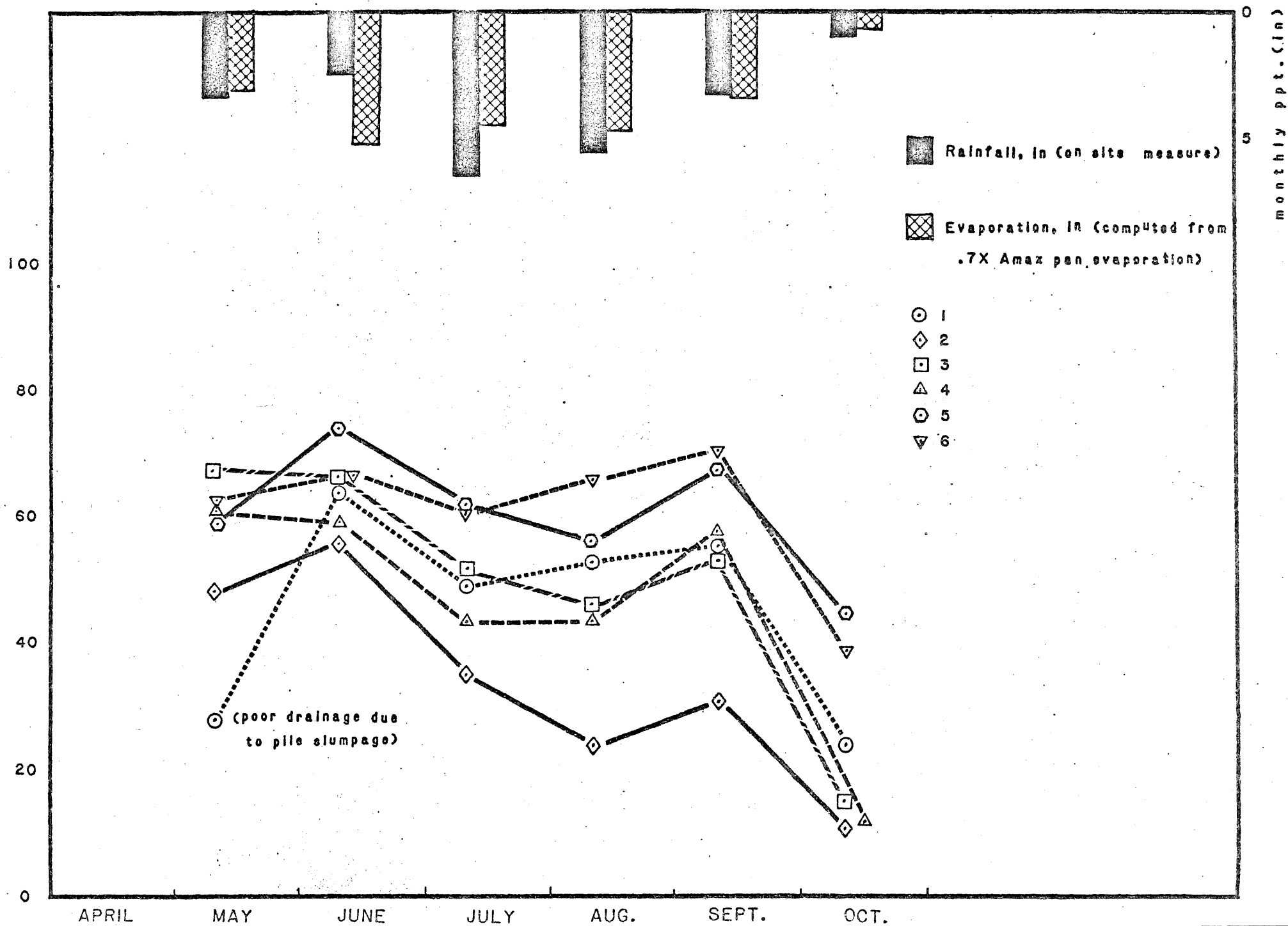


Figure 17 MONTHLY RUNOFF PERCENTAGES AMAX TEST PILES, 1979

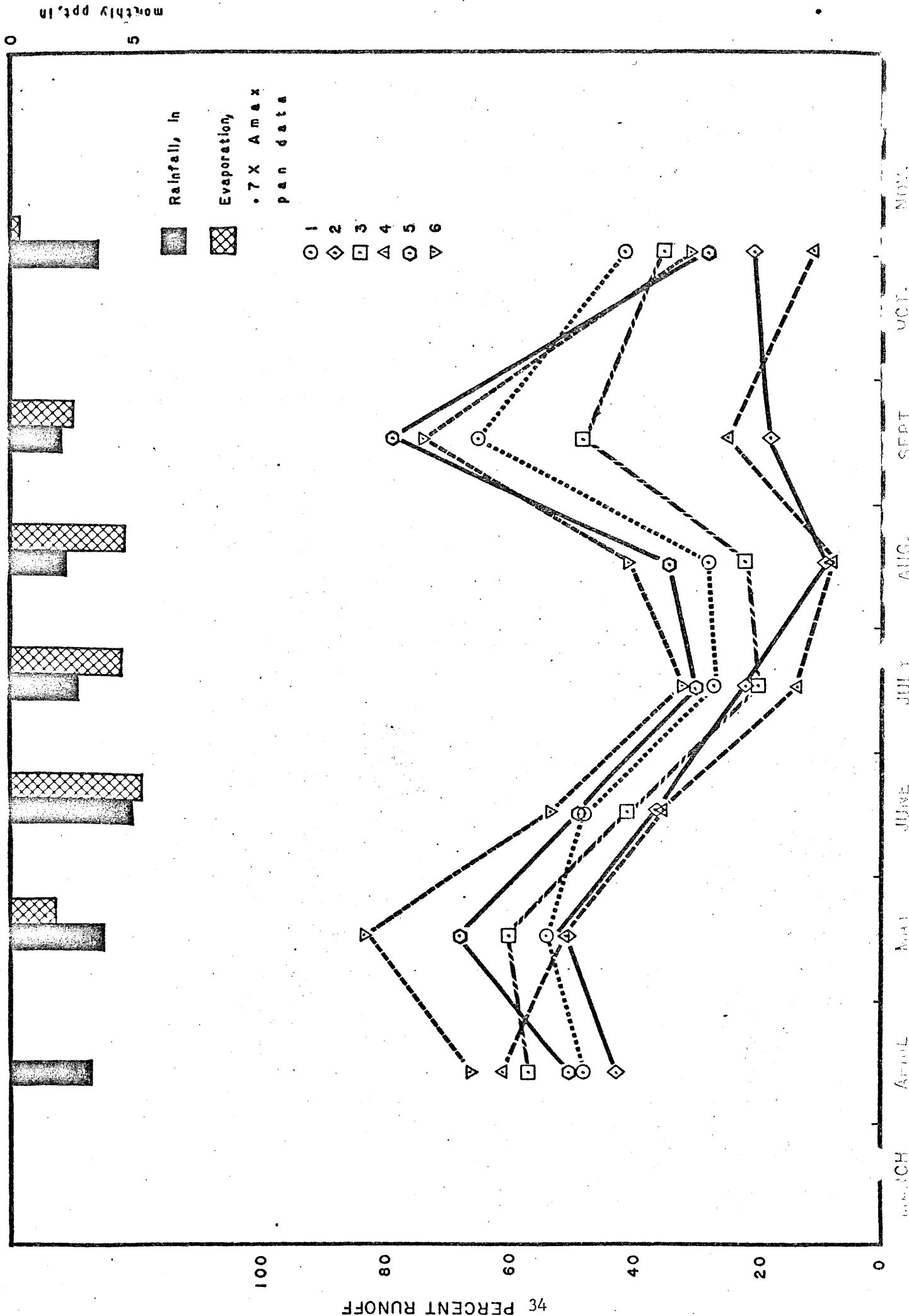


TABLE X

BIOMASS

Year	Mean Biomass (gms dry wgt/.065m ²) ³			
	Pile 2 Topsoil	Pile 3 Glacial Outwash	Pile 5 Glacial Outwash	Dike Glacial Till
1978 ¹	14.13	3.74	3.76	6.15
1979 ²	6.51*	1.88	2.18	3.94

*partial sample

¹1978 data included a large crop of volunteer oats which were present in the mulch.

²Heavy feeding by grasshoppers in late summer may have reduced biomass.

³To convert table values to lbs/acre, multiply table value by 136.

In 1979, the topsoil yielded 24% less water than the control pile FL 1 and the outwash pile FL 3. The drift piles FL 5 and 6 continued to yield more water than the shaft piles. The control pile FL 6 yielded 30% more water than FL 1 in 1978 and 29% in 1979.

There was a reduction in flow for FL 5 relative to the control FL 6, between 1978 and 1979. In 1978 FL5 only yielded 3% less than FL 6, while in 1979 a difference of 12% was observed. Biomass measurements (Table X) indicate that there was less material on the pile in 1979 than 1978. The reason for this decreased flow is not known.

Water Quality

The general trend in the water quality data is a decrease in the mean pH and a corresponding increase in trace metal concentrations over the two years of data.

Median pH values for FL 1-4 increased between 1977 and 1978, but decreased between 1978 and 1979. For FL 5 and 6, pH has continually declined.

Alkalinity shows a continued decrease for all piles, decreasing from around 70 to 20 for FL 1-4. The alkalinity in FL 5 and FL 6 has decreased to 0.

Trace metal concentrations are highly pH dependent, increasing as pH decreases. This trend is very apparent for FL 5 and 6 and is also seen for FL 3 in 1979. FL 2 copper concentrations have increased, presumably due to increased mobility caused by a higher concentration of dissolved organic carbon. Median metal values at FL 1 and 4 do not show any strong trends, although several samples with metal concentrations ($\text{Ni} > 4 \text{ mg/l}$) were collected at FL 4. Sulfate concentration only increased substantially in FL 5, from a mean of 1262 mg/l in 1978 to 2567 mg/l in 1979. A small increase (602 to 684 mg/l) was observed in FL 3 but SO_4 concentrations decreased from 15 to 30% in all other piles. Chloride and nitrate are not present in the gabbro to any large extent, and the major source of these parameters is the residual water on the rock when it was stockpiled.

The constant decline in their concentrations results from a continual washing off of the rock surfaces. Additional analysis of the chloride data is given in Appendix XIV.

The water quality data was analyzed to determine its potential for toxicity to aquatic organisms. Lind, Alto and Chatterton (1978) developed four predictive equations for acute copper and nickel toxicity to the fathead minnow and *Daphnia Pulicaria*:

I. Acute Copper Toxicity

A. Fathead minnow

$$\log 96 \text{ hr LC50} = 1.37 + 1.20 \log \text{TOC}; R^2 = .957$$

B. *Daphnia Pulicaria*

$$\log 48 \text{ hr. LC50} = .301 + 1.33 \log \text{TOC}; R^2 = .925$$

II. Acute Nickel Toxicity

A. Fathead minnow

$$\log 96 \text{ hr. LC50} = 1.95 + 1.05 \log \text{hardness}; R^2 = .707$$

B. *Daphnia Pulicaria*

$$\log 48 \text{ hr. LC50} = 2.07 + .710 \log \text{hardness}; R^2 = .705$$

The Regional Copper-Nickel Study (1980) developed the concept of the copper equivalent unit (CEU):

$$\text{CEU } (\mu\text{g/l}) = \text{Cu} + \text{Co} + .1 + \text{Ni} + .1\text{Zn}$$

where if

CEU = 0-5: no effect
5-30: low probability of measurable effect
30-100: probable chronic
100-600: potential acute
>600 : definitely acute

Median, minimum and maximum concentrations for each pile were selected and used to predict LC50's and compute CEU. (Figure 18,19, Appendix VIII)

The LC50's indicate that for nickel only the leachate from pile 5 exceeds the

Figure 18 ACUTE TOXICITY OF NICKEL (1979)

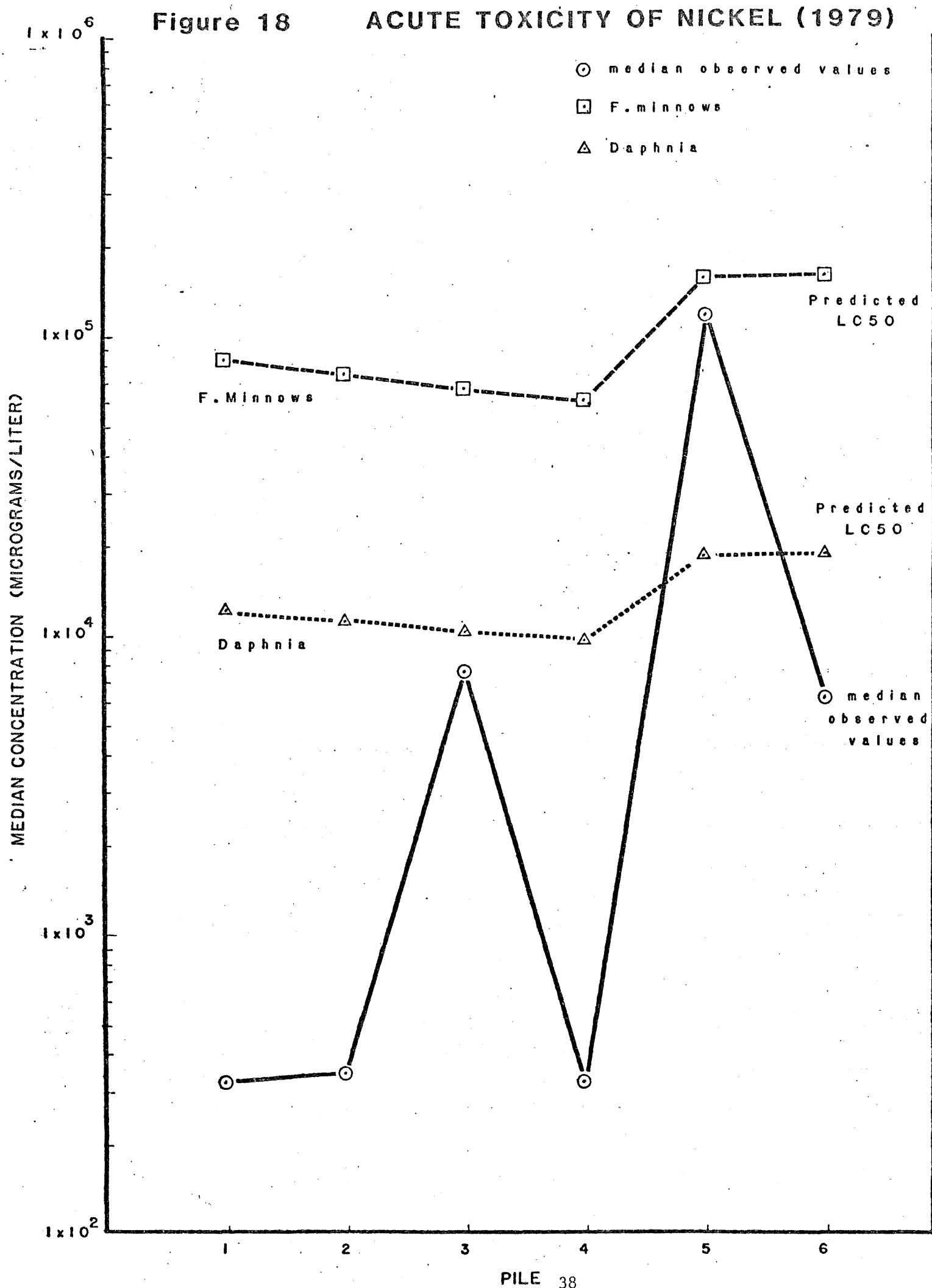
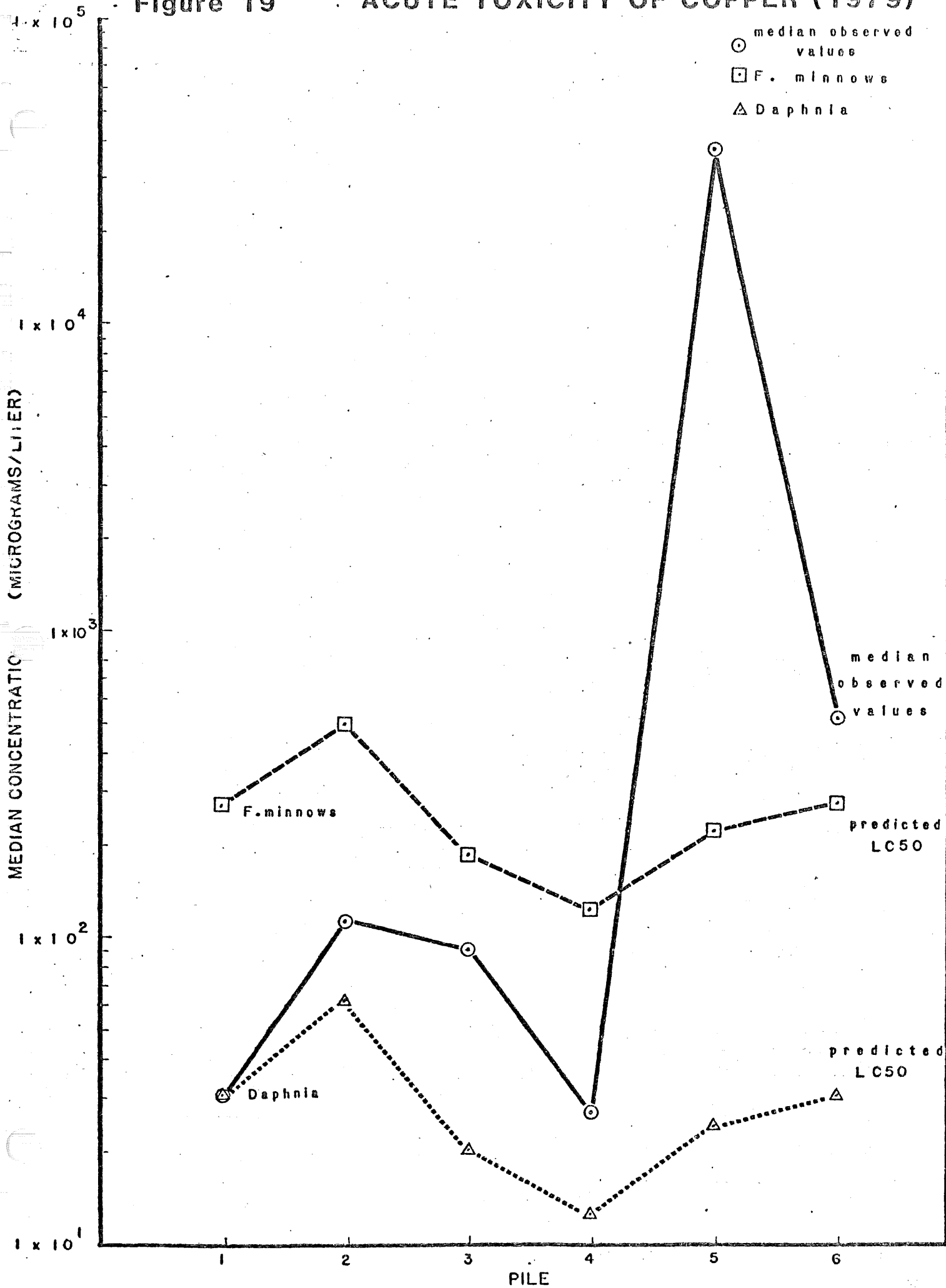


Figure 19

ACUTE TOXICITY OF COPPER (1979)



predicted LC50 values. (The low pH from this pile would be acutely toxic to both organisms). For copper, the leachate generally exceeds the LC50 for Daphnia, but only do FL 5 and 6 exceed the LC50 for the fathead minnow.

Lind et al found that in his tests with actual leachate, that his models tended to overpredict toxicity; the leachate was less acutely toxic than predicted. One possible problem is that none of his experiments were conducted in waters with hardness values as high as the leachate solutions. His maximum hardness value was 200 mg/l as CaCO_3 . The median values in the leachate range from 700 to 3000 mg/l as CaCO_3 . Therefore, the regression equation is being used beyond the range for which it was developed. High hardness values may also reduce the toxicity of copper (Lind, et al 1978). Only the organic carbon concentration was used to predict the copper LC50's.

The CEU calculations (Figure 20 and Appendix VIII) indicate that the leachate from piles 1 through 4 generally is in the range of probable chronic to potentially acute effects. The leachates from FL 5 and 6 are in the range of definitely acute effects. Using the CEU method, the order of leachate toxicity based on the median concentration values is

$$5 >> 6 >> 3 > 2 > 4 \approx 1$$

The prediction is that the leachate from the topsoil pile FL 2 is potentially more toxic than the leachate from the uncovered control piles, FL 1 and 4. This is due to the higher copper concentration in the leachate from FL 2; 65% of the predicted toxicity is due to copper, while for piles 1, 3, and 4 copper only accounts for around 35% of the toxicity. (Figure 21)

The mean concentration of dissolved organic carbon in FL 2 is approximately $1\frac{1}{2}$ times that of FL 1 and 3 times that of FL 4. The ability of organic compounds to complex copper is well documented and leaching experiments by Lapakko (Lapakko, (1980)) Eger and Lapakko (1980), demonstrated an increase in mobility when organic compounds were added to the solution. It is likely that the

COPPER EQUIVALENT UNITS (CEU) $\mu\text{g/l}$

FIGURE 20. COPPER EQUIVALENT UNITS, 1979

57,439

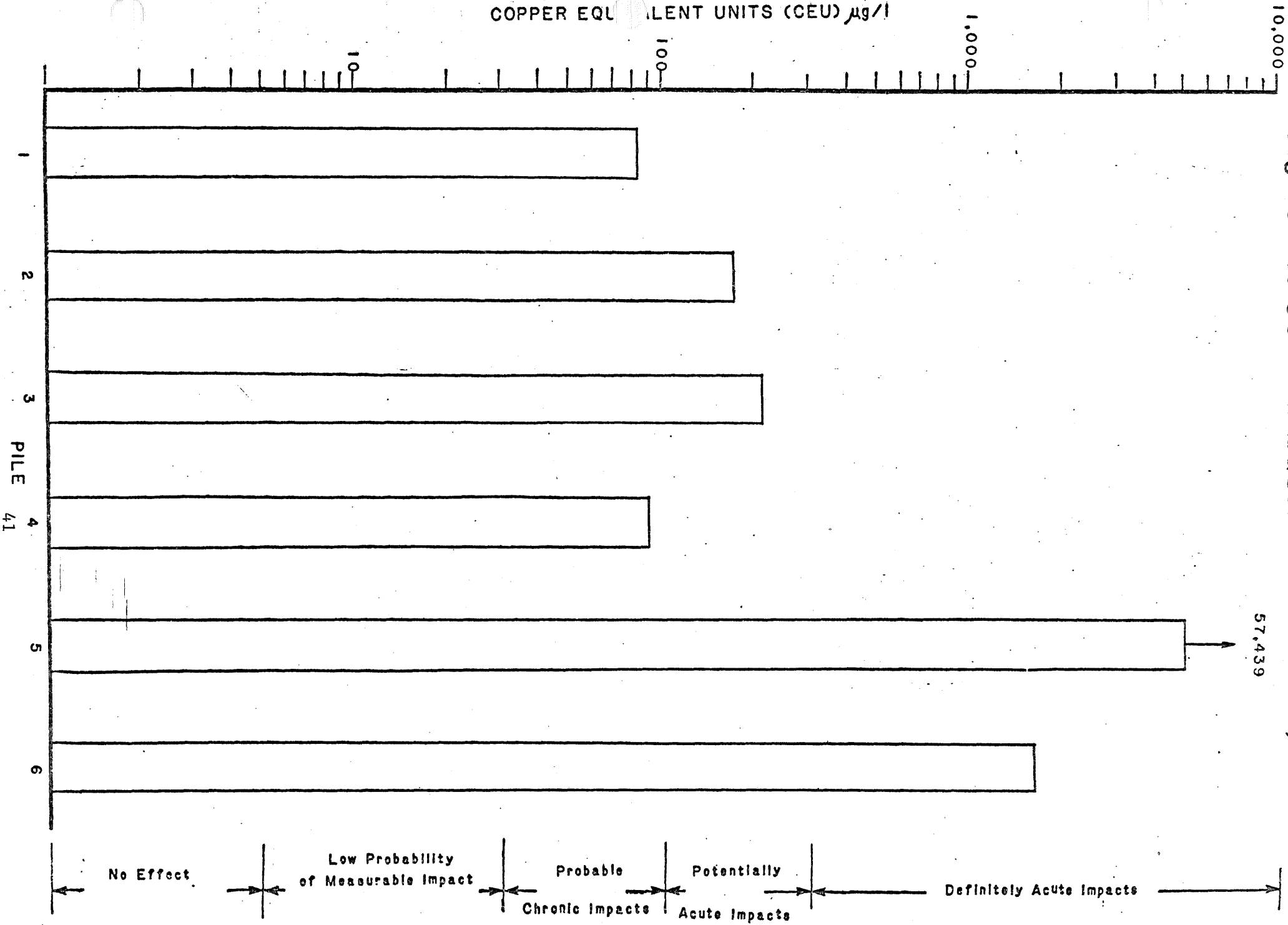
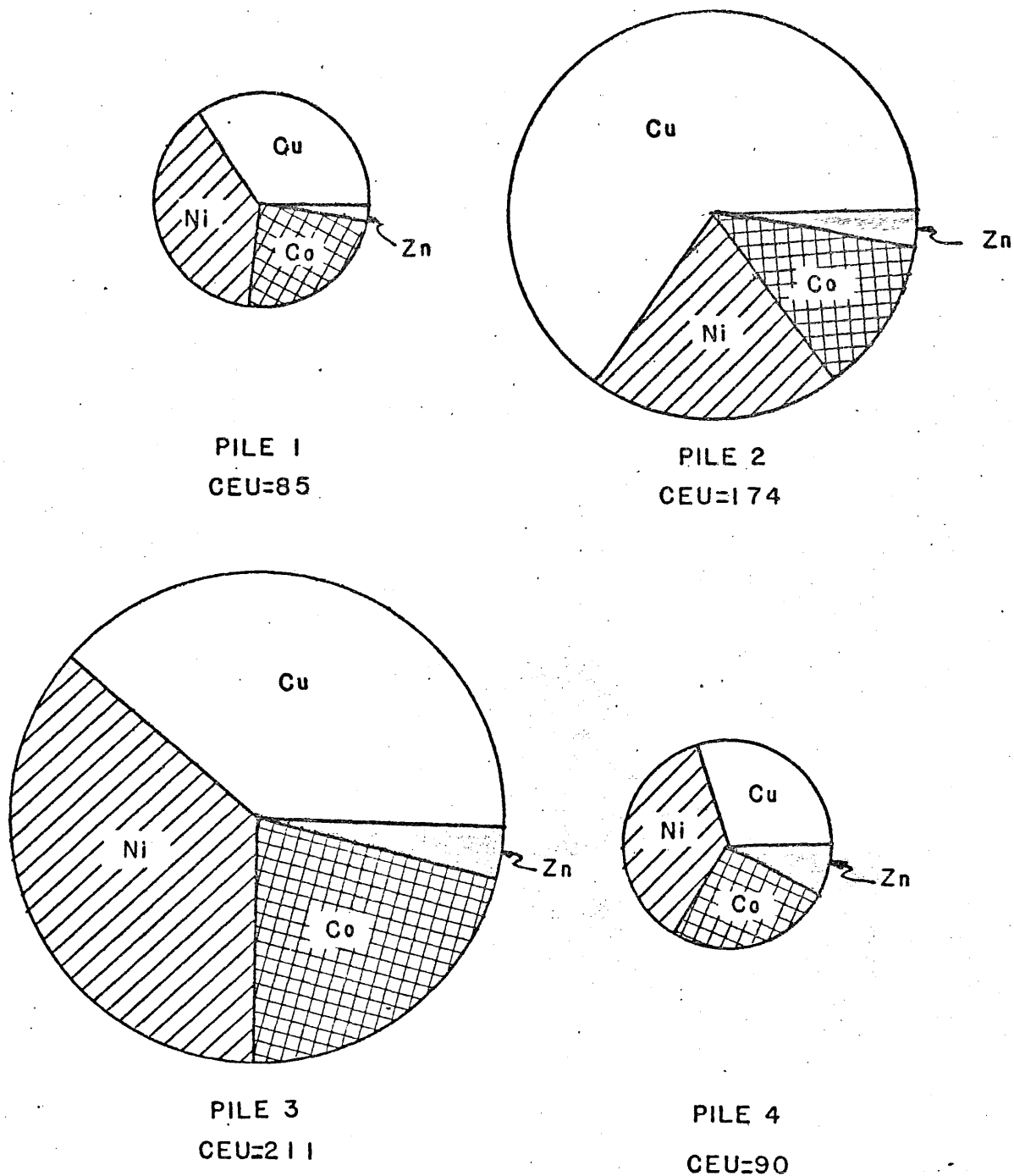


Figure 21.

DISTRIBUTION OF COPPER EQUIVALENT UNITS



Scale:

1 cm represents 28.2 CEU

increased copper is a result of the increased concentration of organic compounds in the runoff.

MASS RELEASE

The rate of mass release (Figures 7-14) normalizes for test pile size and length of season and as a result can be used for comparing the test piles

Sulfate

The rate of sulfate release decreased in all piles except FL 5. The increased sulfate release could be caused by the low pH (3.2 to 3.5) or the action of sulfide oxidizing bacteria. A preliminary sample indicated the presence of *Thiobacillus ferrooxidans* in the runoff from FL 5. FL2 released less sulfate than FL 1 and FL 4 in 1978, and less than FL 1 in 1979. The low sulfate release from FL 4 in 1979 may be the result of lost flow through a hole in the hypalon liner (see flow discussion). FL 3 released less sulfate than FL 2 in 1978, but a slightly greater amount in 1979.

The data suggests that the revegetated topsoil cover has decreased the total amount of sulfate released relative to the control piles but additional analyses is needed to explain the low sulfate release from FL 4 in 1979.

Copper

An increase in the release of copper was observed for all piles except FL 1 which decreased, and FL 3 which remained the same. Declining pH in FL 6 and a sustained low pH in FL 5 explain the increased release observed in those piles. The large increase for FL 4 is the result of the large mass released during the early part of spring runoff and the summer storm of July 30. Concentrations of copper in these three samples were about two orders of magnitude higher than all of the other copper data. The increase in FL 2 is apparently due to the increased mobility of the copper which has resulted from the increase in organic carbon in solution.

Copper release is slowest from the control, uncovered pile FL 1. The runoff from this pile has a low concentration of organic carbon (median = 7.8) and elevated pH value (median = 7.35). Both conditions reduce copper mobility.

Nickel

Nickel release increased from all piles except FL 1 and 2, where the rate remained unchanged. The large increase from FL 4 resulted from the large mass released during spring runoff and the large summer storm of July 30. The pH began to decline in FL 3 with resulting increase in nickel release. The lowest nickel release is from the topsoil covered pile FL 2, which is the result of the smaller runoff volume.

Spring Runoff

Spring runoff can be a critical period for aquatic organisms, particularly if the concentrations of trace metals are increased. During spring runoff, pH and alkalinity are low, thereby increasing the mobility and toxicity of trace metals in solution. Many fish species spawn during the spring and the eggs and larvae are damaged at lower metal concentrations than the adults. Invertebrates are most susceptible when they are emerging and for many species this occurs in the spring (Lind, Halpern, Johnson 1978).

Spring runoff contributed from 29-46% of the total yearly outflow. If a pile remains in a constant condition for the year (eg. pH constant) and there are no chemical transport limitations then the percentage of mass release during spring runoff should equal the percentage of water released during that time period. (Figure 22-28) This is observed for FL 5, Figure 27. pH was in the range 3.6 to 3.2 for the entire season. In this pH range, complete copper and nickel mobility are predicted. For piles 3 and 6 there was a pH decrease during the year which resulted in increasing metal mobility. As a result, a smaller percentage of the mass was released during spring runoff.

Figure 22 MASS RELEASED DURING SPRING RUNOFF FL-1 1979

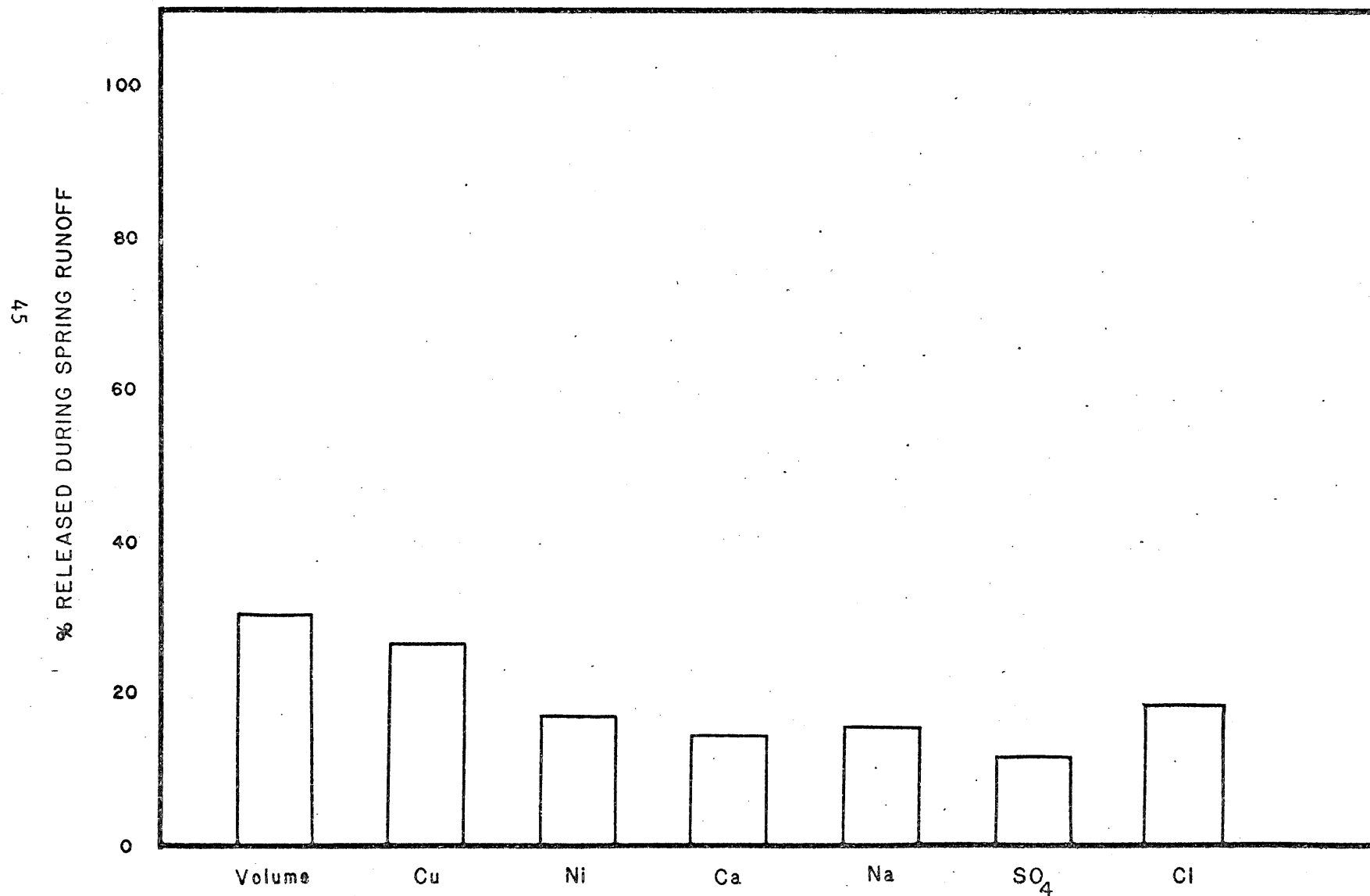


Figure 23 MASS RELEASED DURING SPRING RUNOFF FL-2 1979

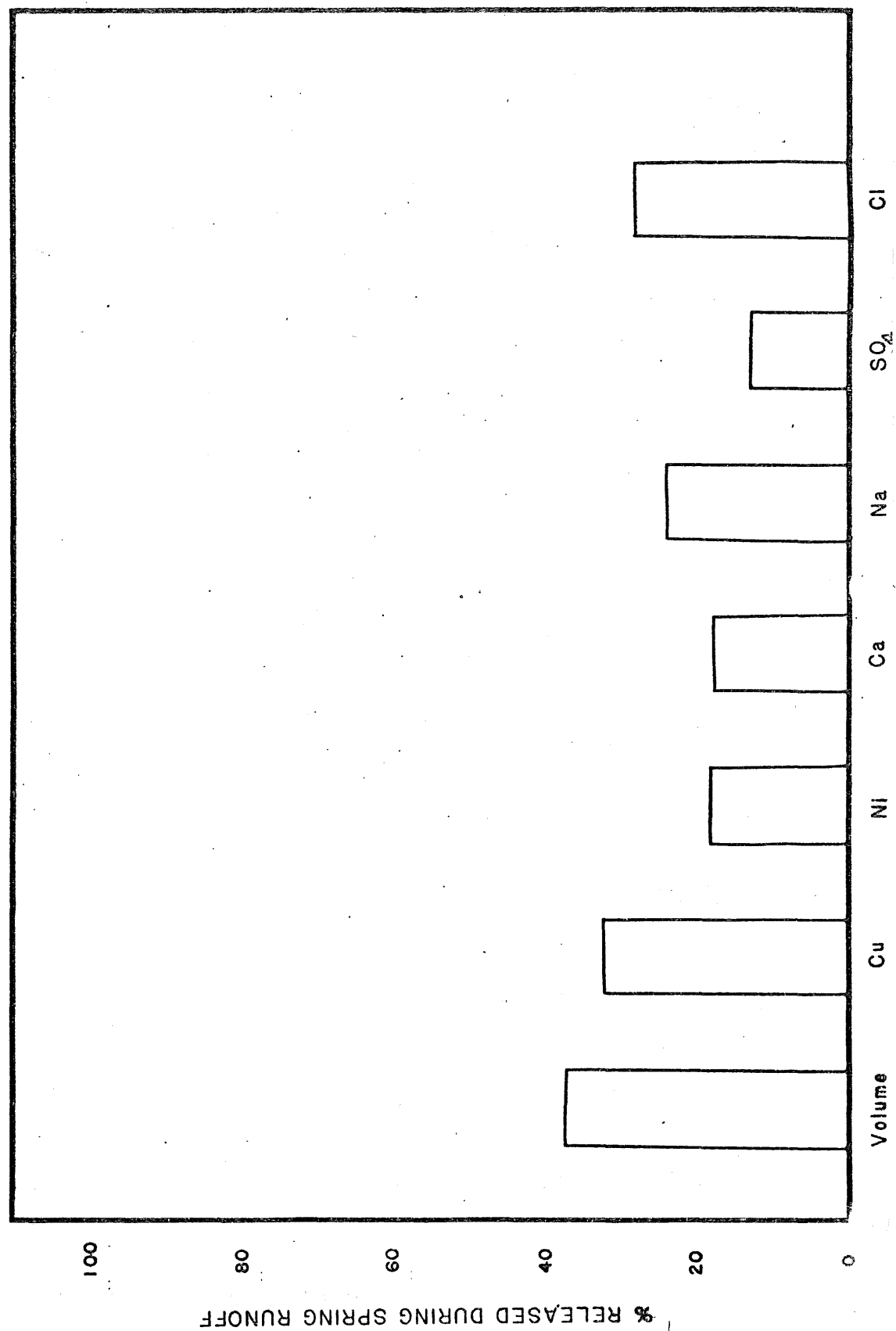


Figure 24 MASS RELEASED DURING SPRING RUNOFF FL-3 1979

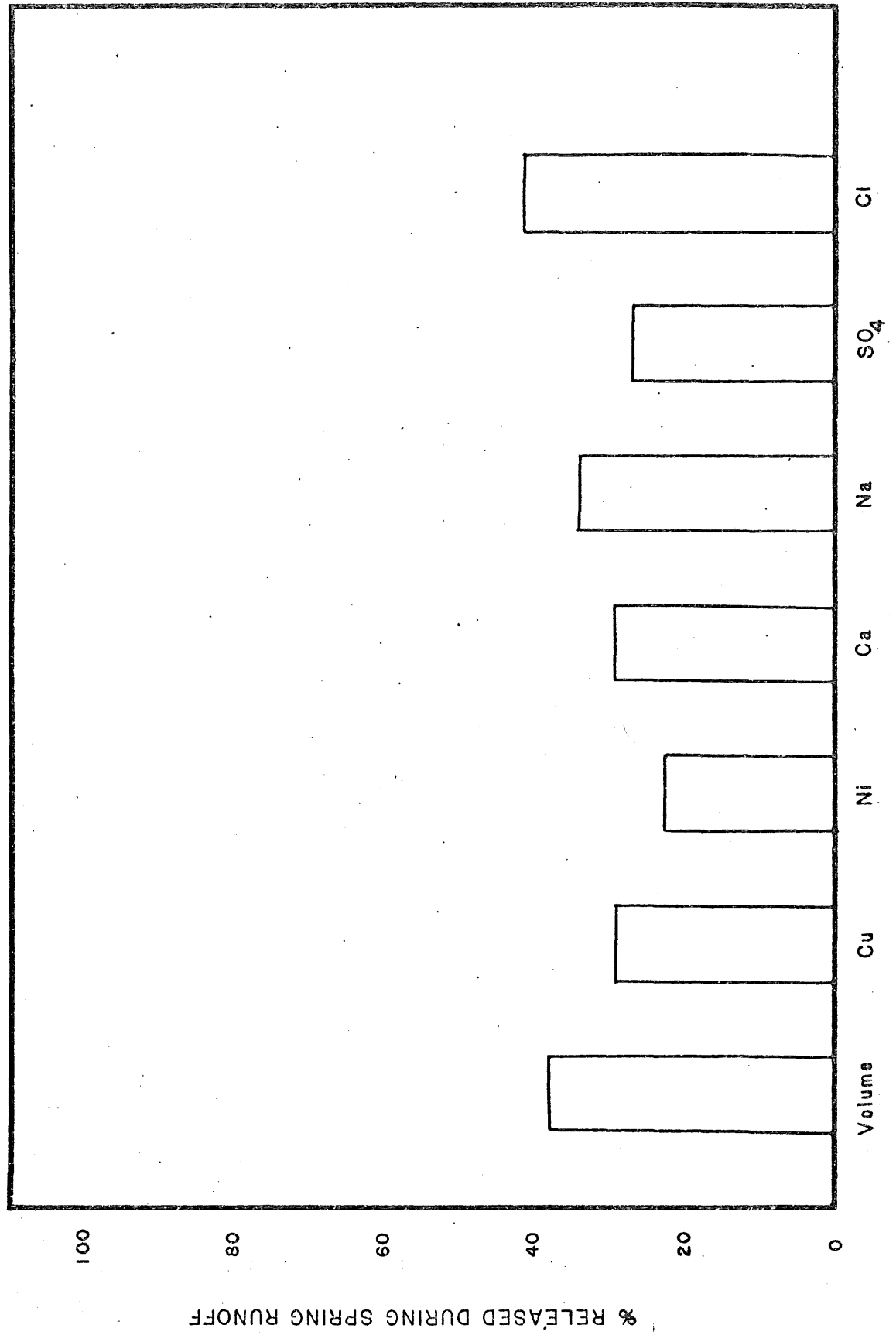


Figure 25 MASS RELEASED DURING SPRING RUNOFF FL-4 1979

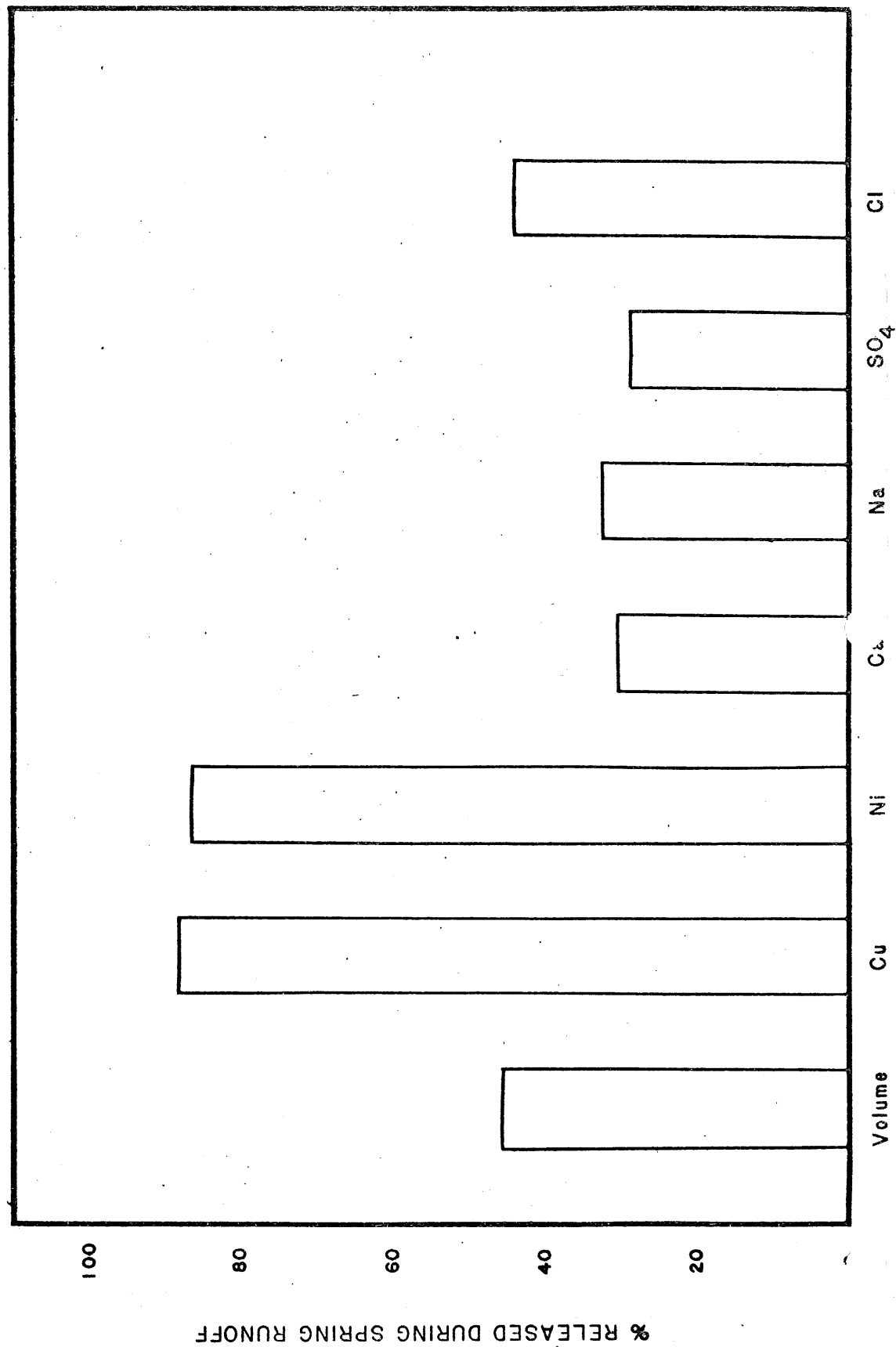


Figure 26 MASS RELEASED DURING SPRING RUNOFF FL-5 1979

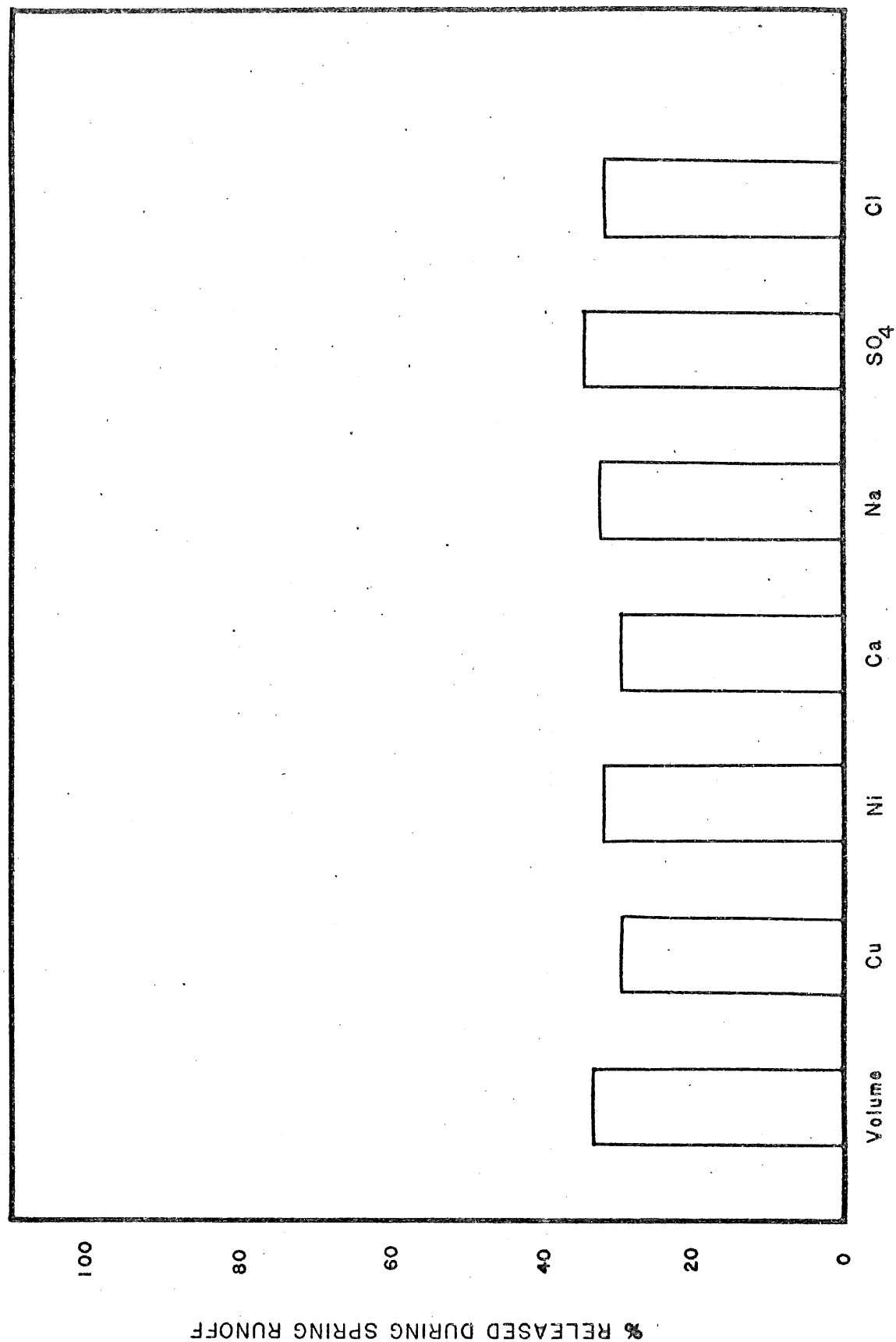
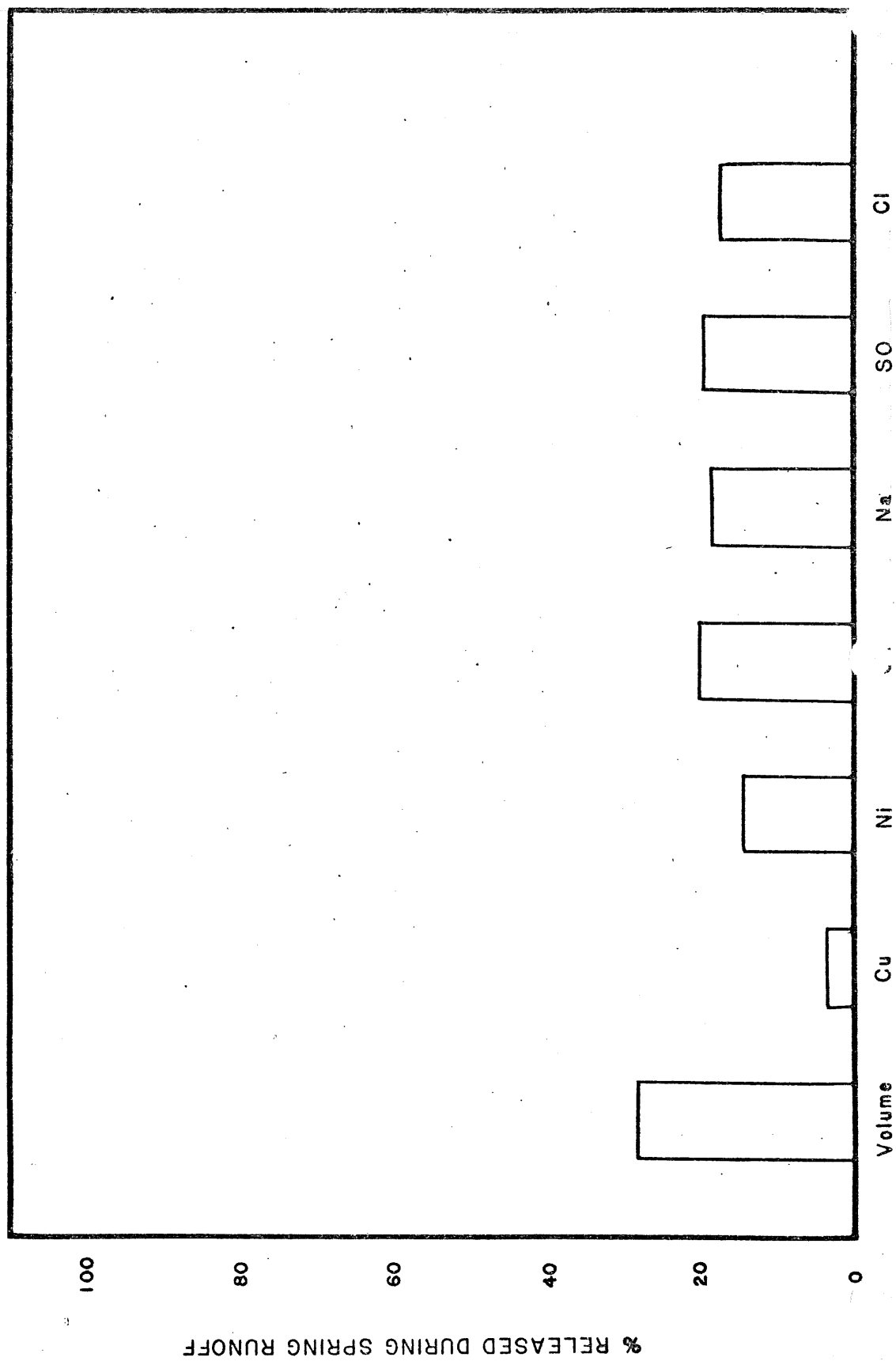


Figure 27 MASS RELEASED DURING SPRING RUNOFF FL-6 1979



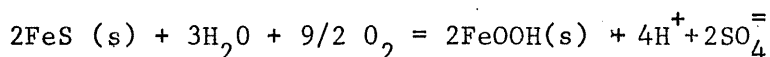
Nickel concentrations increased toward fall in runoff from FL 1 and 2, but pH did not show a trend. More mass was removed later in the season.

For FL 4 greater than 85% of the total mass was transported in the spring runoff. This was the result of the anomalously high concentrations of copper and nickel in the first two spring runoff samples. Careful monitoring of the 1980 runoff will be conducted to see if this pattern is repeated.

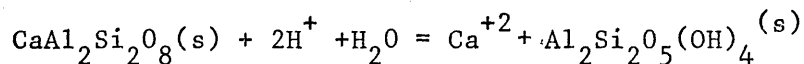
Acid Production

When a pile produces acid leachate, trace metal concentration increases and the mass release increases several orders of magnitude. (Figure 28) The rates of release of copper and nickel from FL 5 are about three orders of magnitude greater than FL 1. (Figures 11-14) Median metal concentration increases as median pH decreases.

To produce acid leachate, the rate of acid generation, which is controlled by the oxidation of the iron sulfides:



must exceed the rate of acid consumption, which for the gabbro is controlled by the silicate minerals



The larger the concentration of iron sulfides, the faster the rate of acid generation and the higher the probability of producing acid leachate. Field data (Figure 29) suggest that when the percent sulfur is greater than or equal to .83% acid conditions can develop. pH did decline in FL 3 towards the end of 1979 (Appendix II), and acid conditions may develop this year.

SUMMARY

Overall runoff percentages generally decreased from 1978 to 1979, due in part to fewer large (>1.2 in) rainstorms and small (<5000l/day) runoff peaks. The revegetated topsoil cover on FL 2 has provided a 25-30% reduction in runoff volume for both years, while the glacial outwash has not been effective in

Figure 28

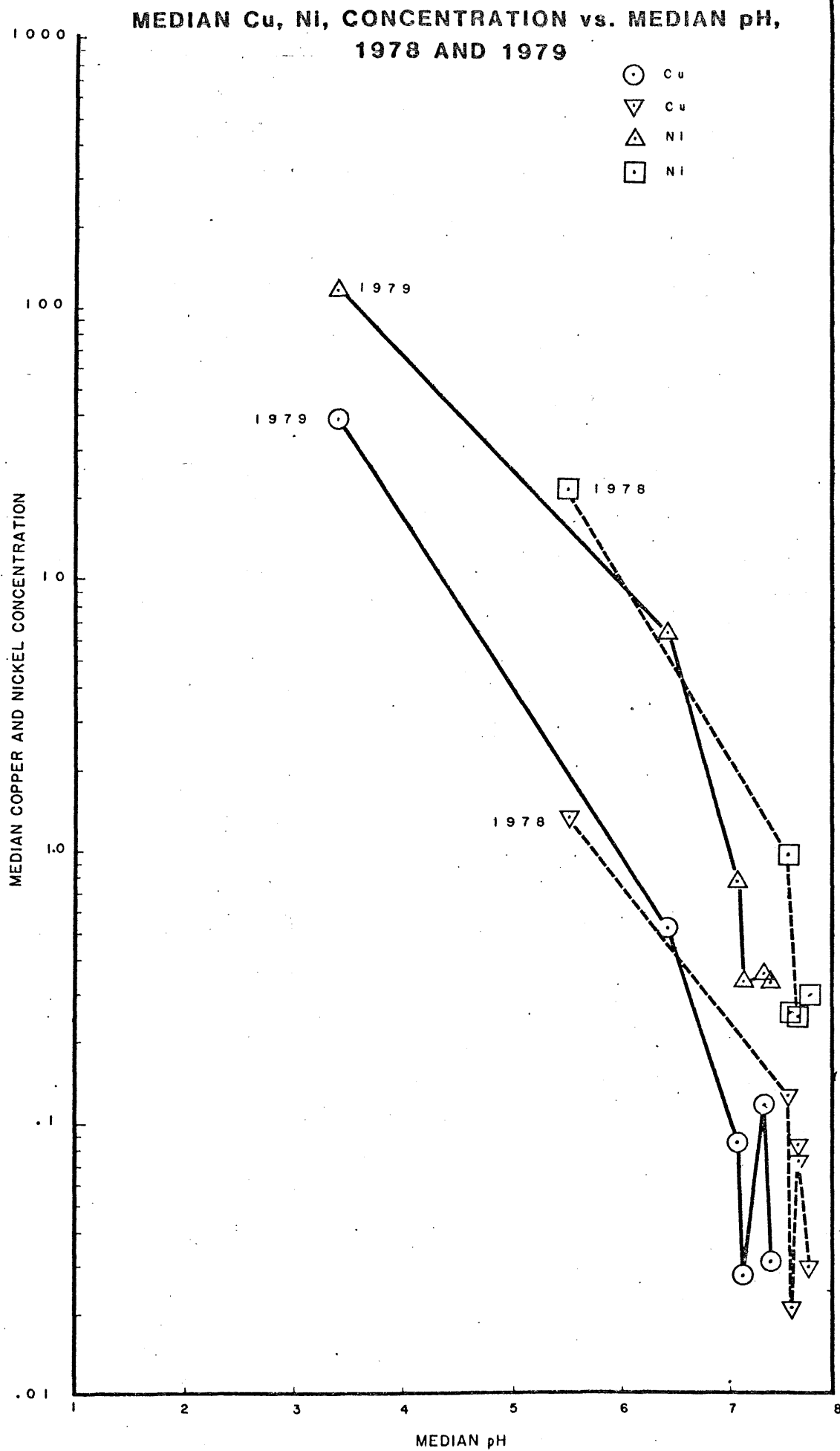
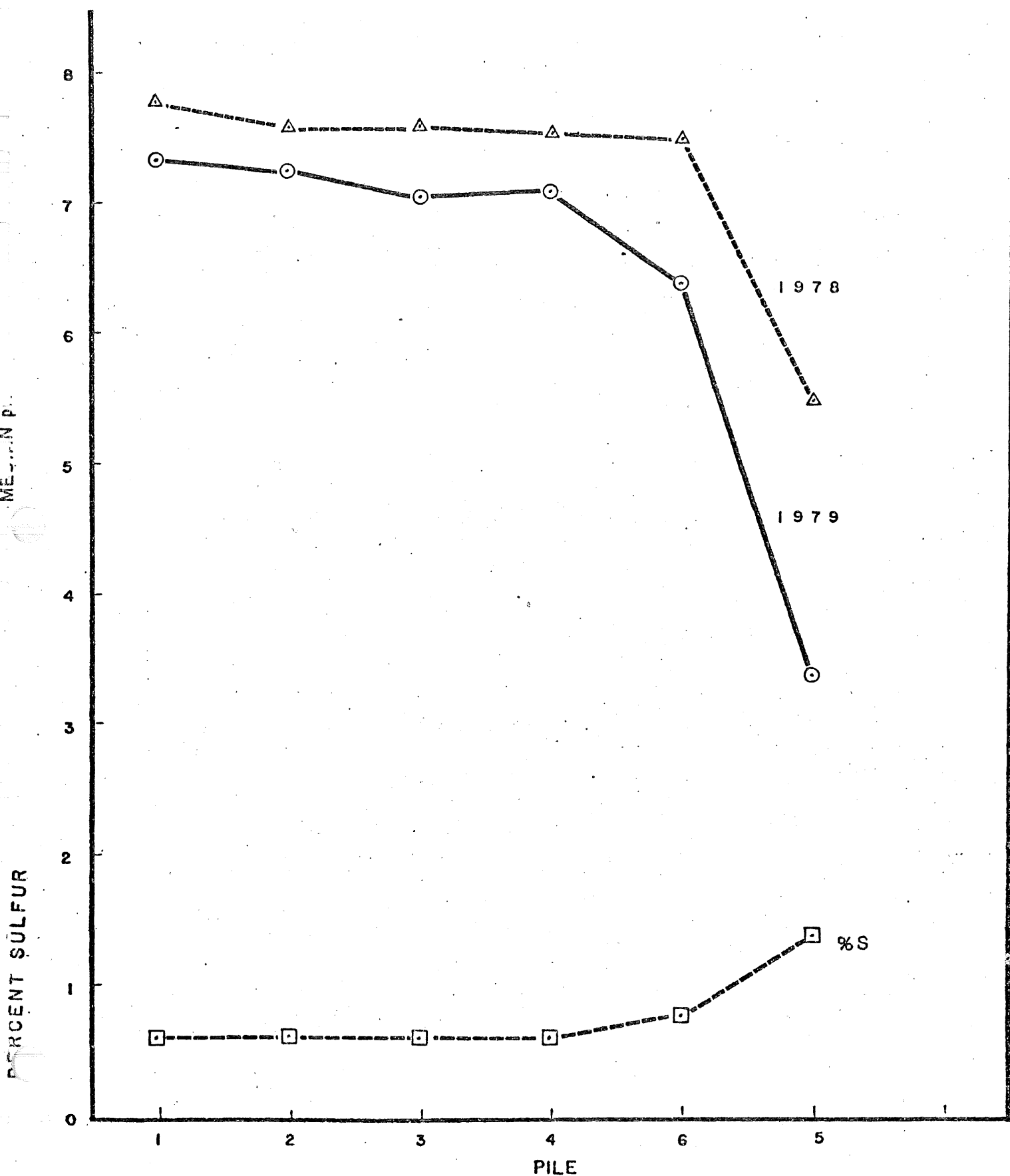


Figure 29

RELATIONSHIP BETWEEN pH AND % OF SULFUR IN PILES



reducing runoff. In 1979, FL 4 produced little or no base flow indicating that a hole may exist in the underlying hypalon liner.

pH was generally lower in 1979 than 1978, and as a result an increase in trace metal mobility was observed. FL 6, which contains .83% sulfur, began to produce acid leachate and the pH in FL 3, .6%S, began to decline in the fall, reaching 6.3 prior to freeze up. Copper concentrations increased in FL 2, probably the result of an increase in complexing organics in solution.

Toxicity calculations indicated that the leachate from all of the test piles could produce biological effects. The leachate from FL 5 and 6 is acutely toxic, due both to high trace metal content and low pH. Leachate from FL 1-4 may produce chronic effects. Ranking the toxicities of the runoff from each pile yields

5>>6>>2>3>1=4

The rate of release of trace metals generally increased as a result of declining pH, but the rate of sulfate release generally decreased. FL 2 had the lowest sulfate release indicating that this revegetated topsoil cover may be reducing the overall oxidation rate.

Spring runoff accounts for 29 to 46% of the total runoff, but for most of piles a smaller proportion of the total mass was released. Exceptions were FL 5 which released an equal percentage of mass and water, and FL 4 which released most of the trace metal mass in the first part of the runoff.

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CHAPTER 2

LABORATORY PROGRAM:

REMOVAL EXPERIMENTS

ABSTRACT

Batch reactor and column experiments were conducted to evaluate the ability of peat, tailings, and sand for removing trace metals (Cu, Ni, Co, Zn) from two types of mining stockpile runoff. One type of runoff (FL5) had trace metal concentration of 2-64 mg/l and pH 3.8, while the second (FL1) had trace metal concentrations less than 0.5 mg/l and pH 7.2. Following metal removal tests, columns were rinsed with distilled water to determine the degree of metal release. Sand was eliminated from experiments when it proved ineffective in removing metals from FL5 leachate in batch experiments.

In batch reactor experiments, peat removed metals from FL5 leachate, but released H^+ to solution. Trace metal data were fit to Langmuir equations, and the result capacities for Cu, Ni, Co, and Zn were 700, 1200, 70, and 50 $\mu\text{g/g}$ dry peat. In column tests the respective net capacities were 1300, 2500, 46, 140. Tailings were not effective in removing trace metals from FL5 leachate, but they did raise the pH slightly.

For FL1 leachate with peat, and tailings, batch data were fit to both Langmuir and Freundlich equations, but agreement was poor in both cases. The peat removed Ni from solution but released H^+ in both batch and column tests. Peat also removed Cu and released Co and Zn in batch tests while the opposite was true in column experiments. The tailings removed Ni, released Co, and had little effect on Cu, Zn, or H^+ in batch experiments. In column tests using tailings all five parameters were removed, but with the exception of Cu and H^+ , removal capacities were only 2-8% those for peat and FL1. The metal removal capacities observed for peat and FL1 were in turn lower than those observed for peat and FL5.

INTRODUCTION

Elevated concentrations of trace metals (Cu, Ni, Co, Zn) have been observed in runoff from mining stockpiles (Eger and Lapakko, 1980). Treatment of this type of runoff may be required since bioassay tests indicate that some leachate samples are toxic to laboratory test organisms (Lind et al, 1978) and the observed metals concentrations exceed proposed EPA water quality criteria (Federal Register, 1979). As a result, experiments were conducted to examine the ability of peat, tailings, and sand to remove trace metals from solution.

Four batch reactor experiments and two column tests were conducted in a joint effort by the Minnesota Department of Natural Resources (DNR) and AMAX. The isotherm experiment (Experiment 4) and the column tests were of primary importance and are discussed to a greater extent than the first three batch tests, which were of a more preliminary nature.

RELATED RESEARCH

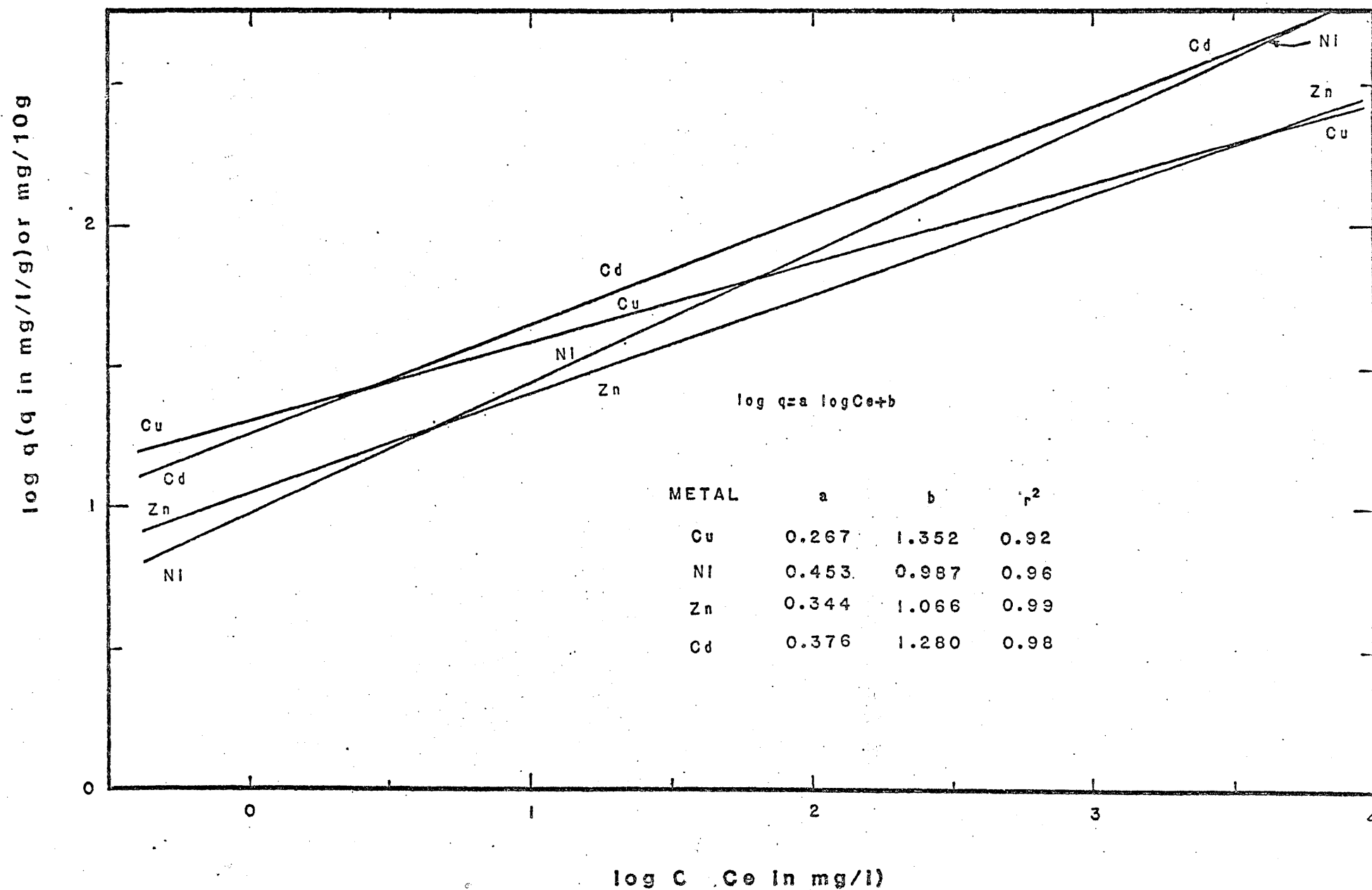
Two treatment studies were conducted in connection with the potential mining of copper and nickel in northeastern Minnesota.

Iwasaki et al., (1975) investigated the feasibility of copper and nickel removal by metal-xanthate precipitation, cementation, and adsorption onto activated carbon. Results indicated that concentrations of free copper and nickel were significantly reduced by metal-xanthate precipitation. Cementation of copper and nickel onto sponge iron appeared to be the most effective of the three methods tested. Initial metal concentrations were reduced from 10 mg l^{-1} to less than 0.01 mg l^{-1} . Activated carbon also adsorbed significant amounts of copper and nickel, but the authors felt this method was not feasible in field application due to the amount of carbon required.

Ryss and Hoffmann (1979) conducted batch reactor experiments using trace metal (Cu, Ni, Co, Zn Pb, Cd) concentrations of 5-300 ppm and five peat samples from northeastern Minnesota which were blended into a homogeneous slurry. Results for Cu, Ni, Zn and Cd were fit to Freundlich plots since Langmuir plots were not linear for any of the metals. Results for cobalt were erratic with $C_e > C_o$ in some cases, while sequestration of Pb was so great ($C_e=0$) that calculation of isotherm constants was impractical.

The ordering of the $\log q$ values for Cu, Ni, Zn and Cd was dependent on the solution concentration. In the lower concentration range, $(\text{Me})_e < 5 \text{ mg/l}$, the ordering was $\text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$, but for $5 < (\text{Me}) < 90 \text{ mg/l}$ the ordering was $\text{Cd} > \text{Cu} > \text{Ni} > \text{Zn}$ (Figure 1). Hoffmann (1980), indicated that the metal removal was probably the result of physical and chemical interaction of metals with the peat.

Figure 1. Log q vs log Ce for Freundlich Plots by Ryss and Hoffmann (1979)



Sturgess (1979) conducted a preliminary experiment using a mixture of peat and sand (111 g dry wt., 3114 g respectively) to remove metals from 1 liter of FL5 leachate ($Q \approx 0.25$ l/hr.). The initial concentrations of Cu, Ni, Co, and Zn were 66, 210, 14, and 9.9 mg/l, respectively. Following the adsorption test the column was rinsed twice with distilled water. The net removals for Cu, Ni, Co, and Zn were 0.52, 0.47, 0, and 0.028 mg/g dry peat.

EXPERIMENTAL

Experimental objectives and methods for batch reactor tests are summarized in Table 1.

Materials

A dark brown, hemic (as determined by visual inspection) peat sample was collected from the upper layer of a bog in the southwest quarter of section 28 at the Minnamax site near Babbitt. The tailings were produced in pilot plant bulk flotation processing of Minnamax shaft material at the Mineral Resource Research Center, University of Minnesota (MRRRC). Sand was collected from a borrow pit at the Minnamax site.

Leachate was collected from test stockpiles at Minnamax. Two samples, with trace metal concentrations ranging from 1 to 220 mg/l at approximately pH4, were collected from FL-5. One sample containing lower concentrations of trace metals at pH 7.2 was collected from FL-1 (Table 2).

Three types of reaction vessels were used in the batch reactor tests. Erlenmeyer flasks (250 ml) were used in Experiment 1 and 250 ml glass bottles with aluminum foil lining the metal caps were used in Experiment 2. The performance of the glass bottles was compared with 250 ml polypropylene (Nalgene) bottles in experiment 3. The polypropylene bottles were used in subsequent experiments.

Table 1. Summary of batch reactor experimental methods.

EXPT NO	SOLN/ADSRBENT	OBJECTIVES	ANALYSES	PROCEDURAL COMMENTS
1	150 ml FL5/1, 5g peat 150 ml FL5/1, 5g tailings 150 ml FL5/1g sand	Compare adsorption of Cu (22mg/l) and Ni(240mg/l) by peat, tailings, and sand at pH 4.	pH, Cu, Ni	24 hour experiment 250ml Erlenmeyer flasks as reaction vessels Eberbach horizontal shaker
2	75 ml FL5/12.5g peat 75 ml FL5/none 75 ml FL1/12.5g peat 75 ml FL1/12.5g tailings 75 ml FL/none	Determine time for adsorption reaction to reach equilibrium Quantify removal of individual metals	pH, Cu, Ni, Co, Zn, Fe, Mn	Samples withdrawn at 0.1, 26, 50, 73, 98, 170 hours. Glass reactors used. Rotating mixer.
3 62	75 ml FL5/none 75 ml FL1/peat 75 ml FL1/peat	Comparison of glass and poly- propylene reactors	pH, Cu, Zn, Fe	Samples withdrawn at 0.1, 72, 166 hrs. Rotating mixer.
4	75 ml FL5/0.25-12.5g peat 75 ml FL1/0.25-12.5g peat 75 ml FL1/0.25-12.5g tailings	Generation of isotherm data to determine the capacity of adsorbents for various metals	pH, Cu, Ni, Co, Zn, Fe, Mn, Ca, Mg, Na, K	Samples withdrawn at 72 hrs. Polypropylene reactors used. Rotating mixer.

Table 2. Composition of leachates

Parameter	Concentrations in mg/l					
	Batch Reactors			Columns		Sturgess, 1979
	FL-5 ^a	FL-5	FL-1	FL-5	FL-1	
Collection Date		7/30/79	8/22/79			
pH	4.0	3.8	7.2	3.8	7.2	3.2-3.4
Cu	22.35	5.80	0.05	11.5	0.060	66
Ni	242	30.1	0.52	64	0.470	210
Co		2.39	0.05	4.36	0.040	14
Zn		1.07	0.02	2.30	0.040	9.9
Fe		0.35	0.02			
Mn		2.74	0.13			
Ca		152	484			
Mg		42.8	38.8			
Na		42.3	213.3			
K		8.2	49.3			
SO ₄						

^aused for experiment 1 only

Mixing was achieved with an Eberbach horizontal shaker in Experiment 1 and with a horizontally rotating mixer (designed by M. Semmens, University of Minnesota) in subsequent batch reactor tests. Samples were filtered through 0.45µm Millipore filters using a Millipore filter unit. An Orion Model 610A/ digital ionalyser was used for pH measurements.

Material Preparation

Sand and tailings were oven dried at 100°C and sieved. The moisture content was determined. In Experiment 1 particle diameter ranged from 20µm to 1000µm and in subsequent experiments, the particle diameter of tailings was greater than 74µm. Peat was similarly dried and its moisture content determined (88%).

Permeabilities for tailings and the peat sand mixture were determined by the Minnesota Department of Transportation. The permeabilities of the tailings at 1.6 and 1.7 g/cm³ were 8.4×10^{-4} cm/s at 20°C. The permeability of the peat-sand mixture was 5.0×10^{-4} cm/s. (at 1.04 g/cm³).

Experimental Procedure

In Experiment 1 five duplicate samples of sand (1g), tailings (1g, 5g) and peat (1g, 2g) were placed into separate Erlenmeyer flasks. To each flask 150 ml of FL5 was added. As controls 150 ml of FL5 and 150 ml of distilled deionized water were added to separate flasks containing no solids. The pH of all solutions was measured, after which the samples were mixed at 144 cycles per minute on the horizontal shaker.

After mixing for 24 hours at room temperature, the pH of the samples was again measured. Samples were filtered (0.45µm), acidified and analyzed for Cu and Ni at the Department of Natural Resources (DNR) laboratory in Hibbing. Metals analysis for all experiments was done on a Perkin-Elmer 603 Atomic Absorption Spectrophotometer.

In Experiment 2 seven samples of tailings (12.5g) were placed into separate glass reactors with 75 ml of FL1 leachate. Fourteen samples of wet peat (12.5 g dry wt.) were also placed into reactors, seven with 75 ml of FL1 leachate and seven with FL5 leachate. Three blanks containing only 75 ml of leachate were prepared for both FL1 and FL5.

Samples were analyzed for pH and filtered and preserved for metals analysis (Cu, Ni, Co, Zn, Fe, Mn). The first sample was taken before reactors were placed on the rotating mixer (t=0.1 hr.), and subsequent samples were taken at t = 26, 50, 73, 98, and 170 hours.

In Experiment 3, six samples of wet peat (12.5 g dry weight) and 75 ml of FL1 leachate were placed into separate reactors, 3 glass and 3 polypropylene. Samples of FL1 and FL5 were also mixed in glass and in polypropylene reactors without peat. Initial water quality samples were taken after 5-10 minutes of contact time. The remaining reactors were placed on the rotating mixer and additional samples withdrawn at three and seven days.

The FL1 leachate in reactors without adsorbent was analyzed for pH only. Other samples were filtered, acidified and sent to the DNR Hibbing laboratory for metals analysis (Cu, Zn, Fe).

Experiment 4 was conducted to determine the theoretical metal sequestration capacity of peat and tailings for Cu, Ni, Co, and Zn. Peat was used with both FL5 and FL1 leachates and tailings with FL1. Each leachate (75 ml) was added to plastic reactors containing variable masses (0.25, 0.5, 1.0, 2.5, 5.0, 7.5, 10.0 and 12.5g dry weight) of adsorbent. After the reactors were mixed for 24 hours, the pH was measured and samples were filtered, acidified and sent to the DNR Hibbing laboratory for metals analysis (Cu, Ni, Co, Zn, Fe, Mn, Ca, Mg, Na, K). A regression analysis was conducted on the data to determine the best fit to Langmuir and Freundlich isotherms.

Column studies were conducted using 2" I.D. acrylic columns (Figure 2) which were placed in cabinets designed to eliminate exposure to light. The columns were packed as follows:

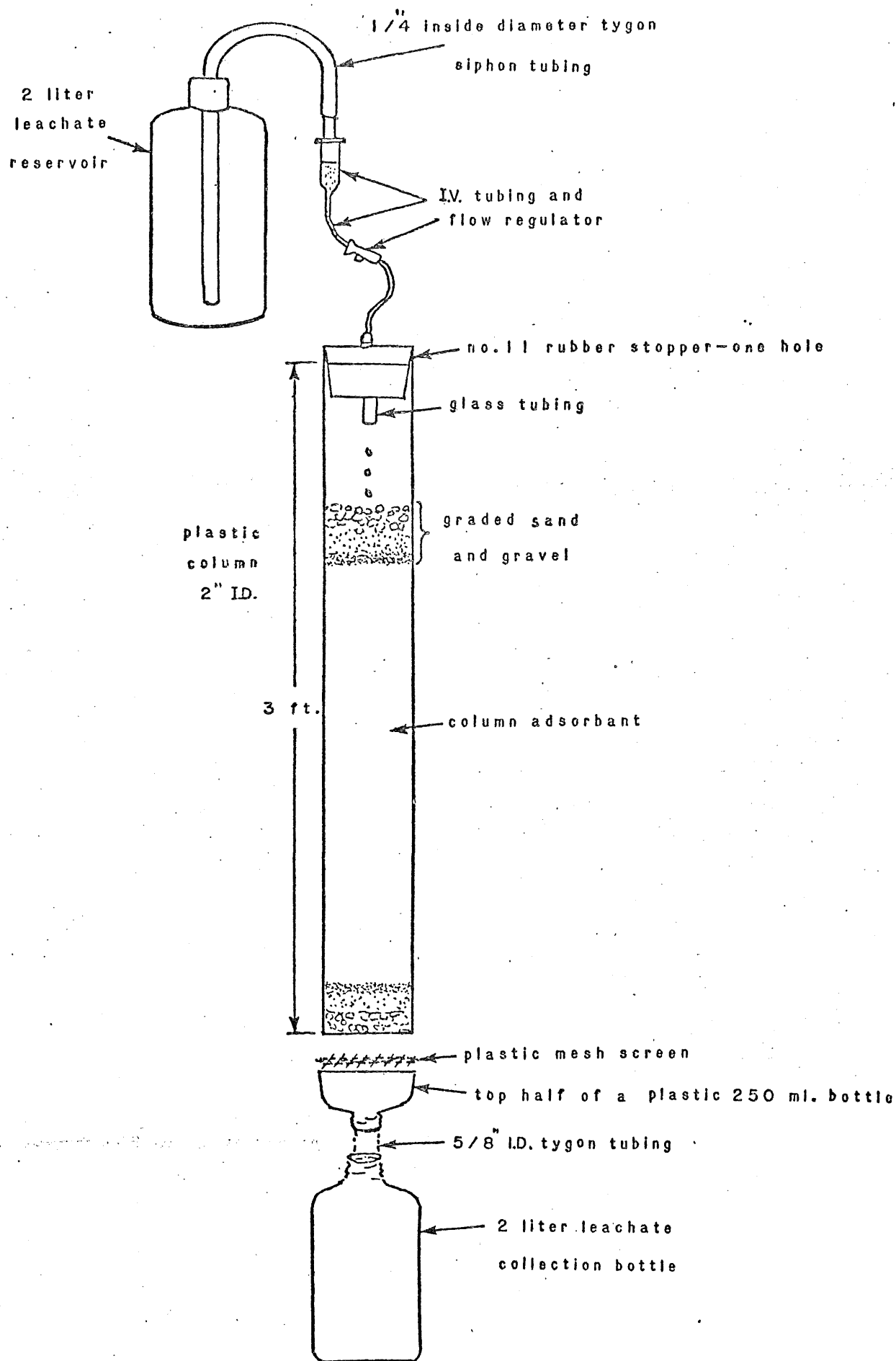
- Four columns which were fed by FL5 leachate contained 575g wet peat (76.7g dry) and 1070g sand (160 cm).
- Four columns fed by FL1 leachate contained 67g wet peat (8.9g dry) and 125g sand (13 cm).
- Four columns fed by FL1 leachate contained 400g sieved tailings (1-13 cm). (all tailings < 200 mesh (74 μ) were discarded).

The peat was mixed with sand to enhance the flow characteristics of the peat. Sand and gravel were layered at each end of the adsorbent for enhanced flow distribution and adsorbent support.

The mass of peat used with the FL5 leachate was determined based on the capacities determined in the batch isotherm experiments and a water quality analysis of FL5 leachate. The leachate used in the experiment had metal concentrations which were twice as high (Table 2). Capacities were not calculated for peat or tailings with the FL1 leachate since the data did not fit isotherm equations. Columns were loaded with a mass judged to be near the minimum for efficient flow. A small mass was selected since a limited amount of leachate was available and breakthrough was desired.

Columns were filled to field capacity with distilled water prior to application of leachate. A flow rate of 17-18 drops/minute (0.7 ml/min.) was used to simulate a fluid loading of 1 inch per hour. The total leachate application was 11 liters with samples collected and pH measured twice daily over a ten day period. The same flow and sampling procedure was used for the column rinsing experiments. The application rate and total treatment volume were used to simulate field conditions (Appendix XVI). Samples were sent to the DNR Hibbing laboratory for metals analysis (Cu, Ni, Co, Zn). No pH adjustments were made in either batch reactor or column experiments.

Figure 2. Column experimental apparatus



RESULTS

Batch Reactor Experiments

Since Experiments 1-3 were preliminary the results are presented only briefly. The results of Experiment 1 (Table 3) indicated that:

- Peat is more effective than tailings or sand in removing Cu and Ni from the FL5 leachate.
- Peat released H^+ to solution as indicated by a pH decrease from 4.0 to 3.25.
- Tailings removed a small amount of nickel but released Cu to the FL5 leachate.
- Tailings removed H^+ from solution as indicated by a pH increase from 4.0 to 4.1.
- Sand removed virtually no Cu or Ni from the FL5 leachate.
- Sand released H^+ as indicated by a pH drop from 4.0 to 3.85.

The results of Experiment 2 (Figure 3, Table 4) indicated that:

- Glass reactors removed Cu, Fe, and H^+ from FL5 leachate and Cu, Zn, and H^+ from FL1 leachate.
- Peat removed Ni, Co, Zn, Mn from FL5 leachate.
- Peat removed Ni from the FL1 leachate but released Zn, Fe, Mn, and H^+ to solution (pH dropped from 7.2 to 3.72).
- Tailings were slightly more effective than peat in removing Ni from FL1 leachate and released only Fe to solution.
- Equilibrium concentrations in almost all cases were approached after one day of reaction.

The results of Experiment 3 supported the observations from Experiment 2, in particular:

- Glass was responsible for removing Cu^{2+} , Fe^{2+} , and H^+ from solution.
- Peat removed Cu from FL1 leachate and released Zn, Fe, and H^+ .

Table 3. Trace metal removal by peat, tailings, sand (Experiment 1)

$$Cu_o = (22.4 + 22.3)/2 = 22.35 \text{ mg/l}$$

$$Ni_o = (215 + 212)/2 = 213.5 \text{ mg/l}$$

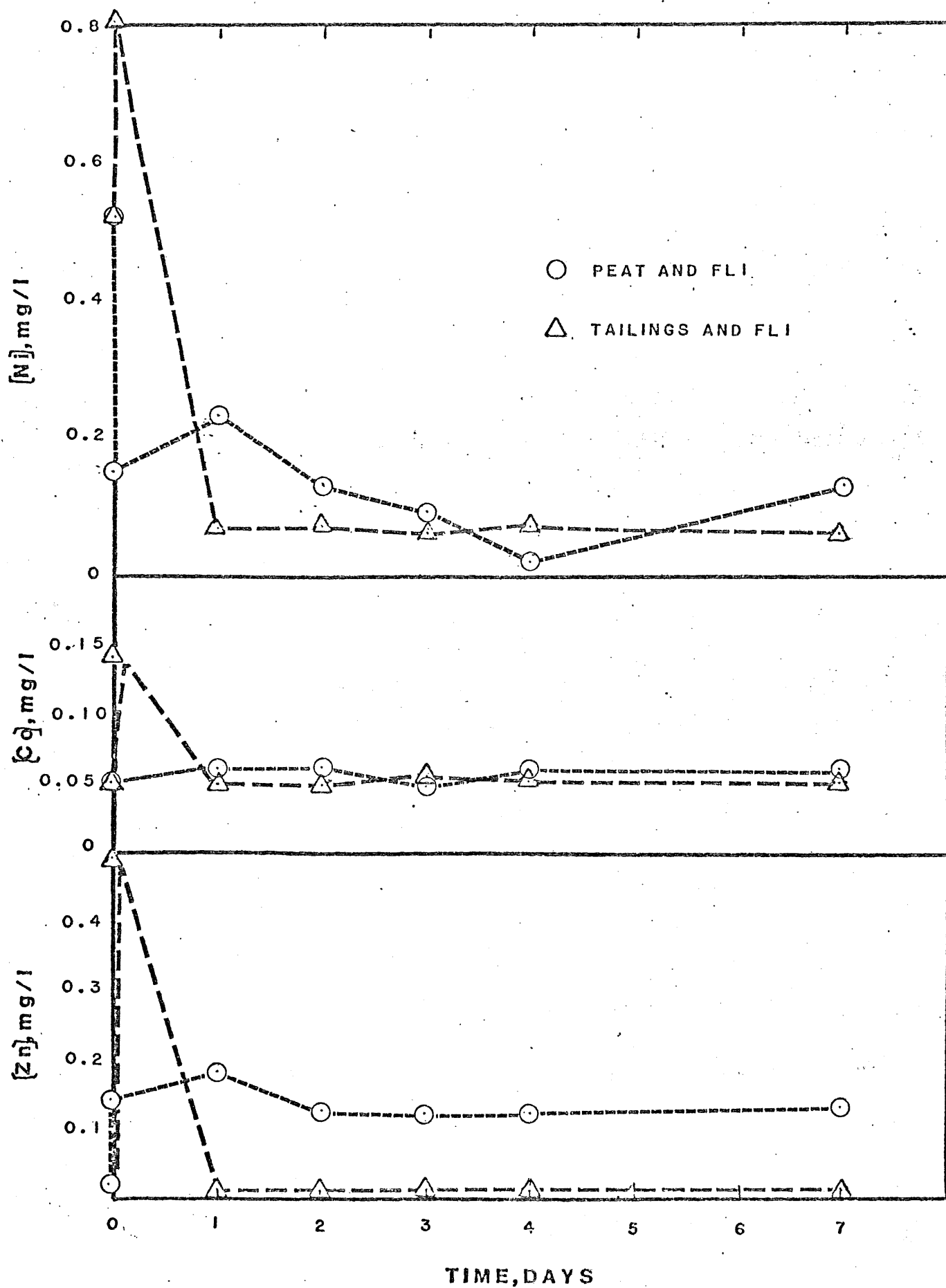
$$v = 0.151$$

ADSORBENT	ADSORBENT LOADING (g/l)	FINAL METAL CONC		ADSORPTION CAPACITY		PH _f
		Cu Mg/l	Ni mg/l	Cu mg/g	Ni mg/g	
PEAT	6.7	14.6	195	1200	2800	3.30
PEAT	6.7	14.5	196	1200	2600	3.25
PEAT	13.3	10.5	182	900	2400	3.20
PEAT	13.3	11.2	183	800	2300	3.20
TAILINGS	6.7	23.2	205	-100 ¹	1300	4.10
TAILINGS	6.7	23.2	205	-100	200	4.05
TAILINGS	33.3	25.4	213	-100	xx	4.10
TAILINGS	33.3	25.1	2.5	-100	-xx	4.15
SAND	6.7	22.4	210	-xx	500	3.85
SAND	6.7	22.5	212	-xx	200	3.85

¹adsorption capacity < 0 implies metal release

xx essentially no change

Figure 3. [Ni], [Co], [Zn], vs time, FL-1 with peat and tailings
(Experiment 2)



Tab. 4. Trace metal removal by peat and tailings, Experiment 2.

ELEMENT	FL5 AND PEAT			FL1 AND PEAT			FL1 AND TAILINGS		
	C _o mg/l	C _f mg/l	Removal eq/g peat	C _o mg/l	C _f mg/l	Removal eq/g peat	C _o mg/l	C _f mg/l	Removal eq/g tailings
Cu	5.80	0.04 ²	0.27 ²	0.05	0.01 ²	0.0019 ²	0.05	0.05 ²	0 ²
Ni	30.1	1.2	1.5	0.52	0.13	0.020	0.52	0.06	0.024
Co	2.39	0.20	0.11	0.05	0.06	-0.0005	0.05	0.05	0
Zn	1.07	0.13	0.044	0.02	0.13 ²	-0.005 ²	0.02	0.01 ²	0.0005 ²
Fe ³	0.35	16.5 ²	-0.58 ²	0.02	17.0	-0.61	0.02	0.40	-0.014
Mn ³	2.74	0.69	0.056	0.13	0.68	-0.015	0.13	0.14	-0.0003
pH ³	3.80	3.71 ²	-0.2 ²	7.2	3.72 ²	-1.1 ²	7.2	7.65 ²	0.0002 ²

$$^1 \text{Removal} = \frac{(C_o - C_f) \times 0.075 \times 10^3}{(MW) \times z \times 12.5} = \frac{(C_o - C_f) \times 6}{(MW) \times z}$$

where MW = molecular wt. and z = ionic charge

²Glass reactors also removed these metals from solution

³Fe assumed to be Fe²⁺, Mn assumed to be Mn⁴⁺

In the isotherm experiment peat removed Cu, Ni, Co, Zn, Mn, Ca, and Na from (Figure 4) and released H^+ , Fe, and K to the FL5 leachate (Table 5). The removal of Cu, Ni, Co, and Zn was consistent with Langmuir adsorption theory (Figure 5), and the capacities (Q_0) and energies of interaction (b) were calculated (Table 6). The capacities decreased in the same order as the initial concentrations ($Ni > Cu > Co > Zn$) and the energies of interaction in the order $Cu > Co > Zn > Ni$. The variation of initial metal concentrations limits strict comparison among the constants for the various metals.

The data were also fit to the Freundlich equation. The K_F values, a rough indicator of capacity, decreased in the order $Cu > Ni > Co > Zn$ and the $1/n$ values, a rough indicator of the adsorption intensity, in the order $Zn > Cu > Co > Ni$ (Table 7).

The degree of trace metal removal from the FL1 leachate was considerably less than FL5 due in part to the low concentrations in the FL1 leachate. Peat removed Cu, Ni, Ca, Na, and K but released Zn, Fe, Mn, H^+ , and Mg (Figure 6, Table 8). The tailings removed nickel, released Mn, Ca, Mg, Na, and K while concentrations of Cu, Co, Zn, Fe, and H^+ remained relatively constant (Figure 7, Table 9). The nickel data for peat and tailings were fit to both Langmuir and Freundlich equations, but agreement with both equations was poor.

Column Experiments

Net removal capacities were determined by the difference between trace metal uptake in the removal experiment and metal release in the distilled water rinse. The calculated capacities were greatest for peat and FL5 (Table 10). With the FL1 leachate, tailings were more effective in removing copper, but peat had a much greater capacity for removing nickel, cobalt, and zinc.

Figure 4. $[Me]_{final}$ vs MASS OF PEAT, FL-5 LEACHATE

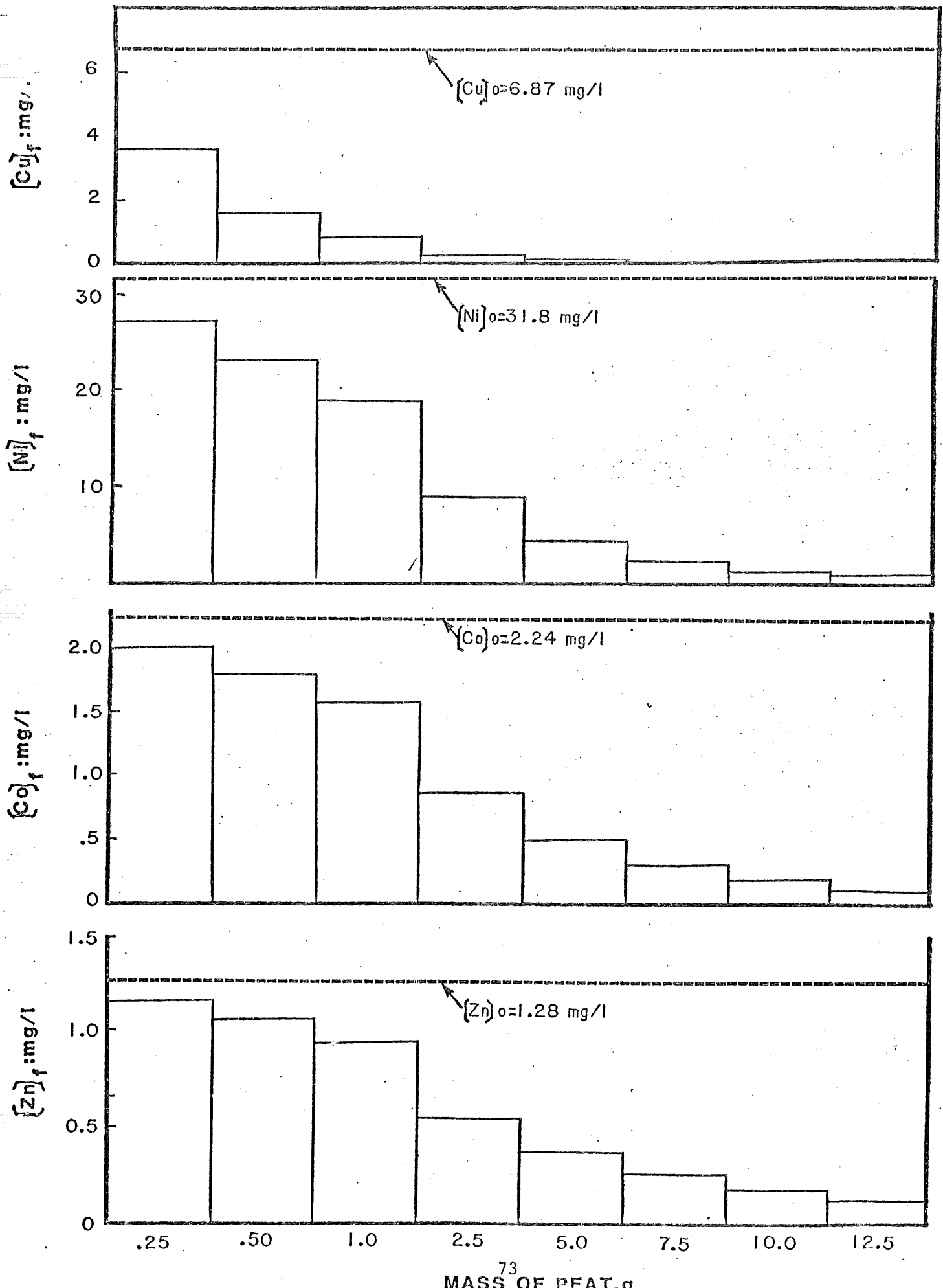


TABLE 5. Equilibrium Concentration(mg/l) For Peat and FL5 (Experiment 4)

Mpeat	Cu	Ni	Co	Zn	Fe	Mn	Ca*	Mg*	Na	K	pH ¹	pH ²
0, Co	6.87	31.8	2.24	1.28	0.16	3.11	152	42.8	42.3	8.2	5.2	4.0
0.25	3.62	27.6	2.00	1.16	0.08	2.83	152*	43.4*	42.8*	8.8*	3.5	3.5
0.5*	1.61	23.6	1.81	1.06	0.20	2.73					3.5	3.4
1.0	0.85	19.2	1.58	0.94	2.98	2.55	130*	46.0*	34.4*	8.6*	3.5	3.25
2.5*	0.22	9.05	0.88	0.56	0.31	1.86					3.6	2.4
5.0	0.10	4.60	0.51	0.36	0.34	1.50	102*	48.6*	27.6*	11.6*	3.6	3.4
7.5*	0.05	2.45	0.30	0.23	0.40	1.17					3.6	3.6
10.0	0.04	1.50	0.20	0.17	0.38	0.92	60*	40.5*	18.0*	12.2*	3.6	3.6
12.5*	0.03	1.13	0.13	0.12	19.8	0.66					3.7	2.5
Blank*	6.77	31.1	2.28	1.26	0.14	3.09	148*	42.0*	41.4*	8.2*	4.0	4.0

*Not Run in Duplicate

All others run in duplicate, average value reported

¹pH in reactor²pH after filtration

Figure 5. Copper, $1/q_e$ vs $1/c$, PEAT AND FL-5

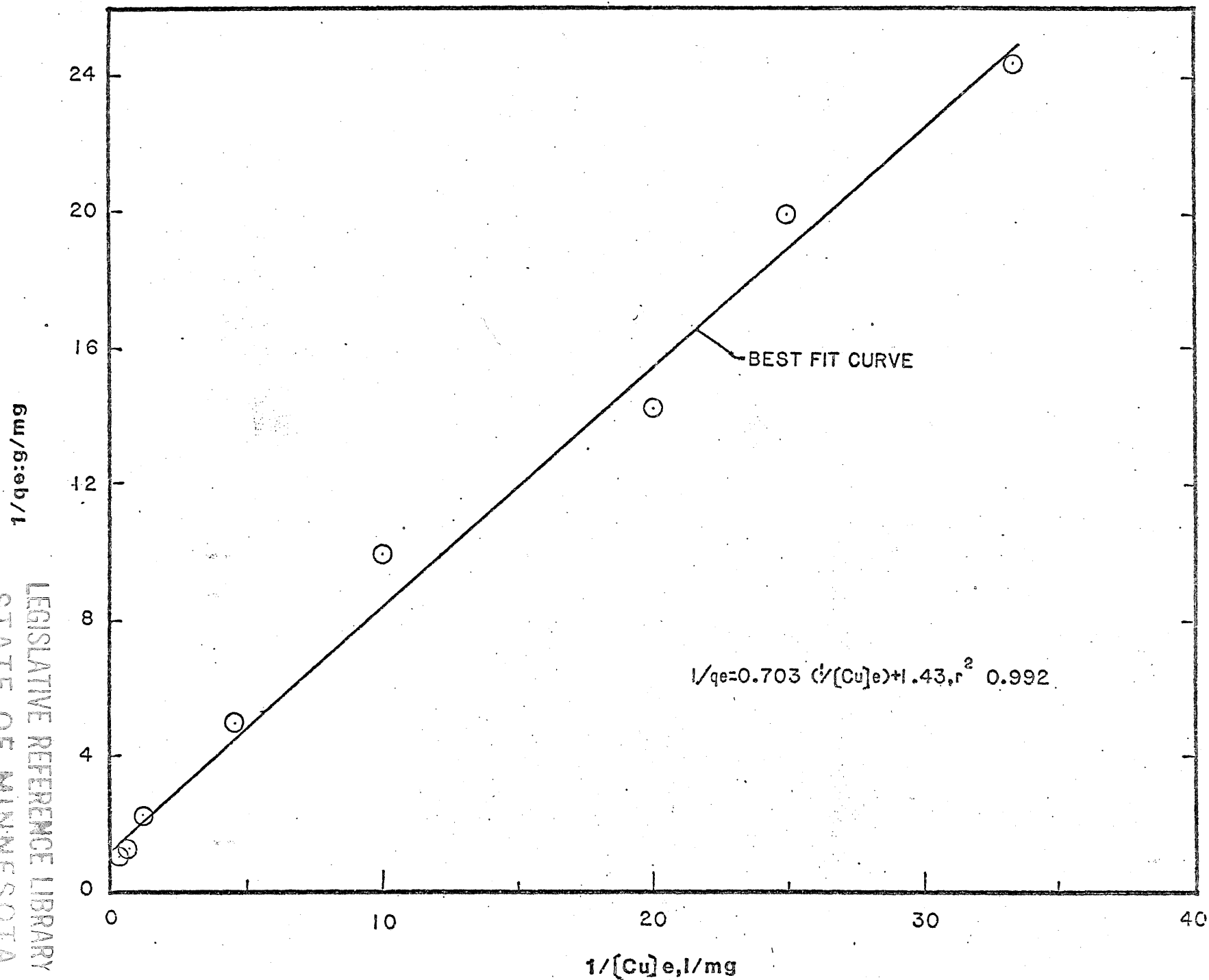


Table 6. Langmuir Constants For FL 5 and Peat, Experiment 4

Metal	b 1/mg Me ads	Q _o mg Me/g peat	r ²	n
Cu	2.03	0.699	0.992	8
Ni	0.155	1.19	0.978	8
Co	1.64	0.0699	0.942	8
Zn	1.26	0.0496	0.972	8
Ca	0.04	3.33	0.569	5
Na	-0.0083	-0.98	0.735	5

TABLE 7. Comparison of Freundlich constants¹ with those from Ryss and Hoffmann (1979).

Metal	FL-5 and Peat			Ryss and Hoffmann (1979)		
	K _F	1/n	r ²	K _F	1/n	r ²
Cu	0.492	0.683	0.991	22.5	0.267	0.92
Ni	0.171	0.603	0.995	9.72	0.453	0.959
Co	0.0424	0.625	0.986			
Zn	0.0306	0.725	0.988	11.6	0.344	0.990

¹ $q = K_F Ce^{1/n}$, $n > 1$ or $\log q = \log K_F + 1/n \log Ce$

q in mg/g

Ce in mg/l

K_F in $\frac{1^{1/n} \text{ mg} (\frac{n-1}{n})}{g}$

K_F is rough indicator of relative sorption capacity

1/n is rough indicator of relative adsorption intensity

Figure 6. $[Me]_{final}$ vs MASS OF PEAT, FL-1 LEACHATE

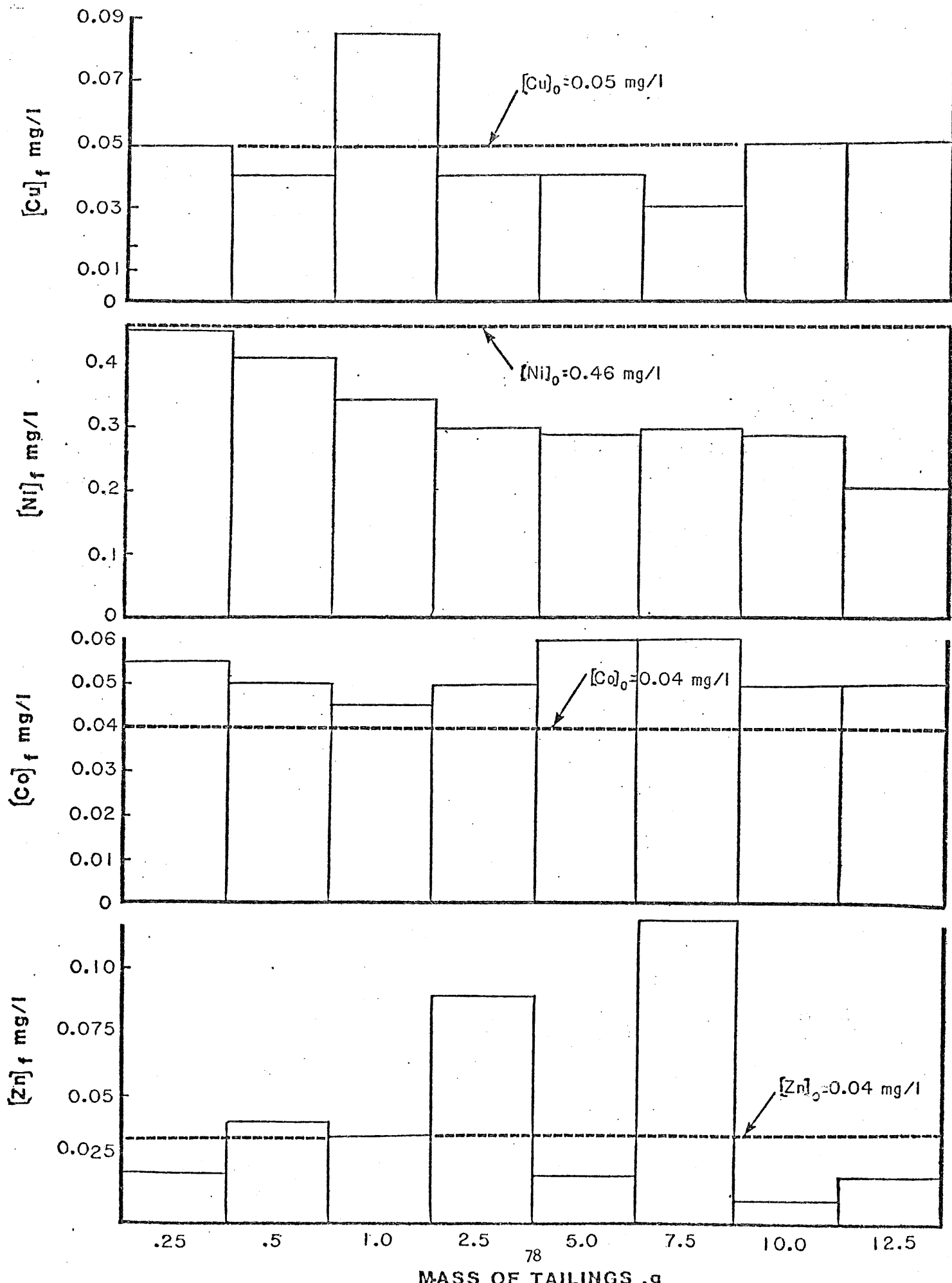


TABLE 8. Equilibrium concentrations, peat and FL 1, Experiment 4

Mpeat (g)	pH ²	pH ¹	Equilibrium Concentration, mg/l									
			Cu	Ni	Co	Zn	Fe	Mn	Ca	Mg	Na	K
0, Co		6.7	0.05	0.46	0.04	0.04	0.02	0.19	484	38.8	213.3	49.3
0.25	4.2	4.2	0.02	0.36	0.05	0.08	0.12	0.20	412	38.6	196.4	44.6
0.50*	3.7	3.9	0.01	0.32	0.05	0.08	0.13	0.25				
1.0	3.3	3.8	0.015	0.26	0.05	0.09	0.14	0.34	318	41.6	170.6	37.4
2.5*	3.3	3.5	0.05	0.34	0.05	0.14	0.17	0.51				
5.0	3.1	3.6	0.02	0.11	0.05	0.11	0.23	0.58	218	53.6	129	31.2
7.5*	3.1	3.6	0.02	0.11	0.05	0.14	0.29	0.68				
10.0	3.6	3.6	0.02	0.09	0.05	0.10	0.51	0.64	178	50.8	100	26.8
12.5*	3.7	3.5	0.04	0.06	0.03	0.09	0.50	0.53				
Blank*			0.08	0.51	0.06	0.05	0.29	0.20	480	38.8	211.6	48.8

*Not Run in Duplicate

All others run in duplicate, average value reported¹In reactor²After filtration

Figure 7. $[Me]_{final}$ vs MASS OF TAILINGS, FL-1 LEACHAT

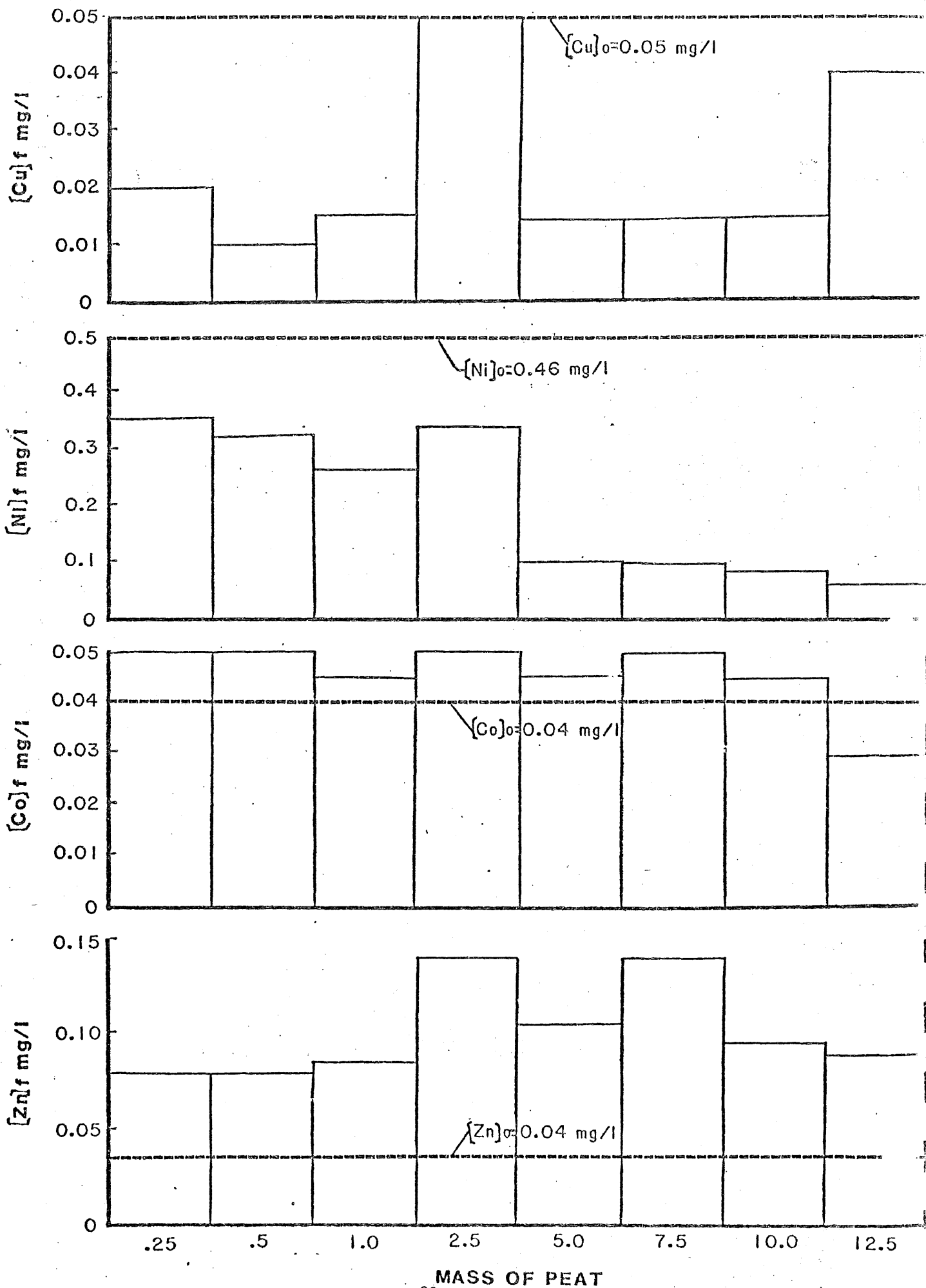


TABLE 9 Equilibrium concentrations, tailings and FL 1, Experiment 4

Mpeat (g)	pH ²	pH ¹	Equilibrium Concentration, mg/l					Mn	Ca	Mg	Na	K
			Cu	Ni	Co	Zn	Fe					
0, Co		6.7	0.05	0.46	0.04	0.04	0.02	0.19	484	38.8	213.3	49.3
0.25	5.4	6.5	0.05	0.50	0.06	0.02	0.02	0.17	448	38.8	204.4	45.8
0.50*	5.3	6.4	0.04	0.42	0.05	0.04	0.03	0.17				
1.0	4.3	6.0	0.09	0.40	0.05	0.04	0.67	0.22	450	41.2	204.8	45.8
2.5*	3.0	6.5	0.04	0.30	0.05	0.09	0.05	0.26				
5.0	4.7	6.5	0.04	0.30	0.06	0.02	0.04	0.50	498	57.6	222	46.8
7.5*	5.6	6.5	0.03	0.30	0.06	0.12	0.02	0.69				
10.0	5.7	6.7	0.05	0.29	0.05	0.01	0.14	0.83	536	72.6	236	49.2
12.5*	5.6	6.8	0.05	0.21	0.05	0.02	0.02	0.96				
Final Blanks*			0.08	0.51	0.06	0.05	0.29	0.20	480	38.8	211.6	48.8

*Not Run in Duplicate

All others run in duplicate, average value reported.

¹In reactor²After filtration

Table 10. Net metal removal capacity of peat and tailings

	Net capacity, $\mu\text{g/g}^1$			
	Cu	Ni	Co	Zn
Peat and FL 5	>1400 ²	2500	46	140
Peat and FL 1	-87 ³	270	20	13
Tailings and FL 1	1.1	7.2	0.8	1.0
Peat and FL 5, Sturgess, 1979.	520	470	0	28
Peat and FL 5, batch reactors	700	1200	70	50

¹On a dry weight basis

²Break through not reached

³Cu was released to solution

With peat and FL5, column effluent pH decreased from about 4.8 to the influent solution pH of 3.8 over the course of the experiment. The net metal removal decreased in the order Ni>Cu>Co>Zn. Effluent copper concentrations were relatively constant at about 0.25 mg/l. Concentrations of nickel, cobalt, and zinc were initially quite low but reached the influent concentration after about 4.5 ℓ (3.7 bed volumes) of leachate passed through the column (Figure 8).

In the column rinse phase the trace metal release was small with most release occurring in the initial sample (Tables 11, 12). The release of Cu, Ni, and Zn was less than 13% of the mass removed in the initial phase of experimentation; cobalt release was 33% of the initial removal. The release of copper was the lowest, suggesting a strong bond between the copper and peat (Table 12). During the rinse phase pH rose from 4.3 to 5.5.

With peat and FL1 the solution pH decreased (6.4 to 4.4) over the course of the experiment, as did trace metal concentrations (Figure 9). The net removal capacity was greatest for nickel and least for copper, for which a net release actually occurred (Table 10). During the column rinse pH rose from 5.1 to 6.2. The release of Ni, Co, and Zn during the column rinse was small, less than 8% of that removed in the initial experimental phase (Table 11). The majority of metal release occurred in the initial sample (Table 12).

During flow through the tailings the FL1 effluent pH increased from 5.6 to 7.3. The net removal capacities for Cu, Ni, Co, and Zn were 1.1, 7.2, 0.8, and 1.0 $\mu\text{g/g}$ tailings. Effluent copper concentrations decreased from 25 to 15 $\mu\text{g/l}$ over the course of the experiment while nickel concentrations increased steadily from 100 to 400 $\mu\text{g/l}$ (Figure 10). Cobalt and zinc concentrations also followed a generally increasing trend. During the column rinse most metal release occurred in the initial sample (Table 12). The total release was small, less than 5% of the mass of metal removed in the initial column phase (Table 11).

Figure 8. CONCENTRATION vs FLOW, PEAT AND FL-5

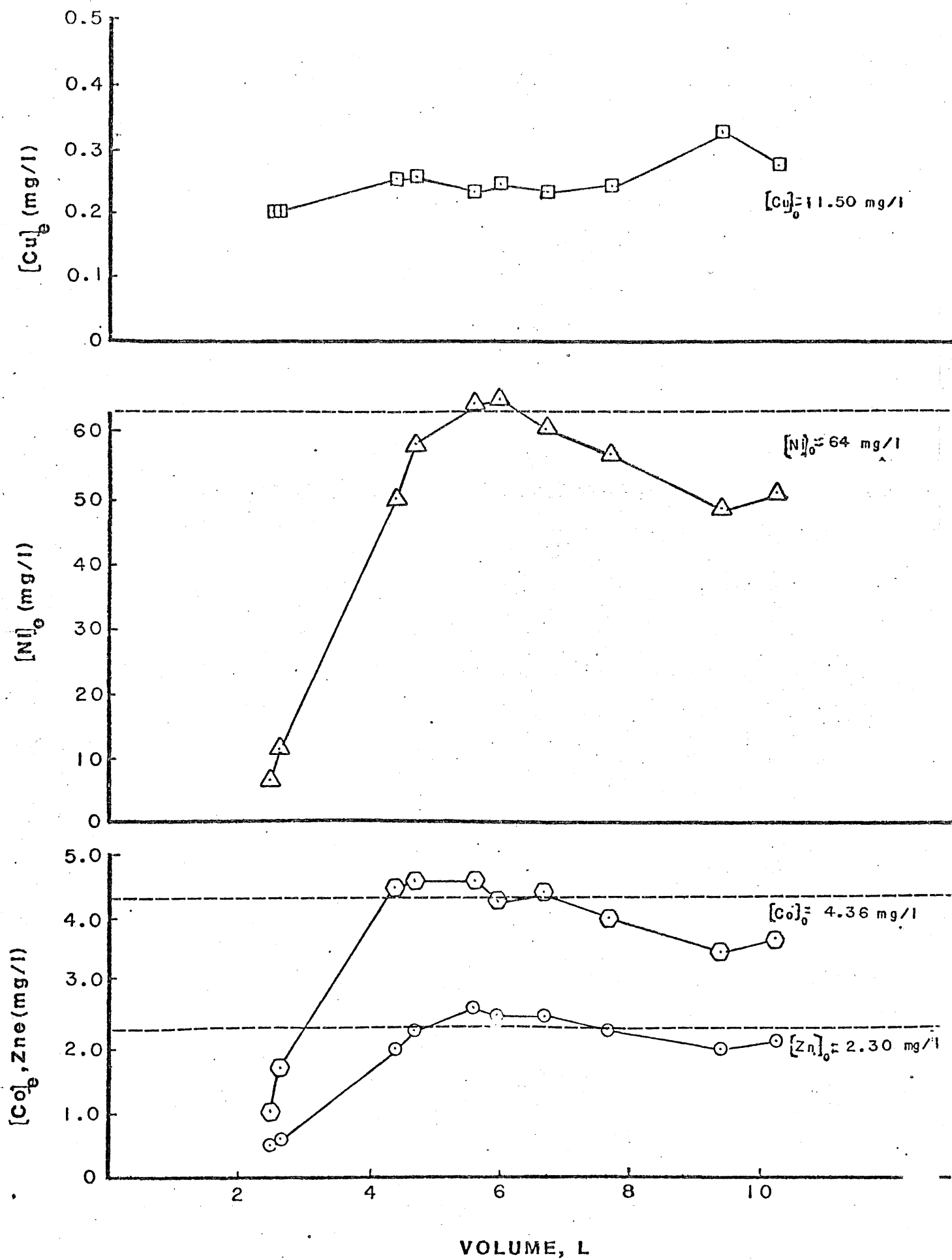


Table 11. Gross trace metal removal, release, and net removal (mg)

	Cu	Ni	Co	Zn
Peat and FL 5 ¹				
Gross Removal	110	230	5.2	11
Release	0.5	29	1.7	0.85
Net Removal	110	200	3.5	10
Peat and FL 1 ²				
Gross Removal	-0.7	2.5	0.19	0.13
Release	0.065	0.065	0.009	0.009
Net Removal	-0.7	2.4	0.18	0.12
Tailings and FL 1 ²				
Gross Removal	0.440	3.0	0.34	0.400
Release	0.010	0.086	0.003	0.008
New Removal	0.430	2.9	0.34	0.390

¹Mean of three values

²Mean of four values

Table 12. Trace metal release from peat into rinse water after sequestration.

Mass Release (μg)				
pH	Cu	Ni	Co	Zn
4.3	420	27,700	1580	800
4.7	10	600	40	20
5.2	30	200	20	10
5.3	30	100	10	8
5.4	10	50	10	3
5.5	20	100	10	6

Peat and FL 1 ²				
5.1	36.1	61.3	6.8	3.0
5.8	5.1	0.6	<0.4	0.7
6.2	7.0	<0.8	<0.8	2.4
6.2	7.6	<0.9	<0.9	0.9
6.2	5.1	0.7	<0.4	0.5
6.2	3.8	1.5	<1.3	1.8-2.0

Tailings and FL 1 ²				
7.5	4.0	80	1.2	0.7
7.0	0.6	1.2	0.4	2.5
6.9	0.8	0.7	0.7	1.4
7.1	2.5	0.8	0.4	1.1
7.0	1.1	1.2	0.2	1.0
7.0	1.4	1.4	0.6	1.4

¹Mean of three values

²Mean of four values

Figure 9. CONCENTRATION vs FLOW, PEAT AND FL-1

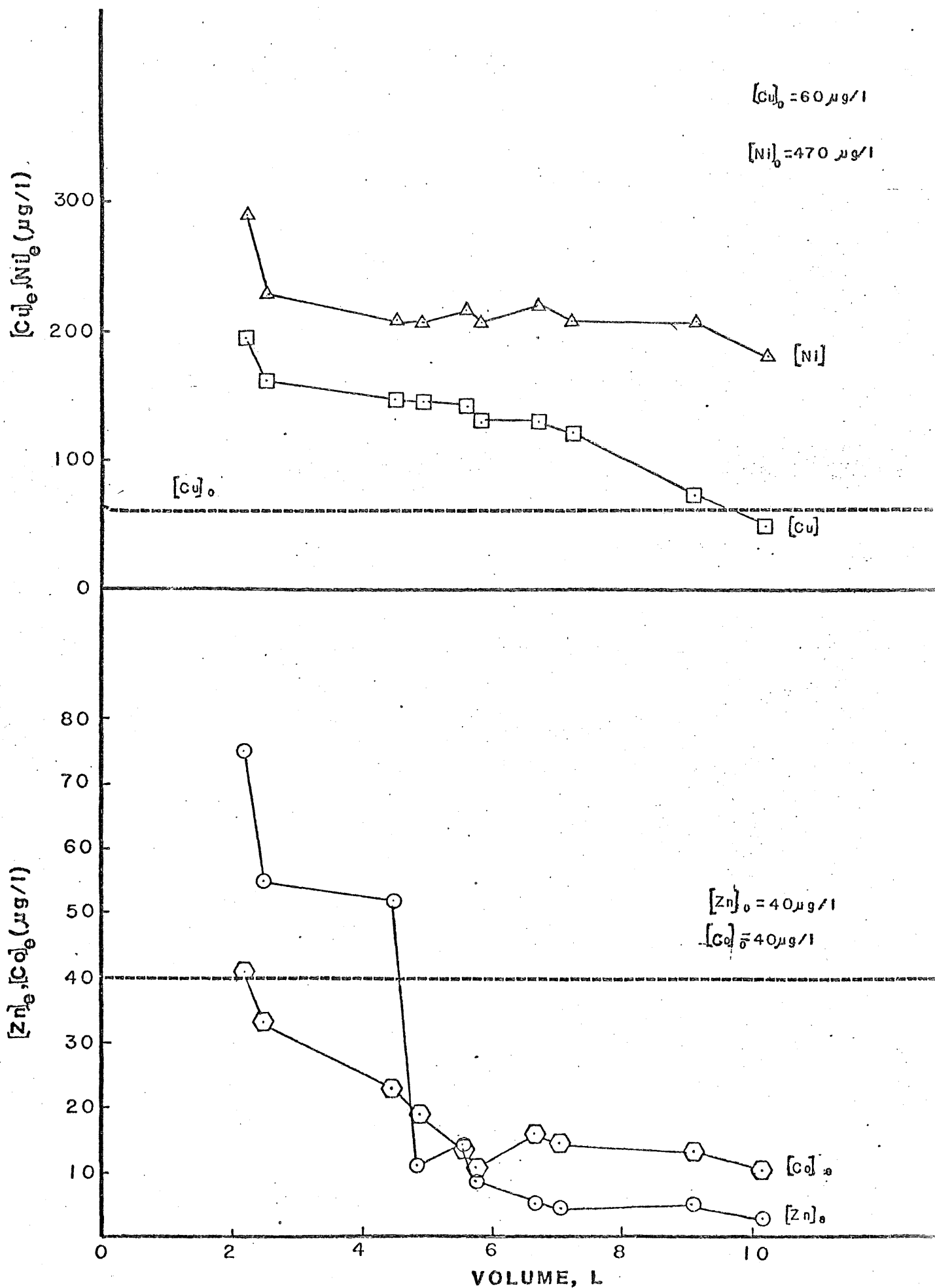
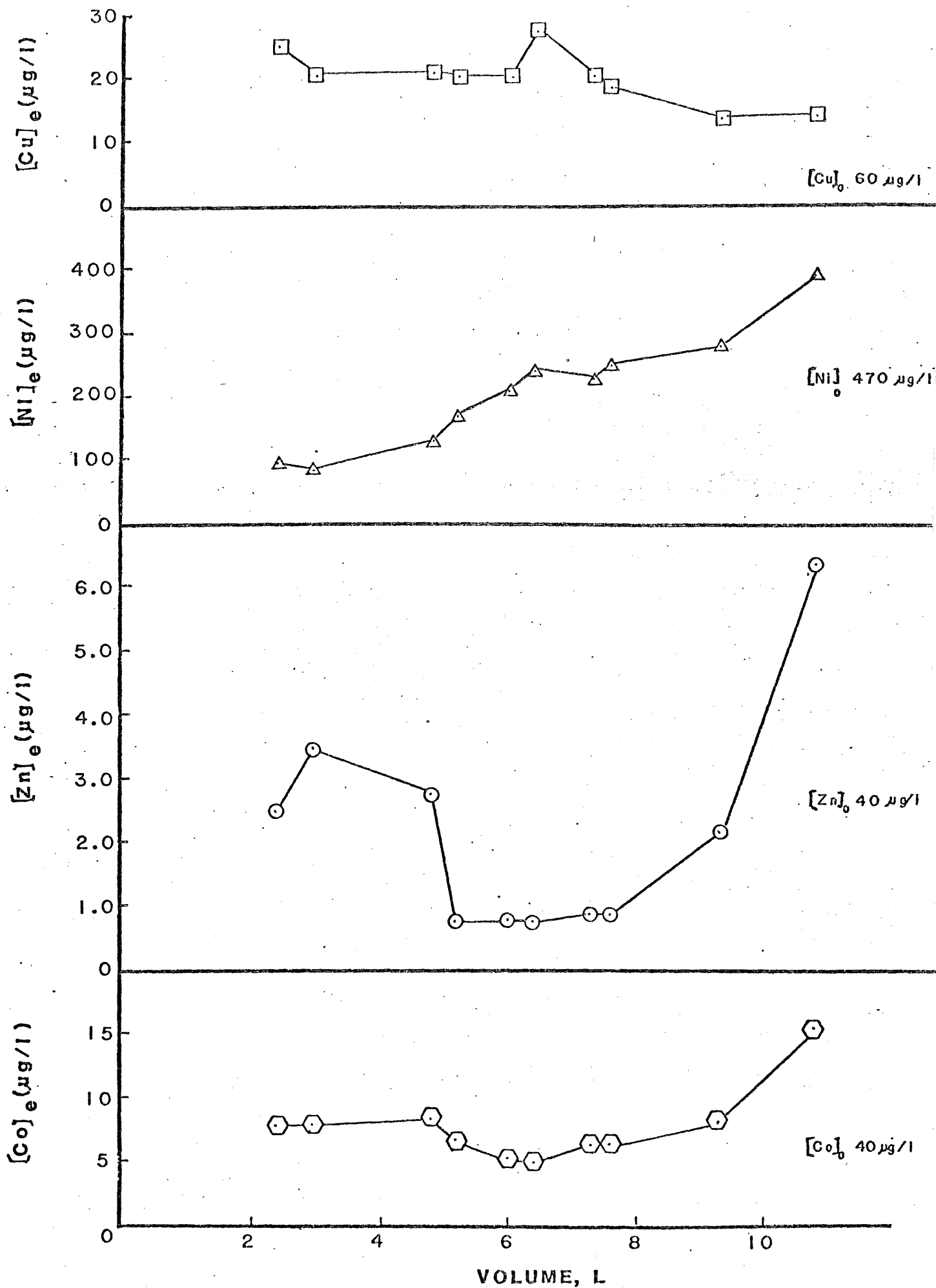


Figure 10. CONCENTRATION VS FLOW, TAILINGS AND T.E.



DISCUSSION

Peat was the most effective material for removing trace metals from the FL5 leachate in column experiments. Copper concentrations were consistently reduced from 11.5 to about 0.25 mg/l throughout the experiment, a 98% reduction. The maximum observed concentration reductions of Ni, Co, and Zn were 99, 94, and 90% respectively, and occurred in the initial sample. Some of the reduction was due to dilution by distilled water present in the peat. Effluent metal concentrations were higher in the subsequent samples, at times exceeding influent concentrations (Figure 8). This may have been an indication that Cu was displacing these metals from removal sites on the peat. High initial concentrations of Ni, Co, and Zn in one of the columns indicated that the flow may have short circuited (Appendix XVII, Table A1, Column 10).

Major cations (Ca, Na, and possible K) and H^+ provide competition for removal sites. Ca and Mg were not analyzed in column experiments, but batch reactor results indicated a significant reduction in the concentrations of these metals (Table 5). Removal of Ca reached 22 mg/g peat and Na 8.9 mg/g peat, values several times higher than those for trace metals. This was due in part to the high concentrations of Ca and Na in the influent in comparison to the trace metals. Potassium was not removed from the FL5 leachate but was removed from the FL1 leachate in which K concentrations were higher (Table 8). H^+ was released to solution in batch reactor experiments but was removed during column tests. The effluent pH decreased from 4.8 to 3.9 over the experiment in comparison with the influent pH of 3.8 (Appendix XVII).

The net trace metal removal capacities in the column experiments ranged from 0.046 mg Co/g peat to 2.5 mg Ni/g peat. The lack of release of Cu, Ni, and Zn to distilled water during column rinse indicated that these metals were strongly bound to the peat; cobalt was less tightly bound. The capacities determined for Cu, Ni, and Zn were 2-3 times greater in the column experiment than in batch tests (Table 10). This was unusual since more intimate contact and a longer contact time occurred in the batch tests. Removal in the column experiments may have been enhanced by trace metal concentrations which were about twice as high as those in the batch tests (Table 2).

The capacities from column experiments were also greater than those observed by Sturgess (1979, Table 10). Although trace metal concentrations in the leachate used by Sturgess were higher than in the present study, a lower mass loading, a higher loading rate and lower pH would tend to diminish the calculated capacities. The trace metal concentrations in the earlier study were 3-6 times as high but, the total metal removed by the peat were only 0.2-0.4 times those in the present study (Table 13). At this low loading it is likely that the capacities of the peat was not reached. The flow rate used by Sturgess were 14-25 times those in the present study. The more rapid flow may not provide sufficient reaction time for effective removal. The lower pH, 3.4 vs 3.8, would also inhibit metal removal due to competition with H^+ for removal sites.

Peat removed nickel and released H^+ to the FL1 leachate in both batch and column experiments (Table 14). Cobalt and zinc were also removed from solution in column experiments while copper was released. The opposite was true in batch reactor experiments, a variation which is not readily explained. Ca, Na, and K competed with trace metals for removal sites. Ca and Na removals reached 288 and 72 mg/g peat respectively in isotherm experiments (Table 8). The removal capacities obtained for Ni, Co, and Zn were 10 to 45% of those observed with the FL5 leachate. Lower concentrations and mass loadings contributed to the lower capacities.

Table 13. Comparison between column experiment and data from Sturgess, 1979.

	Sturgess, 1979 (Value A)	This Experiment (Value B)	Ratio, $\frac{\text{Value B}}{\text{Value A}}$
Input Conc., mg/l			
(Cu)	66.	11.5	0.17
(Ni)	210	64	0.30
(Co)	14	4.36	0.31
(Zn)	9.9	2.30	0.23
Input Volume, l	1	10.3	10.3
Flow Rate, l/hr	~0.25	~0.04	0.16
Mass Dry Peat, g	111	76.7	0.69
Total Mass Loading mg Me/g Peat-HR			
Cu	0.59	1.5	2.5
Ni	1.9	8.6	4.5
Co	0.13	0.59	4.5
Zn	0.089	0.31	3.5
Mass Loading Rate mg Me/g Peat-HR			
Cu	0.15	0.0060	0.040
Ni	0.48	0.033	0.069
Co	0.032	0.0023	0.072
Zn	0.022	0.0012	0.055
Capacity mg Me/g Peat			
Cu	0.52	>1.4	>2.7
Ni	0.47	2.5	5.3
Co	0	0.046	a
Zn	0.028	0.14	5.0

^aundefined due to division by zero

Table 14. Elemental removal summary: batch and column results

+ : ion is sequestered by solid
 - : ion is not sequestered by solid
 o : negligible change
 blank: not analyzed

Experiment	Cu	Ni	Co	Zn	H ⁺	Fe	Mn	Ca	Mg	Na	K
Peat and FL5 column	+	+	+	+	+						
Peat and FL5 batch	+	+	+	+	-	-	+	+	o	+	-
Peat and FL1 column	-	+	+	+	-						
Peat and FL1 batch	+	+	-	-	-	-	-	+	-	+	+
Tailings and FL1 column	+	+	+	+	+						
Tailings and FL1 batch	o	+	-	o	o	o	-	-	-	-	-

In column experiments tailings removed Cu, Ni, Co, Zn, and H^+ from the FL1 leachate but removed only Ni in batch tests while releasing Co. In the column tests the nickel removal capacity of tailings was only 2-3% that of peat.

The advantage of tailings over peat is that tailings do not reduce pH while removing metals. Although pH adjustment prior to contacting tailings may enhance metal removal it is not required to meet effluent pH standards. The tailings may also release metals such as cobalt in the batch reactor tests. This problem could be minimized by using only tailings which are particularly low in metal sulfides. Release of Ca, Mg, Na, and K will also occur when tailings contact leachate due to dissolution of silicate minerals. The amount of release will increase as leachate pH decreases. The calcium release may be limited by formation of $CaSO_4(s)$, which would also remove SO_4 from solutions.

Sand was ineffective in removing trace metals from the FL5 leachate in batch tests, although it may have been improved by influent pH adjustment.

SUMMARY

Peat significantly reduced trace metal concentrations in mining stockpile runoff containing trace metal concentrations of 2-64 mg/l (FL5). The sequestered metals were not readily released to distilled water indicating a fairly strong bond with the peat. Following the sequestration and rinse the peat contained Cu, Ni, Co, and Zn concentrations of at least 0.14, 0.25, 0.005, and 0.014%, respectively. Some of these concentrations may be high enough to consider secondary metal recovery.

The observed reduction in trace metal concentrations may not be adequate to meet discharge requirements so additional treatment may be required. Simple dilution would reduce trace metal concentrations, but is not necessarily environmentally sound. The use of additional columns would tend to reduce effluent concentrations as would pH adjustment. In some cases pH adjustment may be required, regardless, in order to meet effluent pH standards. Lime or perhaps tailings could be used to increase solution pH, although additional study of the latter would be required to determine the degree to which tailings dissolution would affect water quality.

The performance of peat and tailings with leachate having lower trace metal concentrations was less impressive. Per unit mass adsorbent, peat was far superior to tailings in removing Ni, Co, and Zn but released Cu and H^+ . It is likely that influent pH elevation would improve metal removal by peat in addition to helping meet effluent pH requirements. Although the tailings were less effective per unit mass, they merit additional consideration due to their availability and ability to maintain satisfactory pH levels.

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