

Water Geochemistry of Mining and Milling Retention
Ponds in the "New Lead Belt" of Southeast Missouri

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ABSTRACT

The heavy metal content and other geochemical data of the mine and mill waters of two mining operations in the "New Lead Belt" of southeastern Missouri were determined and the efficiency of retention ponds in reducing high metal concentrations was investigated.

The mine waters from two mines of this mining district, which is the largest lead producer in the world, showed a heavy metal content of less than 6 ppb copper, 66 ppb lead and 37 ppb zinc. They do not constitute a major source of pollution to the unspoiled streams of the region.

The heavy metal content from the mill effluents was reduced to values similar to mine water, when the pond sizes were large enough. This refers to effluent flows of up to 10,000 gallons per minute and pond sizes of about 20 acres and up to twenty feet of depths. When the pond size was reduced to about 6 acres, copper and lead concentrations were still reduced sharply, but high zinc concentrations were lowered only slightly.

The concentrations of calcium, magnesium, sodium and potassium and the pH of the mine water are similar to their concentrations in the streams. However, their concentrations are several times higher in the mill water. These elements can therefore be used to trace mine water in the streams.

High zinc concentrations in streams caused by mill water are sharply reduced within 4 miles of stream flow.

The retention ponds are not entirely efficient in preventing transport of metal rich rockflower into the streams.

Key Words: Water pollution*, mining activity*, heavy metals*, retention ponds, mine water, streams, geochemistry.

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PURPOSE OF INVESTIGATION

It was the purpose of this investigation to study in detail the geochemistry of mining and milling retention ponds in the "New Lead Belt" of SE Missouri. Special emphasis was directed toward the behavior of heavy metals.

INTRODUCTION

Previous work (Bolter and Tibbs 1970a, 1970b) in the "New Lead Belt" of southeast Missouri had outlined the background concentrations of copper, lead and zinc as well as several other geochemical parameters in this mining district.

In addition, the influence of the mining and ore milling activity on the chemical quality of the streams during the early stages of the mining development was investigated.

It was found that the early stage of the mining activity did not significantly contribute to the heavy metal content of the streams in the mining district. This suggested a high efficiency of the mining and milling retention ponds. It was therefore decided to investigate the geochemistry of several retention ponds in greater detail.

AREA OF STUDY

The "New Lead Belt" of SE Missouri is located in the Black River basin. This basin is roughly included within the boundaries of Iron and Reynolds counties and is shown in Figure 1.

The mining development of the study area has been very rapid. A few years ago it was sparsely populated and not industrialized. Production of ore started 1960 at a single mine. In 1970, after 4 other mines had started production, the "New Lead Belt" or "Viburnum Trend" became the largest lead producing district in

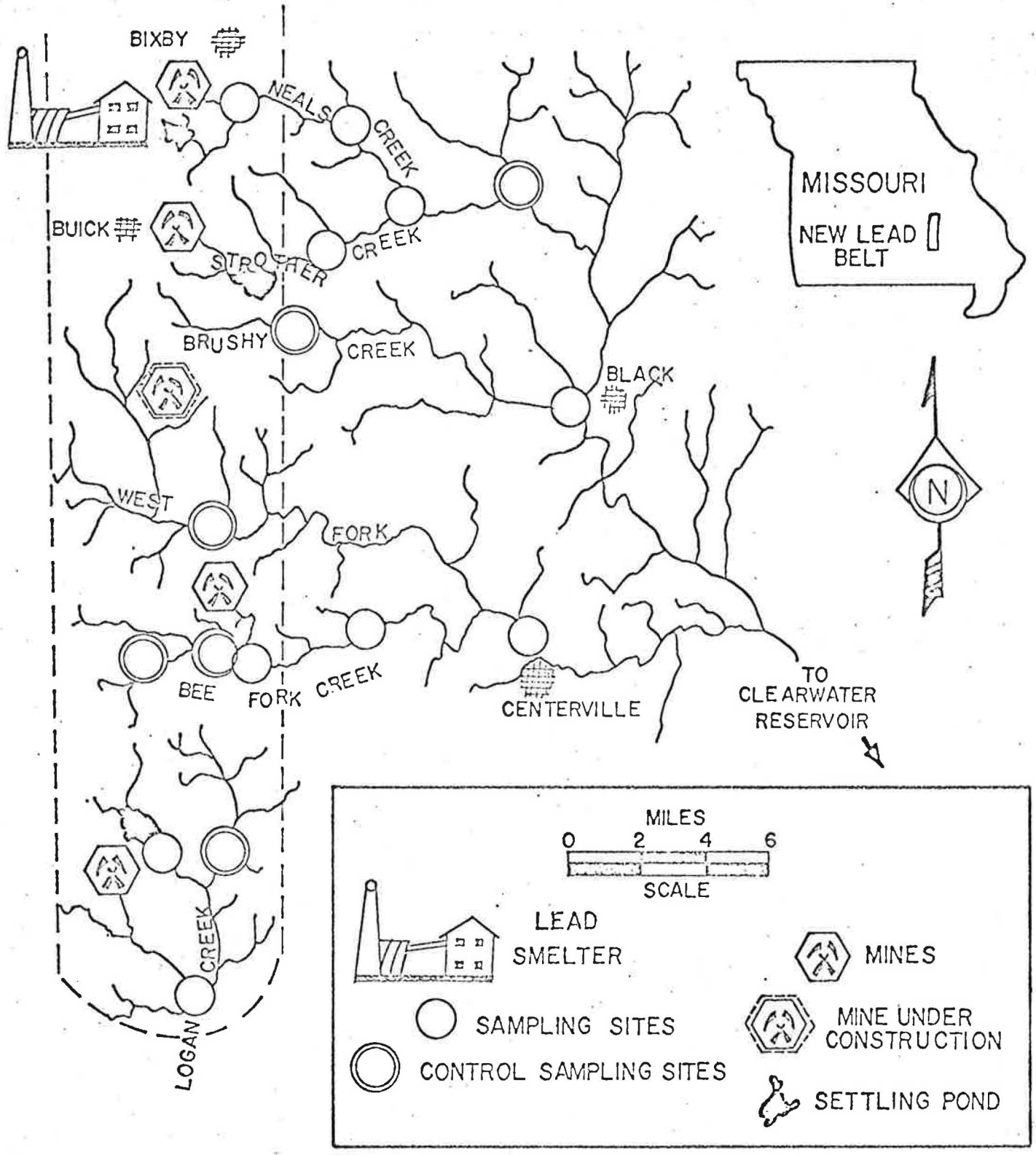


FIGURE 1

THE "NEW LEAD BELT" OF S.E. MO.

the world (Missouri Mineral News, 1971). In addition to lead, the production of ore includes zinc, copper and some silver.

SAMPLING AND ANALYTICAL METHODS

Samples were collected in polyethylene bottles. Analyses with the same number but distinguished as "a" and "b" represent samples taken in two different bottles.

The reported elements were analysed with a Perkin-Elmer 303 atomic absorption spectrophotometer. The analysis is described in greater detail in a previous report (Bolter and Tibbs, 1970b).

All samples were filtered through a 0.45 micron millipore filter on the evening of the collection day and analysed the next day.

Copper was extracted from the water with APDC/MIBK at the ambient pH of the water and then analysed by atomic absorption. The detection limit with this method is about 0.5 ppb.

Zinc and lead were determined by the "sampling boat technique". We found this method a good technique for the low level analysis of these elements in water. However, the analysis must be performed very carefully in a clean laboratory. The method, especially for zinc, is so sensitive that contamination during the analysis is always a strong possibility. Ten repetitive analyses of a 50 $\mu\text{g}/\text{l}$ zinc solution gave a standard deviation of 2.5% of peak height. For 10 repetitions of a 100 $\mu\text{g}/\text{l}$ lead standard all peaks were within 2% of the mean peak height. Detection limit for zinc is less than 0.25 ppb, for lead about 1 ppb. Zinc concentrations higher than 50 ppb were determined directly, without "sampling boat".

For the zinc analysis, the Deuterium Arc Background Compensation System (Perkin-Elmer) was used.

The other reported elements (calcium, magnesium, sodium, potassium and manganese) were determined directly by atomic absorption according to the Perkin-Elmer Standard Methods Handbook.

RETENTION PONDS

The retention ponds of two mines were selected for this investigation. In the subsequent discussion, they will be called "pond system A" and "pond system B"

Both pond systems received water from their respective mine and ore mill.

The ponds are dammed valleys. Their sizes, as noted in the following pages, are estimates from maps. Their depth, according to maps and dead trees in the ponds, probably ranges from 5-20 feet.

A. Pond System A

During the duration of this study, the system was changed. In the subsequent discussion, the system as it existed during the first half of the investigation (1970), will be called "Aa" (Fig. 2,3). The system in existence during the second part of the study (1971) will be called Ab (Fig. 4,5).

Pond System Aa

This system was sampled twice, in June (exact day unknown) and on July 21, 1970.

The system consisted of 3 ponds (pond I, II and III). The combined water from mining and milling operations passed

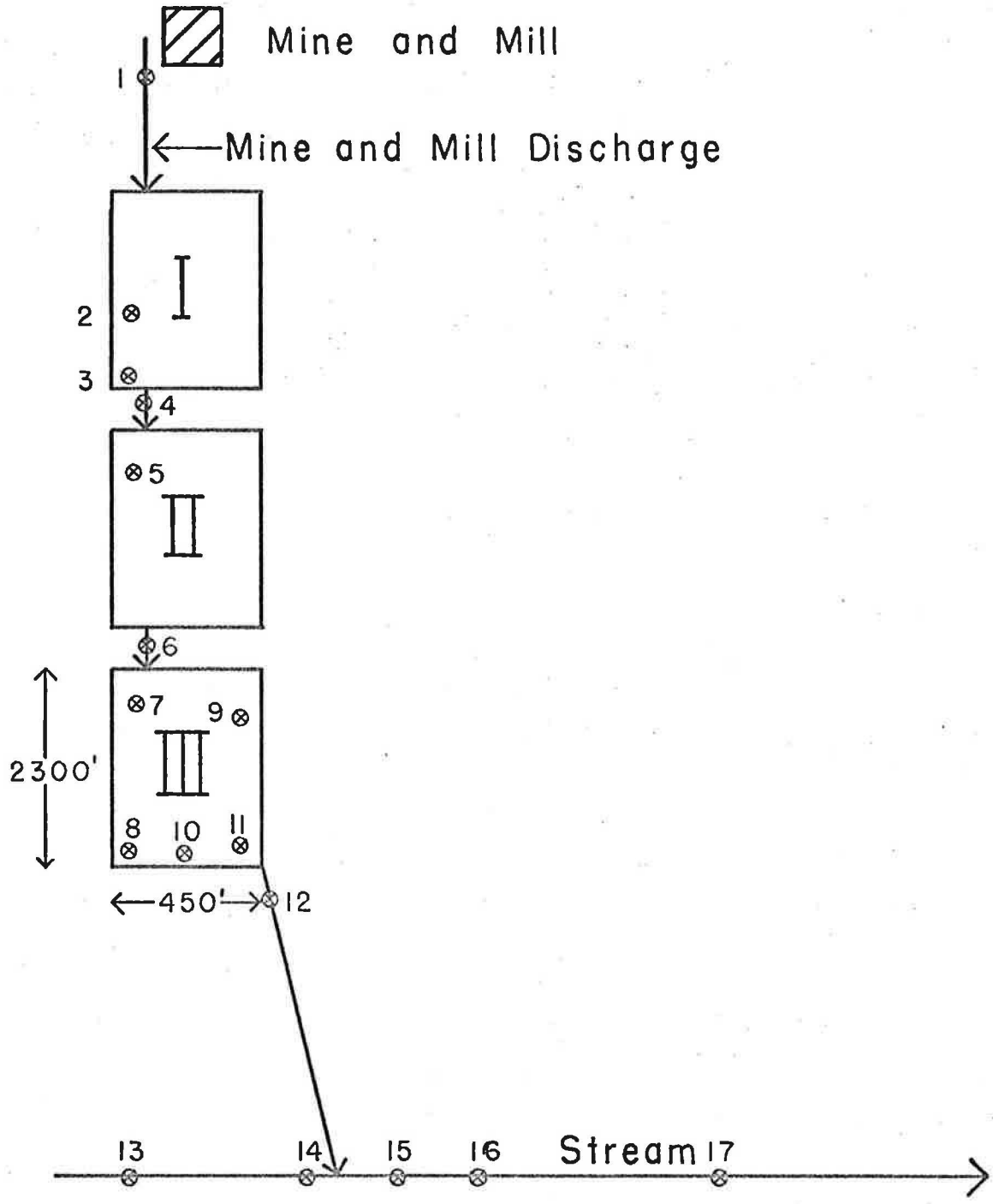


Figure 2 Pond System Aa. Sampling Stations for Table 1. Not to Scale.

TABLE 1 POND SYSTEM Aa
 Sampling Stations in Figure 2. Collected June 1970

Sta. No.	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Remarks
1	0.5	48	21	13	27.75	Mine Water
2	1	70	780	19.75	41	Pond I
3	1	61 68	970	19.5	41	Pond I
4	0.5	55	890	19.75	41	Pond I
5	1	32	390	22.5	42	Pond II
6	2.5	89 109	91	26.5	44	Pond II
7	1.5	52	56	25.75	43.5	Pond III
8	1.5	14.5 17	48	26.5	41	Pond III
9	1.5	20.5	66	25.75	42.5	Pond III
10	1	12	55	25.5	41	Pond III
11	1	15	56	25	41	Pond III
12	1.5	14	56	27	45	Pond III
13a		4	14	13	22	Stream
13b		4	14	13	22	Stream
14	2.5	3	16	13	26.5	Stream
15		9	31	23.5	39	Stream & Discharge
16a	1.5	12.5	30	26	40.5	0.5 miles
16b	1.5	10	21	26	40.5	0.5 miles
17		7	15	21	36	2 miles

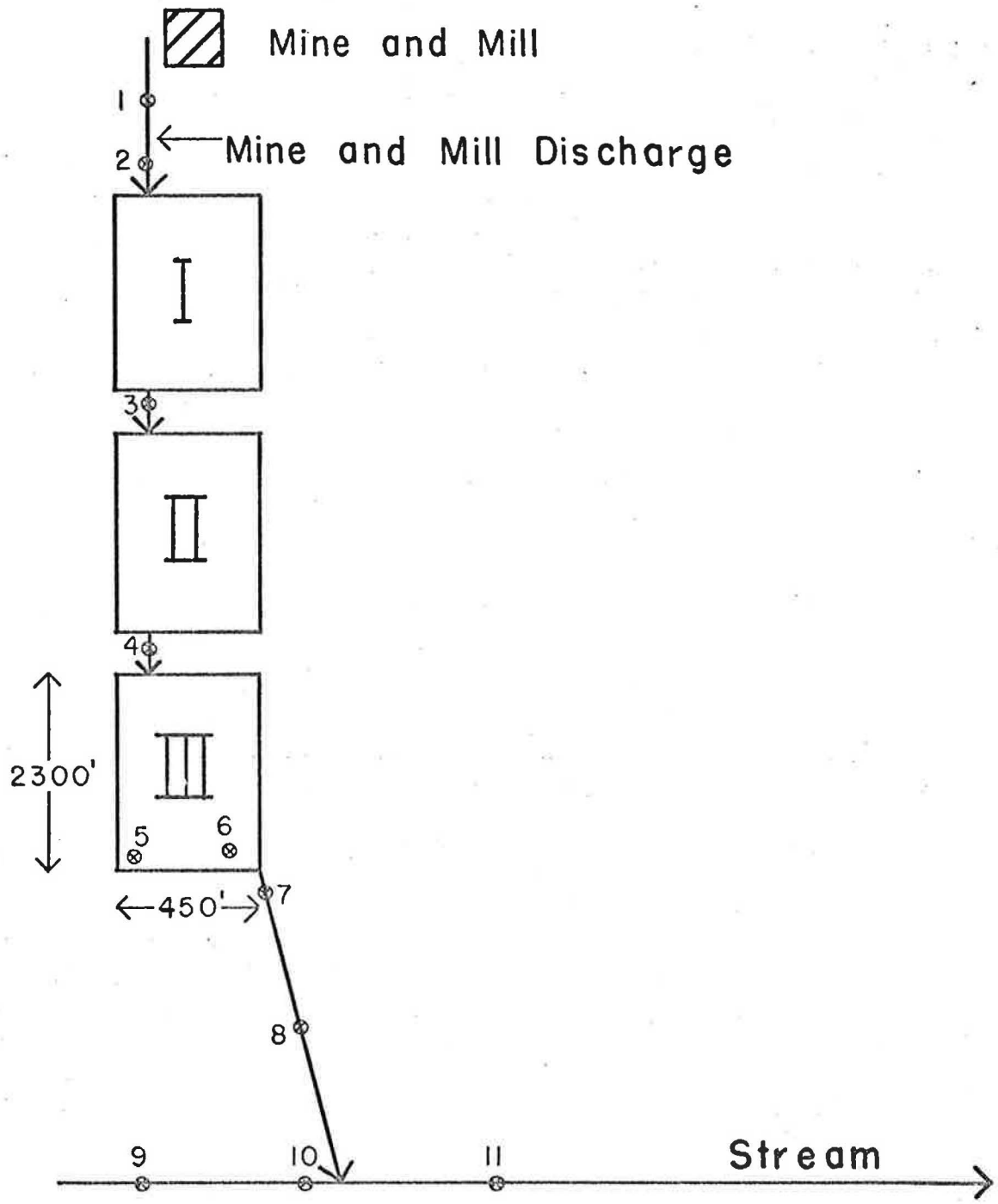


Figure 3 Pond System A. Sampling Stations for Table 2. Not to Scale.

TABLE 2 POND SYSTEM Aa
 Sampling Stations in Figure 3. Collected 7-21-70

Sta. No.	pH	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Remarks
1	7.8	65	8.0	13	29.5	Mine Water
2	7.0	40	928	22	42	Mine & Mill Water
3	7.6	96	27.0	30	46.75	Pond I exit
4	7.3	10.0	28.5	28.75	43.5	Pond II exit
5	8.0	14.0	13.0	29	38.8	Pond III
6	7.8	20.0	13.0	28	38.9	Pond III
7	7.9	21.5	11.0	29	40	Pond III exit
8	8.0	18.5	11.0	28	41.25	Pond III exit
9	7.7	12.0	8.0	15.5	25.5	Stream
10	7.4	9.5	14.0	17.5	26.5	Stream
11	7.8	9.75	11.0	28	39.75	Stream & Discharge (0.5 miles)

through all ponds in succession and was discharged to a stream from pond III (at Station #11, Fig. 2). Pond III had an estimated size of 20-25 acres. The other 2 ponds originally were of the same size, but at the time of this investigation, were partially filled with tailings.

Analytical Results (Aa)

a. Mine Water: The heavy metal content in the mine water collected from 2 effluent pipes on the surface (#1, Table 1,2) was low with less than 1 ppb copper, 48 and 65 ppb lead and 8 and 21 ppb zinc. The magnesium and calcium contents with 13 ppm and 27.75-29.5 ppm respectively are comparable to the contents in the stream (#13 a,b in Table 1 and #9 in Table 2). The pH of 7.8 is also similar to the stream water in this area.

b. Mine and Mill Water Combined: Pond I, which represents the combined effluent, has 1 ppb copper and a range of 40-96 ppb for lead (Table 1,2). However, the zinc concentrations approach 1000 ppb in some samples. At the exit of pond I (#4, Table 1), the zinc concentration is not much reduced in the samples from June, while Table 2 indicates a reduction of the zinc concentration to 27 ppb at a later date. This is probably due to the relatively small size of the pond due to the filling up with tailings and a periodic, rather than continuous, discharge of the mill water.

Of interest is the observation that the magnesium and calcium concentrations in the mill water increase significantly compared to the mine water.

In pond II, copper and lead show little change, but the zinc concentration has values below 100 ppb. Calcium and magnesium do not decrease.

The discharge from pond III shows a further reduction of the heavy metal content. The copper concentration is 1.5 ppb, the range for lead is 14-21.5 ppb and the values for zinc are 11 and 56 ppb. The values for calcium and magnesium show little reduction.

c. The Receiving Stream: The receiving stream, above the point of confluence with the mine-mill discharge, has a pH of 7.7. The concentrations for copper, lead and zinc were found to be 2.5 ppb, 3-12 ppb and 8-14 ppb respectively. The contents of calcium with 22-26.5 ppm and of magnesium with 13-17.5 ppm are similar to the mine water (Table 1,2).

The flow rate of the stream varies with season. However, an average stream flow of 1500 gallons per minute is a reasonable assumption. This compares with a mine water discharge flow rate of 4000-7000 gallons per minute.

d. Stream and Discharge after Mixing: A further reduction of the heavy metal content in the combined stream-discharge water within a relatively short distance down stream will be discussed in more detail in a later section.

Pond System Ab

This system was sampled twice, on March 17, 1971 and April 13, 1971.

a. Mine Water: Since the heavy metal content of the mine water was found to be low, it was decided not to mix mine water and mill water. In the new system, the mine water

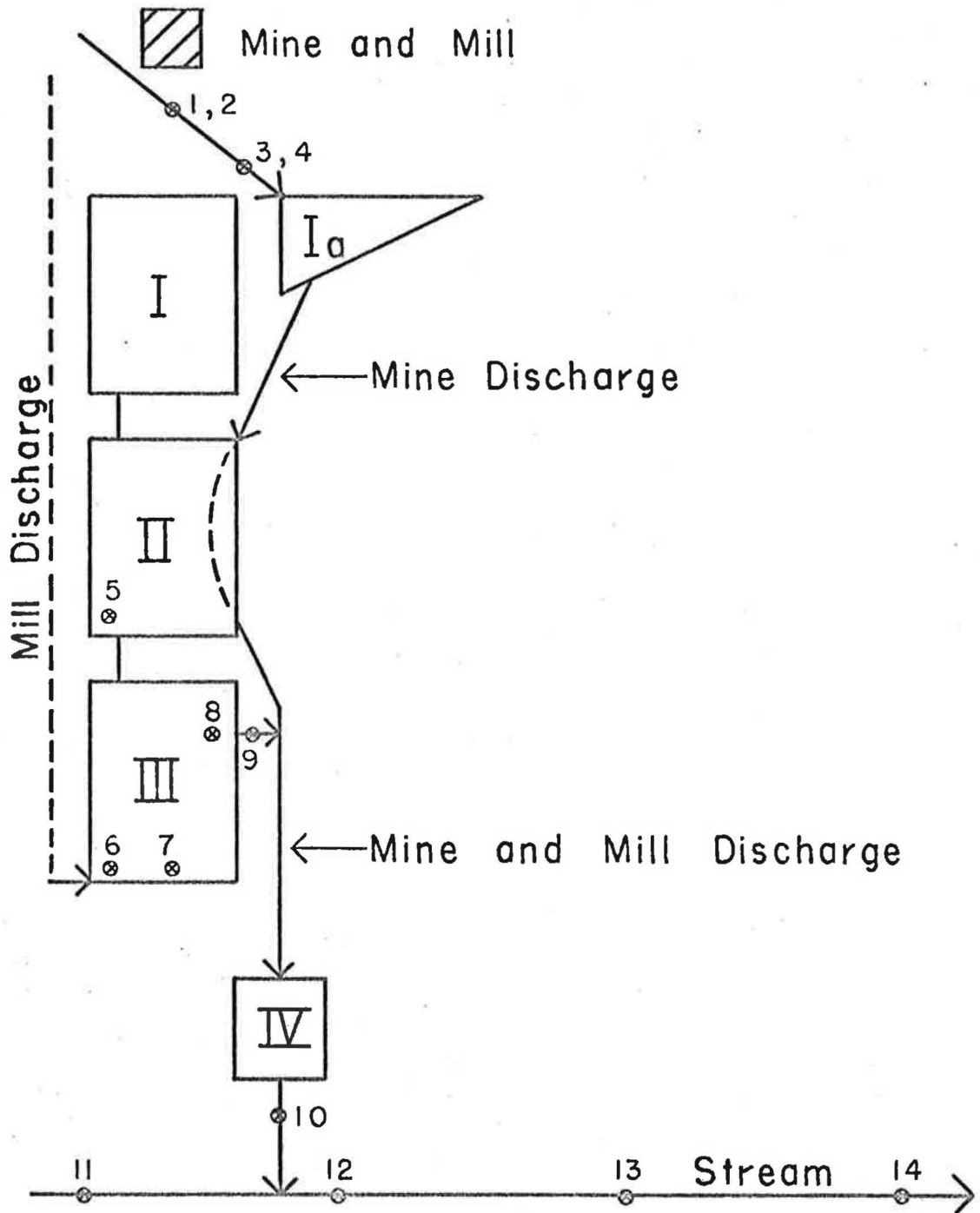


Figure 4 Pond System Ab. Sampling Stations for Table 3.
Not to Scale.

TABLE 3 POND SYSTEM Ab
 Sampling Stations in Figure 4. Collected 3-17-31

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Remarks
1		7.8	4	20	15	14	26.75	32	4.2	Mine Water
2		7.8	4	36	19	15	28.5	42	3.8	Mine Water
3	18°	7.0	720	18	2600	19.5	39.5	42	3.8	Mine & Mill Water
4			580	~10	2200					Mine & Mill Water
5	15	7.5	15	21	1400	21	40	40	4.1	Pond II
6		8.3	280	54	7.5	51	22.5	94	11	Pond III, Near Inflow
7a	14.5	8.1	8	48	27	47	49	58	8.6	Pond III
7b				48	28					18
8		8.1	13	56	14	42	45	60	8.7	Pond III, Exit
9		7.6	11	36 31	23	42	45	58	8.6	Pond III, Exit
10a	12.5	7.6	20	14 12	1150	28	41	53	5.5	Combined Effluent
10b			32	38	1200					Combined Effluent
11a	10	7.7	10	<10	16	6.5	9	0.8	0.8	Stream
11b			10	<10	24					Stream
12a	11.5	7.6	7	<10	310	13	18	14	2.5	Stream & Discharge (0.5 mi.)
12b			8	<10	310					Stream & Discharge (0.5 mi.)
13a	11.5	7.6	9	<10	215	17	25	16	2.4	2 miles Downstream
13b			8.5	<10	205					2 miles Downstream
14a	10	7.6	7	<10	90	14	22	12	2.3	4 miles Downstream
14b			8	<10	110					4 miles Downstream

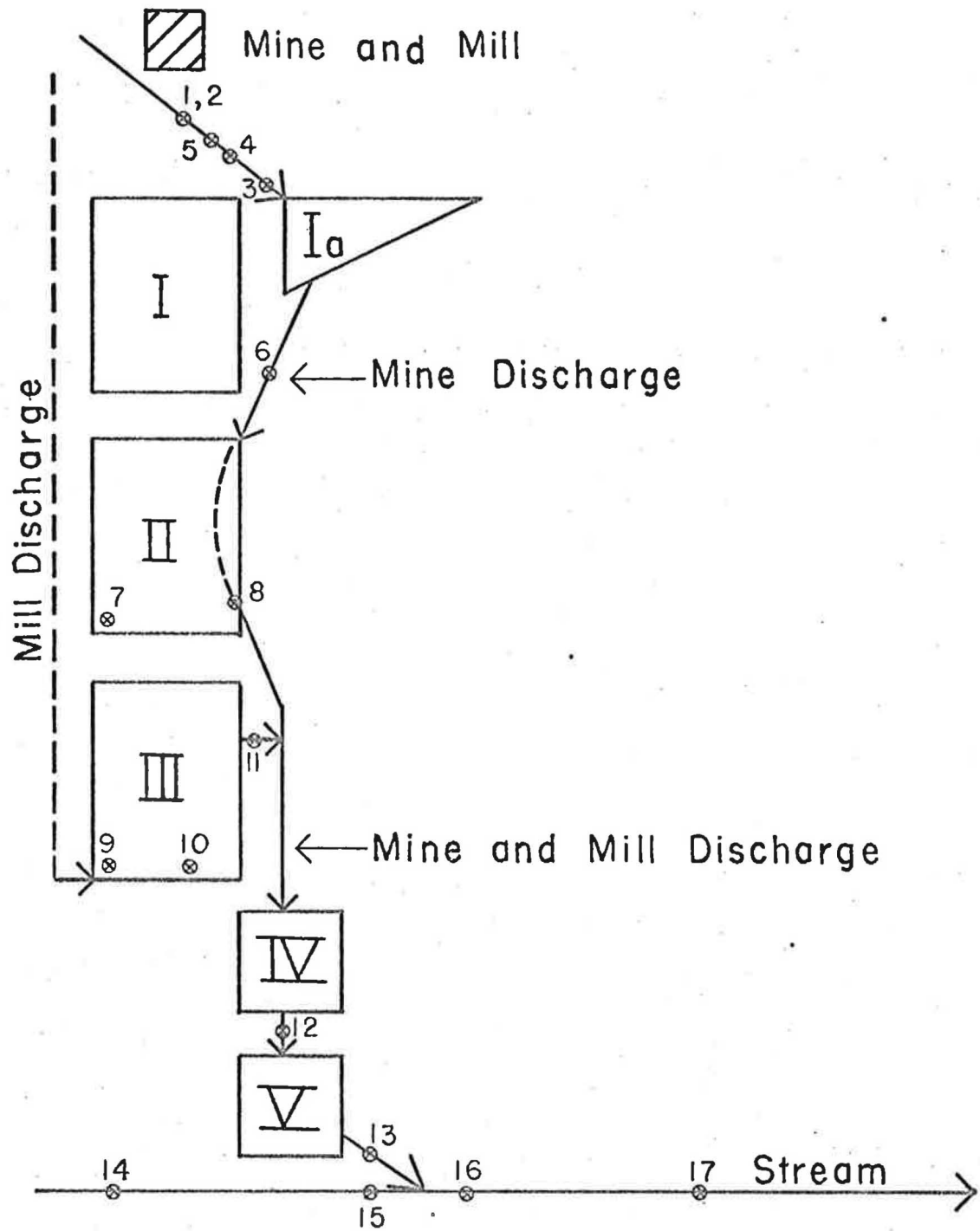


Figure 5 Pond System Ab. Sampling Stations for Table 4.
Not to Scale.

TABLE 4 POND SYSTEM Ab
 Sampling Stations in Figure 5. Collected 4-13-71

Sta. No.	pH	Cu ppb	Pb ppb	Zn ppb	Ag ppb	Cd ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Mn ppb	Remarks
1	8.1	0.5	31	22			12.0	30	52.5	3.2	<15	Mine Water
2	8.1	0.7	52.5	36			13.0	30	53.5	3.0	<15	Mine Water
3a	7.8	7.0	67	525			19.5	39	58	3.5	80	Mine & Mill
3b		11.5	75	610			19.5	39.5	58	3.6	90	Mine & Mill
4	7.9	0.7	103	80			67	66.5	100	12.4	50	Mine & Mill
5	7.6	18.5	40.5	1730			15	34.5	53.5	3.0	95	Mine & Mill
6a	8.1	2.0	⁴⁹ 69	3100			18.5	45	52.5	3.4	215	After Pond Ia
6b		2.0	³⁴ 40	3000			18.5	43.5	52.5	3.6	215	After Pond Ia
7a	8.1	1.6	245	1140			19.5	38.5	52.5	3.5	540	Pond II
7b		1.8	28	1150			18.5	38	52.5	3.4	540	Pond II
8a	8.1	1.4	27	1240			19.0	38.5	52.5	3.5	550	Pond II
8b		1.2	26.5	1260			19.0	38.5	52.5	3.4	560	Pond II
9	8.1	1.2	⁷⁵ 75	88	<1	<1	70	70	102	12.0	40	Pond III
10a	8.2	0.7	52.5	27			52.5	47	119	9.5	60	Pond III
10b		1.0	48	27			52.5	47	118	9.6	80	Pond III
11a	8.2	2.0	28	47			51.5	48	85	8.9	500	Pond III, Exit
11b		2.0	29	51			51.5	48	85	8.9	500	Pond III, Exit
12a	7.9	1.0	23	940			27	42	58	4.6	600	Pond IV, Exit
12b		1.2	17.5	940			27	41.5	58	4.6	600	Pond IV, Exit
13a	7.9	0.8	¹⁴ 14	790			26	41.5	57	4.5	475	Pond V, Exit
13b		1.0	22	800			26	42	57	4.5	460	Pond V, Exit

(Cont'd)

(Table 4 cont'd)

Sta. No.	pH	Cu ppb	Pb ppb	Zn ppb	Ag ppb	Cd ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Mn ppb	Remarks
14	8.2	<0.4	5.0	9	<1	<1	6.5	10		0.4	<15	Stream
15	8.2	0.4	3.0	24			9.0	19	7.5	0.8	~15	Stream
16	8.0	0.5	10	152			16.5	40	31	2.6	95	Stream & Discharge
17a	8.0	1.0	7.5	75			16.5	30.5	29	2.2	45	Stream & Discharge
17b		2.0	9	80			16.0	29	29	2.2	55	Stream & Discharge
18		5.0	24	6			16.0	23.5	1.5	1.1		Mine Water
19		1.2	8.5	16			9.5	22	50	2.1		Mine Water

was directed into pond Ia, a dammed side arm of former pond I. From there, it runs through the partially filled pond II, bypasses pond III and, after passing through 2 small ponds IV and V, is discharged into the stream. However, the water sampled on March 17 did not pass through pond V, since the pond was still under construction (Fig. 4,5).

Pond Ia has the function of removing suspended solids. It's size is 6 acres. However, due to the location of entrance and exit probably only a part of it is effective as far as retention time is concerned.

Ponds IV and V are smaller, with a size of about 1 acre or less. They are shallow (about 3 feet) in order to promote organic growth.

b. Mill Water: In the new system, the mill water bypassed ponds I and II and entered pond III at a point near Station #9 (Fig. 5). It leaves the pond at Station #11 (Fig. 5) and is combined with the mine water. It is planned to stop in the near future the discharge of mill water into the stream. The water will be recycled and used again for the milling operation.

c. Results: Mill water - No analysis of the mill water before it reached pond III is available. However, a sample from the pond near the point of entrance shows a pH of 8.1 and heavy metal concentrations of 75 ppb lead, 88 ppb zinc and 1.2 ppb copper. The calcium and magnesium values of 70 ppm each are high. The sodium content is 102 ppm, potassium is 12 ppm and manganese is 40 ppb (Table 4, #9, Fig. 5).

Comparison of the samples from the pond exit (Table 3, #8, and Table 4, #11) with the sample near the entrance as described above show that the content of lead and zinc is reduced approximately by half. But the reduction of magnesium, calcium, sodium and potassium is less.

Mine Water - The heavy metal concentrations in the mine water discharge are shown in Table 3 (#1,2) and Table 4 (#1,2), which are samples from two discharge pipes on the surface. Samples #18 and 19 (Table 4) represent two samples collected underground. As in previous mine water samples, the concentrations are surprisingly low, with copper being 0.5-4 ppb, lead 20-52.5 ppb and zinc 20-36 ppb.

However, samples collected between the effluent pipes and pond Ia show a much higher heavy metal content. The values range up to 720 ppb for copper, up to 103 ppb for lead and up to 3100 ppb for zinc. Inquires with company officials indicated that a small volume of water from thickener overflows in the mill was permitted to mix with the mine water. The volume of mill water (a few hundred gallons per minute or less) was considered insignificant compared to the flow of mine water (3000-7000 gallons per minute).

During the subsequent flow of the polluted mine water through the small settling ponds, the copper and lead concentrations were reduced sharply. However, the zinc concentration of the effluent before reaching the stream was still around 1000 ppb.

d. Summary: Pond system Aa, while in operation, worked well in reducing the heavy metal content of the combined

mine-mill discharge. The ponds, especially pond III, were large enough to provide enough retention time.

Pond system Ab would probably have worked well, since the mine water needs little if any reduction of the metal content. However, the three small retention ponds, while sufficient for the reduction of copper and lead, do not provide enough retention time for the removal of zinc, if water with a high metal content is permitted to mix with the mine water.

B. Pond System B

The pond system consists of a large retention pond with an estimated size of 20 acres and a small stilling basin (Fig. 6). A seasonal stream enters the pond at Station #1.

The mill water and probably some of the mine water enters the pond at Station #3. The company recycles much of the water for reuse in the mill. This water leaves the system at Station #11.

At Station #10, mine water enters the discharge stream without entering the pond.

The amount of water leaving the pond system is smaller than in pond system A. The volume depends on the rainfall, volume recycled for the mill, etc.

The pond system was sampled six times during the investigation (dates: 6-18-70, 7-14-70, 10-13-70, 1-7-71, 1-11-71, 4-13-71). During this time, the retention pond started to fill up with tailings progressing from Station #3 toward the exit stations. During the late part of the study, the discharge entering at Station #3 passed through

the tailings as a stream. The retention time of the water was probably reduced accordingly (Fig. 7,8).

During this time, the out flow pipe of the pond was moved from Station #4 to #5.

Also during the two sampling visits in January, the remaining pond was covered with ice. This probably enhanced the "channeling" of the water from entrance to exit and reduced retention time.

Results: The heavy metal content of the mine water (sample #10, Table 5,6) is relatively low, similar to the mine water of the other investigated mine.

The mill water is represented by sample #3 (Tables 5-10).

The pH of the incoming water generally ranged from 6.8-8.5. The one sample which showed a slightly acidic pH of 6.8 also has the highest copper, manganese, and especially zinc values (Table 9).

The concentration ranges in the water entering the pond (Station #3) were:

pH	6.8-8.5
Cu	31-1900 ppb
Pb	51-125 ppb
Zn	42-85000 ppb
Mn	40-2600 ppb
Mg	31.5-95 ppm
Ca	37.5-85 ppm
Na	55-98 ppm
K	5.4-22 ppm

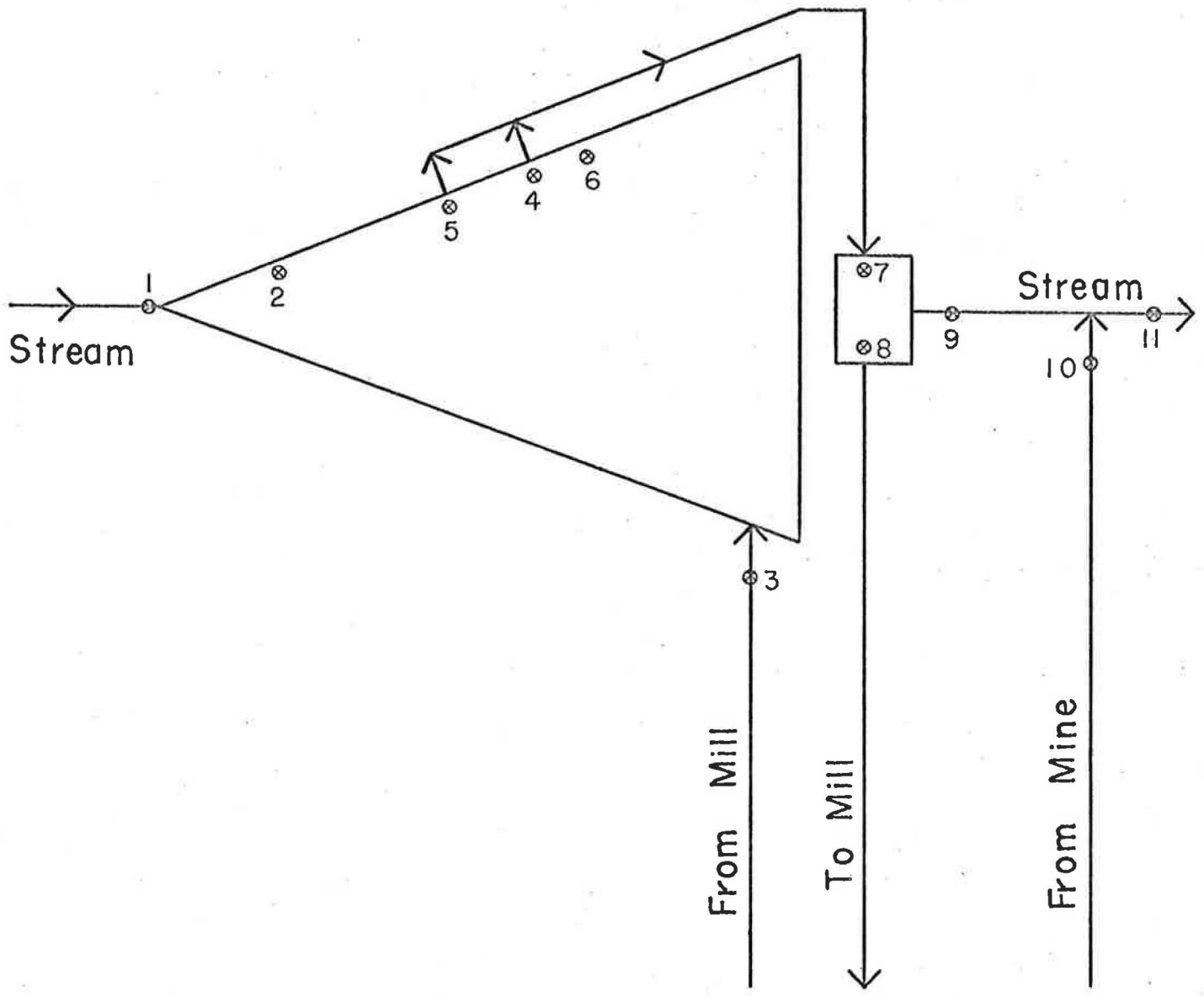


Figure 6 Pond System B. Sampling Stations for Table 5 and 6. Not to Scale.

TABLE 5 POND SYSTEM B
 Sampling Stations in Figure 6. Collected 6-18-70

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Remarks
2	28.5	7.2	5.5	20	31	21.5	27.5	Pond
3	30.5		950	51	42	68.5	85	Mill Water
4a	28.0	8.7	3.5	7.5	21	31	40	Pond, Exit
4b	28.0	8.7	5.5	5	16	27.5	41	Pond, Exit
6			3.5	9	22	32.25	41	Pond
9a	29	8.3	3.5	9	24	30	40.5	Pond Discharge
9b	29	8.3	4	14.5	20	30.5	40.5	Pond Discharge
10	26	8.2	1.5	43	36	25.75	37.5	Mine Water
11	26	8.25	2	30	28	26	37.5	Discharge from System

TABLE 6 POND SYSTEM B
 Sampling Stations in Figure 6. Collected 7-14-70

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Remarks
3	30	8.5	380	98	76	80	59	Mill Water
4	28	8.4		21.5	110	51	53	Pond, Exit
9	27	8.2		32.5	97	51	51.5	Pond Discharge
10	25	8.1		14	22	36.5	44.5	Mine Water
11	25	8.2		21	33	41.5	48	Discharge from System

The retention pond was during the early part of the investigation quite effective in reducing the metal content. Following is a comparison of the mill water entering the pond (#3) with the water discharged (#9,11, Table 5). The quality of the discharge water is compared to the water entering the pond as a stream during the wet season (samples #1, Tables 8,9,10).

	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm
mill water (entering pond)	950	51	42	68.5	85
discharge (leaving pond)	2-4	9-30	20-28	26-30.5	37.5-40.5
stream (entering pond)	1.4-2.5	5-11	19-21	1-1.5	1.5-3

The heavy metal content of the discharge leaving the pond approaches the low metal concentrations of the entering stream. The magnesium and calcium concentrations are reduced by about one half in the pond.

The data from July 14, 1970 (Table 6) show essentially the same picture.

However, subsequent sampling showed a change. Copper and lead values were still reduced in the pond, though not always to a desirable level. However, the zinc concentrations were reduced only to a small extent, permitting water with 230-430 ppb zinc to leave the pond system. This decrease in efficiency is obviously correlated with a decrease in retention time caused by the filling of the pond with tailings. Also, the freezing of the pond in January probably increased this

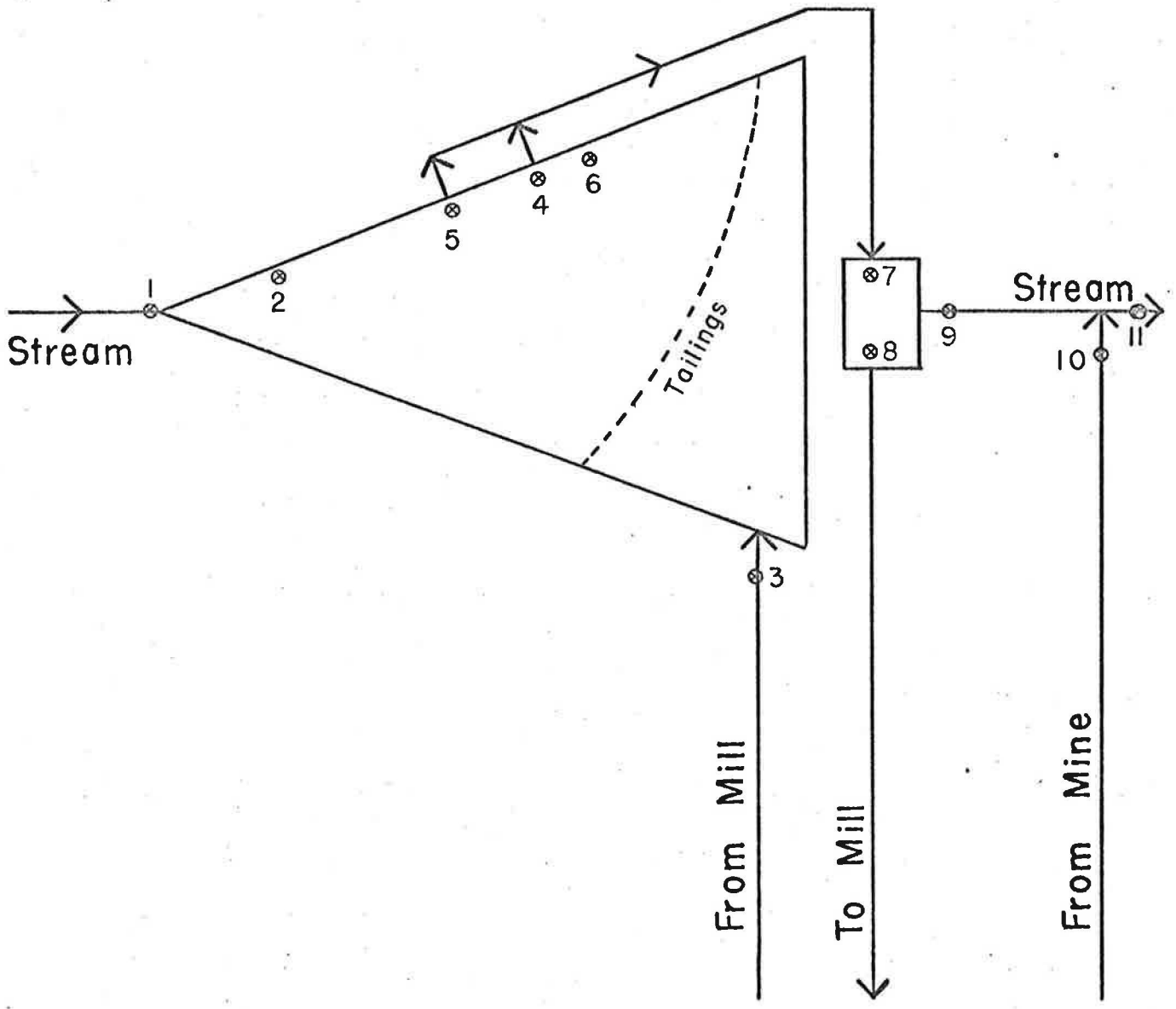


Figure 7 Pond System B. Sampling Stations for Table 7. Not to Scale.

TABLE 7 POND SYSTEM B
 Sampling Stations in Figure 7. Collected 10-30-70
 Pond Partially Filled up with Tailings.

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Remarks
3	20.0	8.3		126 124	300	57.6	53.5	Mill Water
4	17.8	8.1		187	280	58.4	51.8	Pond, Exit
9	15.0	7.6		31	280	21.7	21.9	Pond Discharge
11	15.5	7.5		34	235	21.3	21.9	Discharge from System

TABLE 8 POND SYSTEM B
 Sampling Stations in Figure 8. Collected 1-7-71

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Mn ppb	Remarks
1	8.0	8.0	2.5	<5	21 19	1.5	3.0	0.8 0.8	0.5	<20	Incoming Stream
3		8.0	1200	102	570	95	73	98	22	40	Mill Water
4	0.25	8.4	660 680	73	400	86	67	97	19.2	30 50	Pond, near Exit
5			370	32	470	64	53	76	13.5	260	Pond, near Exit
8	2.0	7.6	280	46	530	56.5	51	67	11.5	680	Small Pond
9	2.0	7.6	230 240	29	530	55	49	65	11.8	700	Discharge from Small Pond
11	0	8.1	170	26	430	48.5	44	60	10	300	Discharge from System

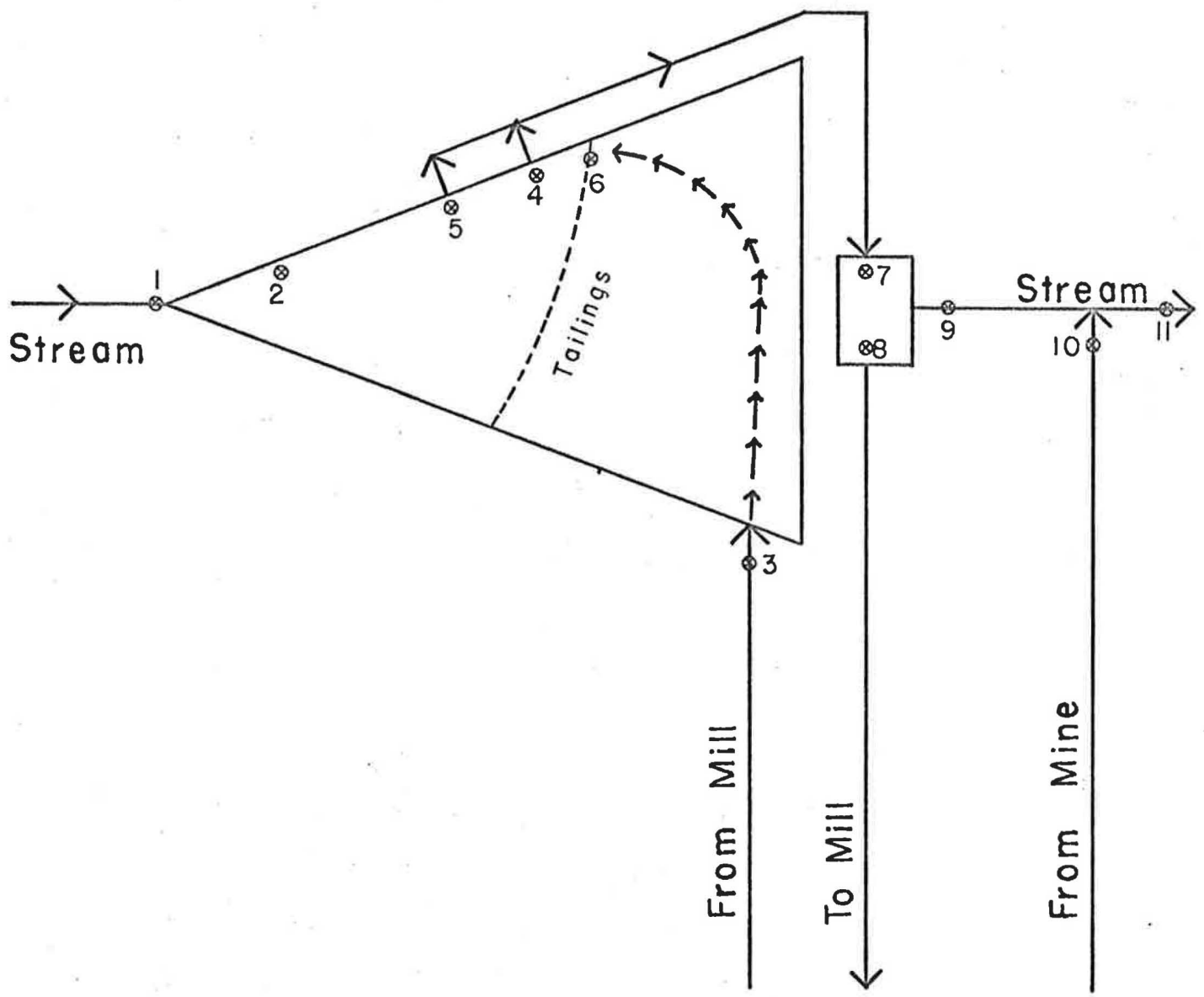


Figure 8 Pond System B. Sampling Stations for Tables 8, 9 and 10. Not to Scale.

TABLE 9 POND SYSTEM B
 Sampling Stations in Figure 8. Collected 1-11-71

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Mn ppb	Remarks
1	13.0	7.9	2.0	<5	21	1.5	2.5	1.2	0.9	<20	Incoming Stream
2	1.5	7.8	8.0	9	38.5	59	142	11.9	<0.5	140	Pond, near Stream
3	11.0	6.8	1900	64	85000	75	85	94	15.5	2640	Mill Water
4	0.5	8.2	450	72	310	52.5	46	72	10.0	140	Pond, near Exit
5	0.5	8.0	7.5	26	120	7.3	7.5	6.2	0.6	80	Pond, Exit
7	2.75	7.7	140	56	430	38.5	34	56	5.6	480	Small Pond
8	2.75	7.4	110 120	59	380	37.5	32.5	51	6.9	340	Small Pond
9	2.75	7.7	100	50	320	37.5	32.5	51	6.9	540	Small Pond Exit
11	3.0	8.0	60	13	320	35	32.5	55	5.6	1060	Discharge from System

TABLE 10 POND SYSTEM B
 Sampling Stations in Figure 8. Collected 4-13-71

Sta. No.	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Mn ppb	Cd ppb	Ag ppb	Remarks
1a	8.1	1.7	8.5		1.0	1.5	5	0.6				Incoming Stream
1b		1.4	11	20	1.0	1.5	3.8	0.7	<15			Incoming Stream
2a	8.0	50	53	210	33	33	43	6.2	315			Pond, near Stream
2b		45	48	222	33	34.5	43	6.2	320			Pond, near Stream
3	7.9	31	98	328	31.5	37.5	55	5.4	450			Mill Water
4	8.1	26	97	134	40.5	43	70	8.3	40			Pond, near Exit
5a	8.1	62	68	250	34.5	35	45	6.7	265			Pond, Exit
5b		77	59	258	34	34.5	45	6.8	250			Pond, Exit
7a	7.9	60	76		33.5	37	47	6.3				Small Pond
7b		56	80	310	33.5	35.5	46	6.5	595			Small Pond
8a	7.9	56	80	298	33.5	35.5	47	6.7	570			Small Pond
8b		70	81	310	34	36	47	7.2	585			Small Pond
9a	7.7	56	75	292	34.5	35.5	47	7.0	585			Small Pond, Exit
9b		67	83	310	34.5	35.5	47	7.2	585			Small Pond, Exit
11a	8.2	51	55	230	33	35.5	45	6.8	710	<1	<1	Small Pond, Exit
11b		45	70	226	33	35.5	44	6.2				Small Pond, Exit

effect. The out flow pipe from the pond (Station #4, later on #5) is in a location which does not utilize most of the remaining pond for retention.

Presumably, the retention efficiency of the pond can be restored by relocating the outflow pipe towards the area of Station #1.

REDUCTION OF HEAVY METALS IN STREAMS

A previous investigation (Bolter and Tibbs 1970b) had shown that the mining-milling discharge raised the heavy metal contents of a stream on the average by a factor of 2-3. Samples collected at distances below the point of confluence of stream and discharge water showed a marked decrease in heavy metal concentrations. This suggested a "self-cleaning capacity" of the streams.

Table 11 shows the average of our stream water data over a period of 2 years before the start of this project from the stream which receives the discharge from pond system A. The relatively high copper concentrations reflect data obtained before the installation of a copper circuit in the mill.

Since during the duration of the present project the zinc concentrations in the discharge water increased, the sampling of the stream was repeated.

Table 12 shows the metal content of the stream to a distance of 4 miles from the point of confluence of stream and mine discharge.

The same data for Zn, Mn, Ca, Mg and Na are also presented in Fig. 9.

TABLE 11 Average of 2 Years Data (Prior to This Project) for Cu, Pb and Zn in Stream Water, Mine-Mill Discharge and in Water Downstream from Point of Confluence. Mill-Mine Discharge from Pond System A.

Sta. No.	Cu ppb	Pb ppb	Zn ppb	Miles	Remarks
A	6.4	5.8	7.3	0.5	Upstream
B	30.6	14.4	12.2		Mine & Mill Discharge
C	17.4	15.3	15.9	0.1	Downstream
E	7.4	9.1	14.1	2	Downstream

TABLE 12 Chemical Composition of Stream Water, Mine-Mill Discharge and Stream Water Downstream from Point of Confluence. Discharge from Pond System A. Collected 1-11-71.

Sta. No.	T°C	pH	Cu ppb	Pb ppb	Zn ppb	Mg ppm	Ca ppm	Na ppm	K ppm	Mn ppb	Mi.	Remarks
A	4.0	7.8	1.5	<5	8	6.0	10.5	<1	<1	30	0.5	Upstream
			1.3	<5	19.5	5.5	9.5	<1	<1	<20		
B	4.75	7.6	4.5	22	580	25.0	42.0	115	14.5	540		Mine & Mill Discharge
			6.0	22	550	26.0	41.5	116	14.5	540		
D	4.5	7.6	2.5	9	200	14.5	23.5	51	4.5	220	1	Downstream
			3.0	9	200	15.5	24.0	53	3.5	220		
E	5.0	7.7	5.0	<5	240	15.0	25.0	48.5	7.0	180	2	Downstream
			2.5	<5	200	16.0	26.5	49.5	4.0	160		
F	5.5	7.7	4.0	10	51	15.0	25.0	39.0	3.0	50	4	Downstream

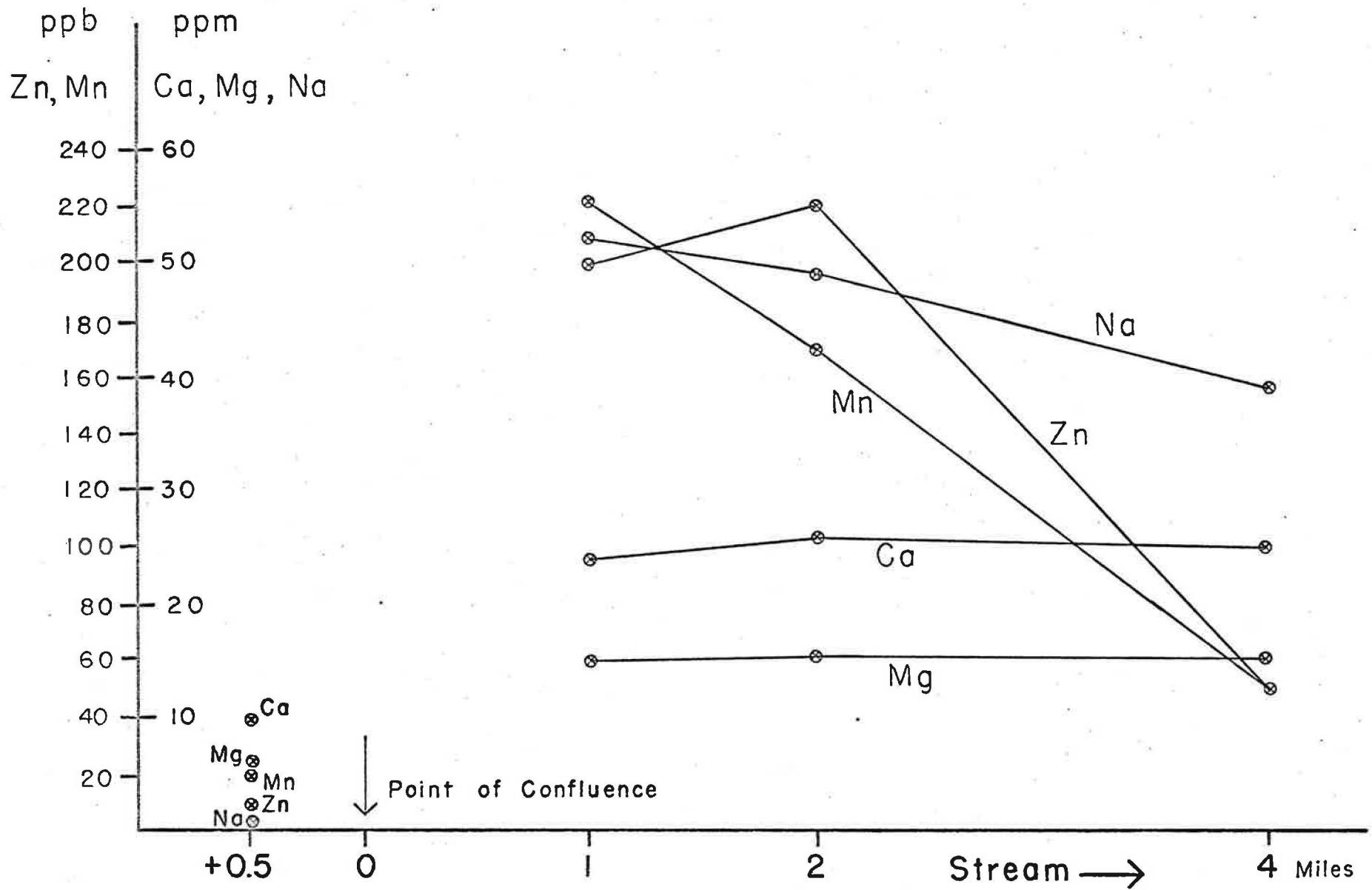


Figure 9 Concentrations of Some Elements Downstream from the Point of Confluence of Stream and Mine-Mill Discharge.

Zinc, which has a high level of 200-220 ppb at 1 and 2 miles distance from the point of confluence is reduced to 51 ppb at 4 miles distance.

A possible explanation for the reduction of the zinc content could be dilution of the metal rich stream by spring water or by tributaries with low zinc content, especially during the wet winter season. We know of no major source of water for dilution. However, the stream is not easily accessible between sampling stations. Some dilution by spring water is therefore possible in this somewhat karst area.

Removal of zinc by precipitation or adsorption is probably the more important process. Our previous data, especially from the dry summer season, when dilution should be small, support this. More instructive are the values for calcium, magnesium, sodium and potassium. The concentrations of these elements in the stream waters and probably spring waters of the region are low compared to their concentrations in the mill effluent. They can therefore be used as internal standards. The reduction of sodium and potassium over a 4 mile distance is small compared to zinc. The concentrations of magnesium and calcium do not decrease at all after they have reached their highest values (Fig. 9). If dilution would be an important factor in the lowering of the zinc values, these elements should be affected also.

Manganese tends to follow zinc closely.

DISCUSSION

The results show that under the geochemical conditions which exist in the mine and surface waters of the "New Lead Belt", removal of excess heavy metals from mill water is possible. A

critical factor in their removal is obviously the retention time. We have no exact measurements of retention times of the investigated ponds, but ponds with a size of about 20 acres and 5-15 feet depth were sufficient to reduce the zinc content. Reduction of lead and copper was even effective in ponds with sharply reduced size, as can be seen in the results of the second half of the study.

Previous experiments in the laboratory have shown, that when excess heavy metals are added to the stream water, the heavy metals are precipitated as carbonates (Handler 1969). This indicates, that the relatively high pH and the concentration of dissolved carbonate create conditions which are favorable for the precipitation of the heavy metals. This is not surprising considering the fact that the rocks of the area consist mainly of limestones and dolomites.

However, as other investigations show, a certain amount of heavy metals is transported down stream in form of metal-rich rockflower and possibly finely ground ore minerals. The stream bottoms consist of coarse gravel. Fine sized tailings therefore vanish in the openings of the gravel. However, the mill effluents produce an intensive growth of algae in the receiving streams, probably caused by organic reagents used in the milling process. This algae growth catches some of the transported tailings material. Analysis of the material shows heavy metal concentrations of .001-1%, (Handler 1969). The retention ponds should normally permit the rockflower to settle out before reaching the streams. Apparently the ponds are not entirely effective with regard to removal of solids.

Interesting is the observation that the milling process increases the contents of calcium, magnesium, sodium and potassium in the mine and stream waters. Since these elements are not easily removed from solution, they can serve as internal standards. Their concentrations can be used to estimate the amount of mill water in streams, the degree of dilution of a polluted stream by clean water, etc.

In spite of the fact that excess heavy metals can be removed in the retention ponds, our investigation shows two cases where relatively high concentrations of zinc reached the streams. This was due to carelessness or lack of knowledge. The two described cases probably represent the two possibilities which exist in this area for heavy metal pollution of the streams. In the first case, a small volume of water with a high metal content was permitted to contaminate a large body of clean water. The amount of polluting water was considered too insignificant to do any damage. In the second case, a retention pond of sufficient size was permitted to fill up with tailings, thus reducing its size and retention time considerably.

In both cases of pollution the solutions fortunately are rather simple.

CONCLUSIONS

(1) The concentrations of heavy metals in the mine waters of the "New Lead Belt" of SE Missouri are surprisingly low and do not constitute a major source of stream pollution.

(2) The high heavy metal content of mill water can be reduced sufficiently by passing the water through retention ponds of sufficient size and retention time.

(3) The mine-mill discharge water must be analysed frequently to detect a reduction of the retention time in the ponds.

(4) High concentrations of copper and lead can be reduced even in relatively small ponds. In order to reduce high zinc contents relatively large ponds are necessary.

(5) The mill water contains much higher concentrations of calcium, magnesium, sodium and potassium than the mine and stream water. These elements can therefore be used to trace the mill water in the streams.

ACKNOWLEDGEMENT

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