Heavy Metal Analysis of Dillon Reservoir,

Central Colorado

A Thesis

Presented in Partial Fulfilment of the Requirements

for the Degree of Bachelor of Science

By

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INTRODUCTION

The extraction of mineral resources is usually accompanied by secondary impacts that could result in environmental pollution or degradation of other resources. One of these resources that can be impacted is surface water and the associated sediments. This impact could be particularly important in reservoirs that are used for public water supplies and sport fishing. Dillon Reservoir (fig. 1), central Colorado, represents an area where this problem has developed; it is the area of study for this project.

Dillon Reservoir serves as Denver's water supply and is fed by streams from several mining areas. Included in the study is the Frisco Bay arm of the reservoir which is fed by Tenmile Creek. The Climax Molybdenum mine is approximately 14-15 miles southwest of the point where Tenmile Creek empties into Dillon Reservoir. Also included in the study is the Blue River Arm, fed by the Blue River which encounters many mining areas and dredge tailings along its path. The Breckenridge mining district is approximately 6.5 miles from the reservoir along the Blue River. Dillon Reservoir represents an ideal opportunity to investigate the impact of metal mining on water resources in the drainage basin.

The purpose of this study was to determine heavy metal concentrations and their areal distribution in bottom sediments of two arms of Dillon Reservoir, Colorado, and to relate these data to possible sources within the respective drainage basins.

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As indicated by Table 1, mining has played an important role in the economy of Colorado.

Table 1.   Selected Mineral Resource Production for Colorado

Metallics	1973 Production	Cumulative Production
Zinc	$15,890,102	$535,718,983
Silver	8,764,824	643,491,318
Lead	7,596,107	407,419,390
Copper	3,312,705	142,999,979

The county (Summit) in which the study area is located produced $2,010,115 (1973) in mineral production including metallics and nonmetallics.

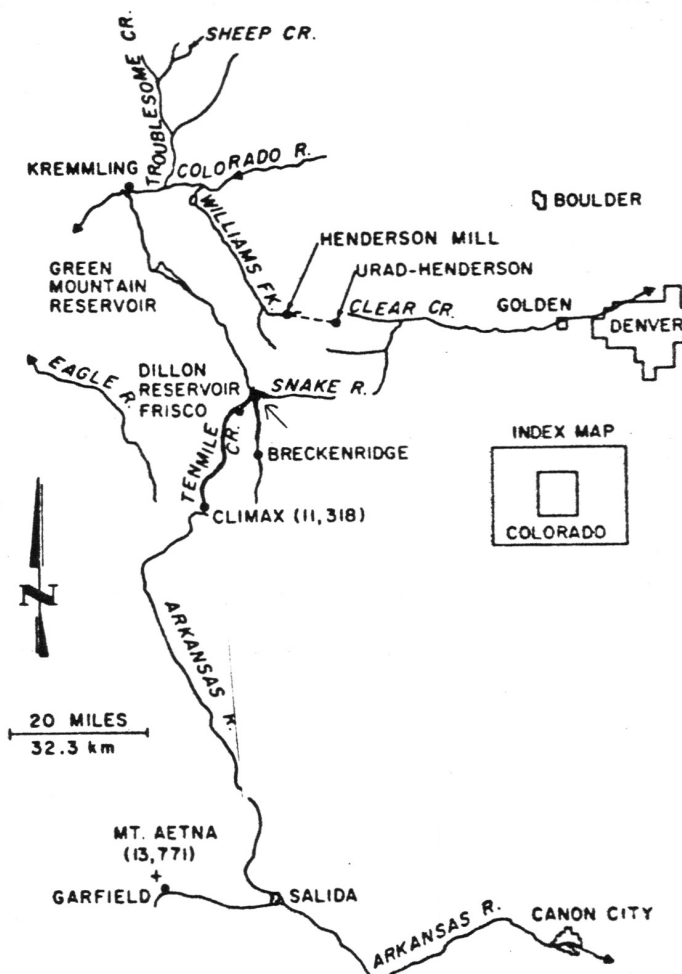Source: Summary of mineral industry activities in Colorado 1973: Colorado Division of Mines.

Fig.(1) Dillon Reservoir in Central Colorado, 60 miles west of Denver.

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Mining and its Impact in Colorado

The non-sedimentary metal deposits of Colorado are generally considered to be of three distinct ages (Tweto, 1968): Precambrian, late Cretaceous to early Tertiary (Laramide), and Oligocene (post Laramide). The majority of the metallic ores being mined in Colorado are termed "complex ores" (U.S. Congress, 1964, p. 29). According to Wentz (1973), complex ores are a combination of base metals (usually copper, lead, and zinc) and precious metals (gold and silver). The base metals and silver occur most commonly as sulfides, with all of the gold and some of the silver occuring in elemental form.

Large-scale metallic mineralization of central Colorado and the resultant mining of these resources presents a potential for pollution problems in that area of the state (fig. 2). Studies by Wentz (1973) have shown that the pollution due to the mineralization is compounded because of oxidation of pyritic material. Not only is the acid that forms harmful in itself, it also dissolves metals from ores and tailing piles and releases them to streams.

Runnells, et al., (1974) have found through analysis of sediments from Tenmile Creek below the Climax mine, that concentrations of molybdenum up to nearly 2,000 ppm. are present. These analyses stand in sharp contrast to what was considered normal background concentrations (between about 1 and 10 ppb.) in Runnells' study.

Geology of the Dillon Reservoir Area

Blue River near Breckenridge is affected by drainage from several mines. Extensive tailings are also located in the area, but most are the result of placer activity and

probably do not significantly contribute to the degredation
of the surface water (Wentz, 1973). At Breckenridge, load
ores have been mined from veins in Precambrian schist, gneiss,
and granite, and from Paleozoic and Mesozoic sedimentary rocks
(Vanderwilt, 1947).

At Climax, Precambrian schist, granite, and gneiss are
intruded by dikes and at least one large stock of Tertiary
age (Vanderwilt, 1947, Del Rio, 1960). The largest molyb-
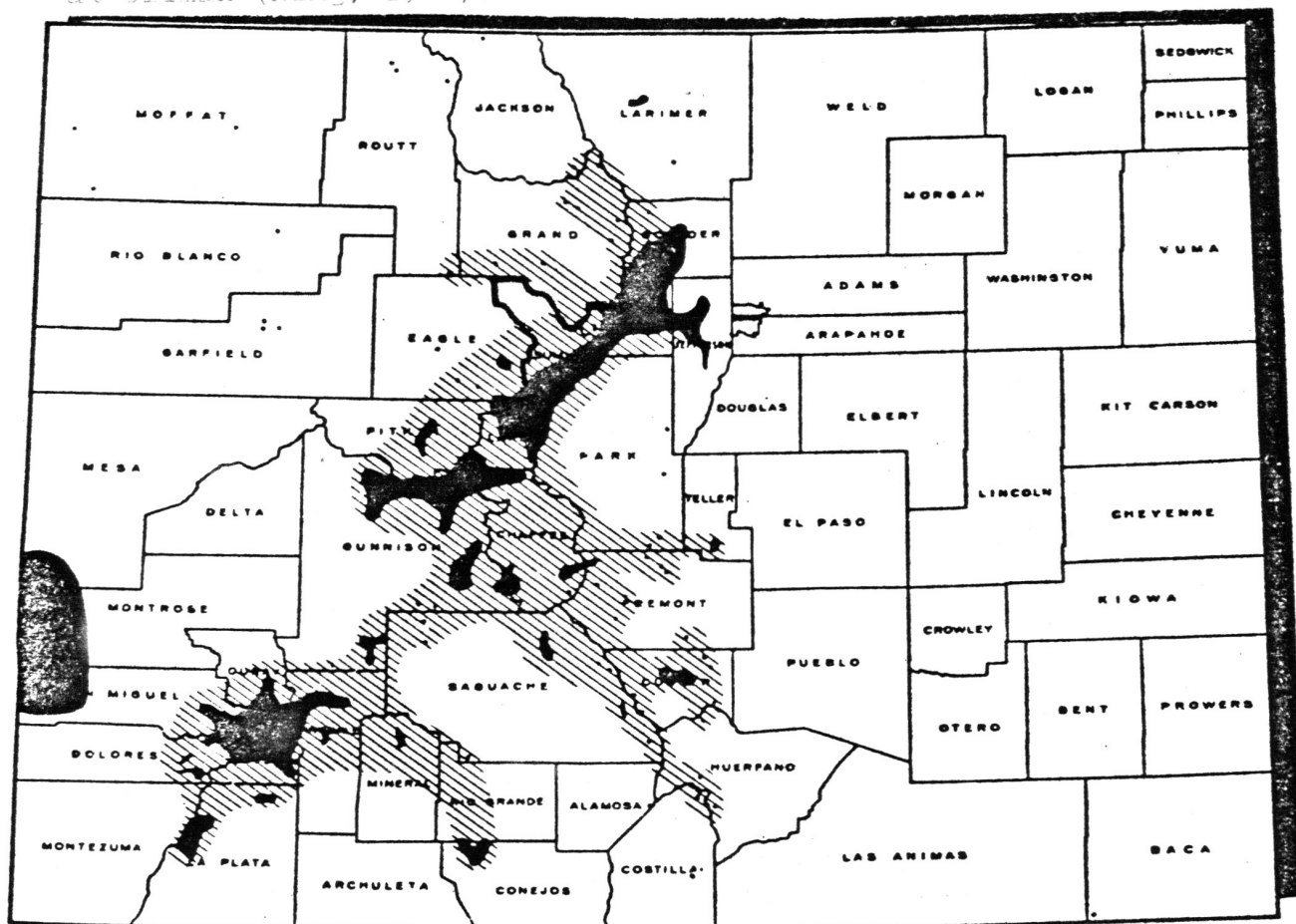denum deposits in the U.S. and possibly in the world occur
at Climax (King, 1964).

Fig. (2). Metallic mineral occurences in Colorado. The black
represents metallic mining districts and areas of mineralization.
The hachures represent the extent of possible mineralization
adjacent to the Colorado mineral belt. (after Shelton, 1977).

SAMPLING METHODS

Sediment samples were collected by Dr. Garry D. McKenzie and Dr. Douglas E. Pride in August 1979 with use of a 12" sampler tube (fig. 3). The samples were put in plastic bags and the collection sites were recorded on rough sketches of the study areas (figs. 5 and 6). The samples were stored in a refrigerator until analysis.

Fig. (3). Sampler Tube
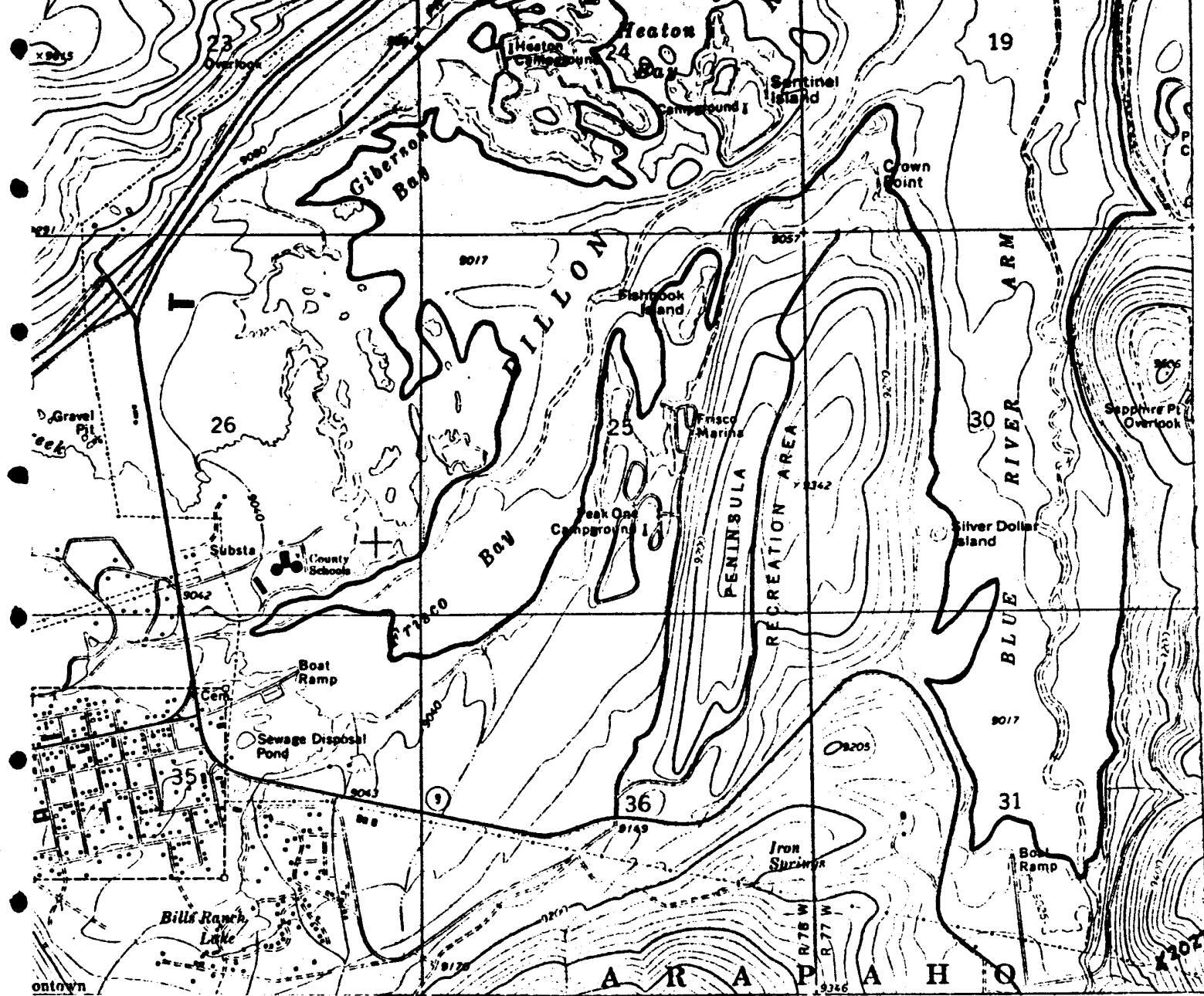
SCALE 1:24000
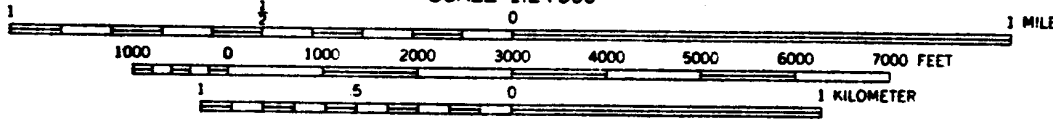
CONTOUR INTERVAL 40 FEET
DATUM IS MEAN SEA LEVEL

FRISCO, COLO.
SE/4 DILLON 15' QUADRANGLE
N3930—W10600/7.5

1970

COLORADO

QUADRANGLE LOCATION
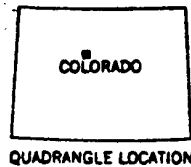
Fig. (4). Frisco Bay and Blue River arms of Dillon Reservoir.

·8,9   · 10,11

·12

· 13,14

·3,4
23,24

· 2,3
21,22

· 6,7,25

· 1,20

approximately
6.5 miles to
Breckenridge dredge
tailings.

approximate scale 1"=250'
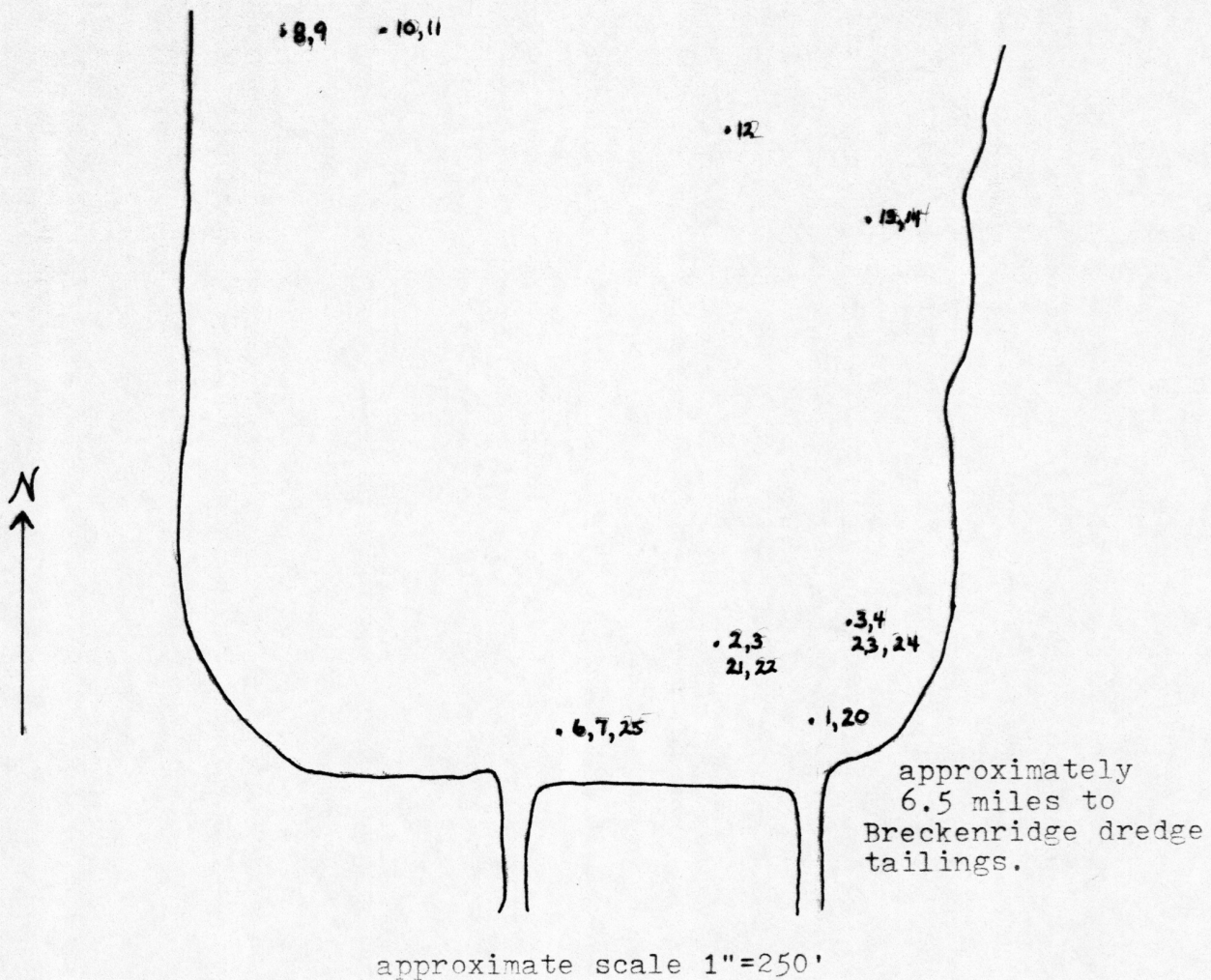
Fig. (5). Sketch of the Blue River Arm sampling sites.

14 miles to
Climax

⊘ 15,16   ⊷ 17,18   ⊷ 19

Tenmile Creek

N
↑
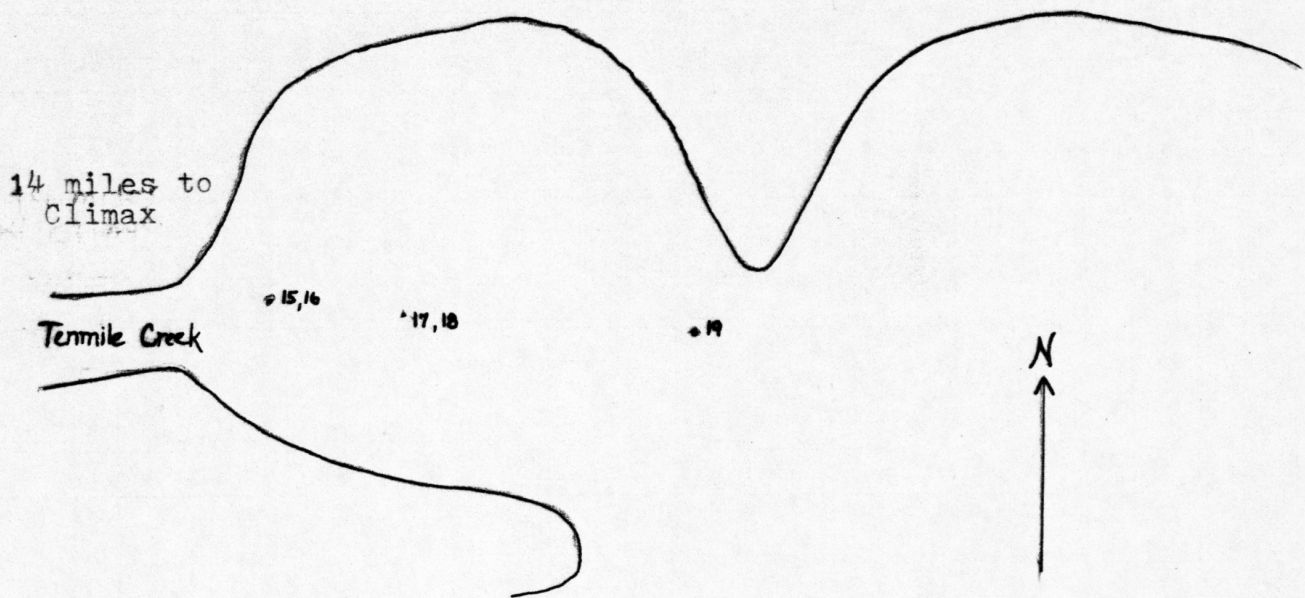
approximate scale 1"=100'

Fig. (6). Sketch of the Frisco Bay Arm sampling sites.

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LABORATORY PROCEDURES

Two portions of approximately 0.5 grams of sediments were taken from each sample, one portion for organic analysis and the other for atomic absorption analysis. The samples were put in crucibles and then heated overnight in a Precision Thelco 18 oven. After drying, each sample was weighed to four decimal places. For accuracy five extra samples representing the first five collection sites were prepared for both organic and atomic absorption analysis.

Organic Analysis

Hydrogen peroxide (30%) was added to each sample in increments of about 1 ml. per. Small additions of hydrogen peroxide were necessary to avoid spattering of a sample with a high organic content. Whereas most samples required 4-6 mls. to digest the organic material, others necessitated up to 11 mls. After the reactions had gone to completion the crucibles were placed on a hot plate until all liquid was evaporated. The samples were then left in the Thelco 18 oven overnight to insure dryness. The crucibles and samples were reweighed and the organic weight percent was determined according to the following formulae:

$$\% \text{ inorganics} = \frac{\text{sample weight (dry)} - \text{organics}}{\text{sample weight (dry)} + \text{organics}}$$

$$\% \text{ organics} = 100\% - \text{inorganics}$$

Preparation for Atomic Absorption Analysis

Four ml. of nitric-percloric (HNO$_3$ as buffer) were added to each sample and digested at medium heat for three hours. After three hours the temperature was increased and the acid mixture was evaporated. The metals in the samples were then taken into solution with 10 ml. of 1 M HCl and digested for about thirty minutes making sure that none of the liquid was allowed to evaporate. The liquid and residue were washed from the crucibles into filter paper in separate 150-ml. beakers. The crucibles were rinsed three times with double-distilled demineralized water and the liquid was transfered to 50-ml. volumetric flasks and diluted to volume with 10% HCl.

Preparation of Standard Solutions for Atomic Absorption Analysis

Solutions of 20, 10, 5, 2, and 1 ppm were diluted from a stock solution of 1000 ppm for each metal to be determined.

.* Two "blank" specimens were prepared without any solid sample. These were used to determine the concentration of metals within the acids themselves and subtracted from the sample concentrations,

Standard Curve

Values of absorbance were obtained through use of a model 303 Perkin-Elmer Atomic Absorption Spectrophotometer. A standard "working curve" for each metal was obtained by plotting absorbance versus concentration (ppm.) of the standard 20, 10, 5, 2, and 1 ppm. solutions. The absorbance value of each sample was found on the Y axis and projected horizontally to the intersection of the standard curve. The point of intersection is then projected vertically to the

X axis and a concentration value is found. The concentration (ppm.) of each sample is then determined through use of this equation:

$$\text{element (ppm.)} = \frac{\begin{array}{c}\text{(concentration in sample solution)}\\ \text{X}\\ \text{(volume of dilute sample solution)}\end{array}}{\text{weight of sample (grams)}}$$

$$*\text{element (ppm.)} = \frac{\begin{array}{c}\text{(dilution factor)}\\ \text{X}\\ \text{(concentration in sample solution)}\\ \text{X}\\ \text{(volume of dilute sample solution)}\end{array}}{\text{weight of sample (grams)}}$$

*equation used for zinc only

Absorbance vs. Concentration
Ag
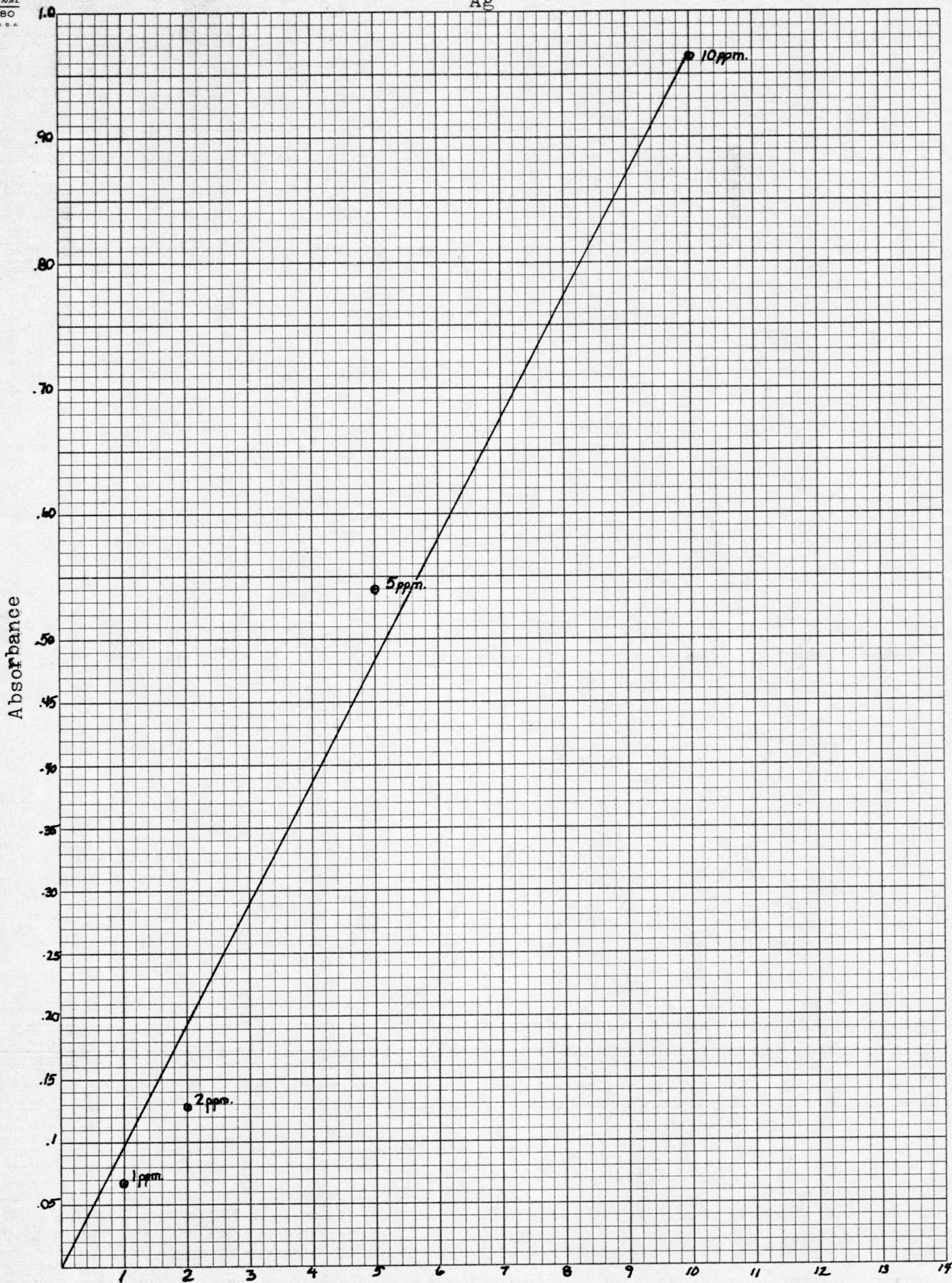
Absorbance vs. Concentration
Cu

Absorbance (y-axis): .020, .0400, .0600, .0800, .1000, .2000, .3000

Concentration (ppm.) (x-axis): 2, 4, 6, 8, 10, 12, 14, 16, 18, 20

Data points: 1 ppm, 2 ppm, 5 ppm, 10 ppm, 20 ppm

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Absorbance vs. Concentration
Pb

Absorbance

Concentration (ppm.)

10 Squares to the Inch
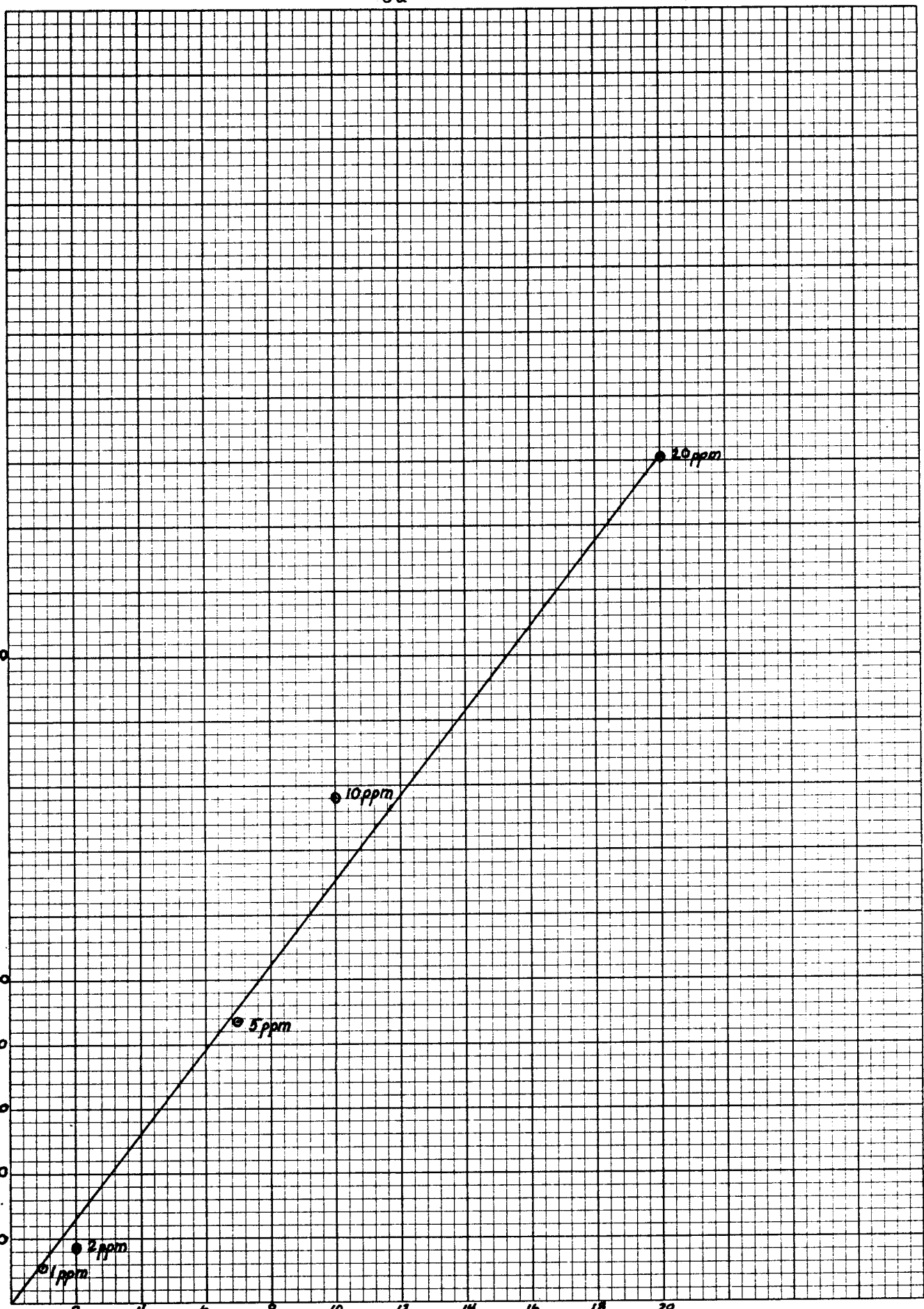
.1000
.0900
.0800
.0700
.0600
.05
.0400
.0350
.0300
.0250
.0200
.0150
.0100
.0050

20 ppm
10 ppm
0.5 ppm
2 ppm
0.1 ppm

2 4 6 8 10 12 14 16 18 20

14
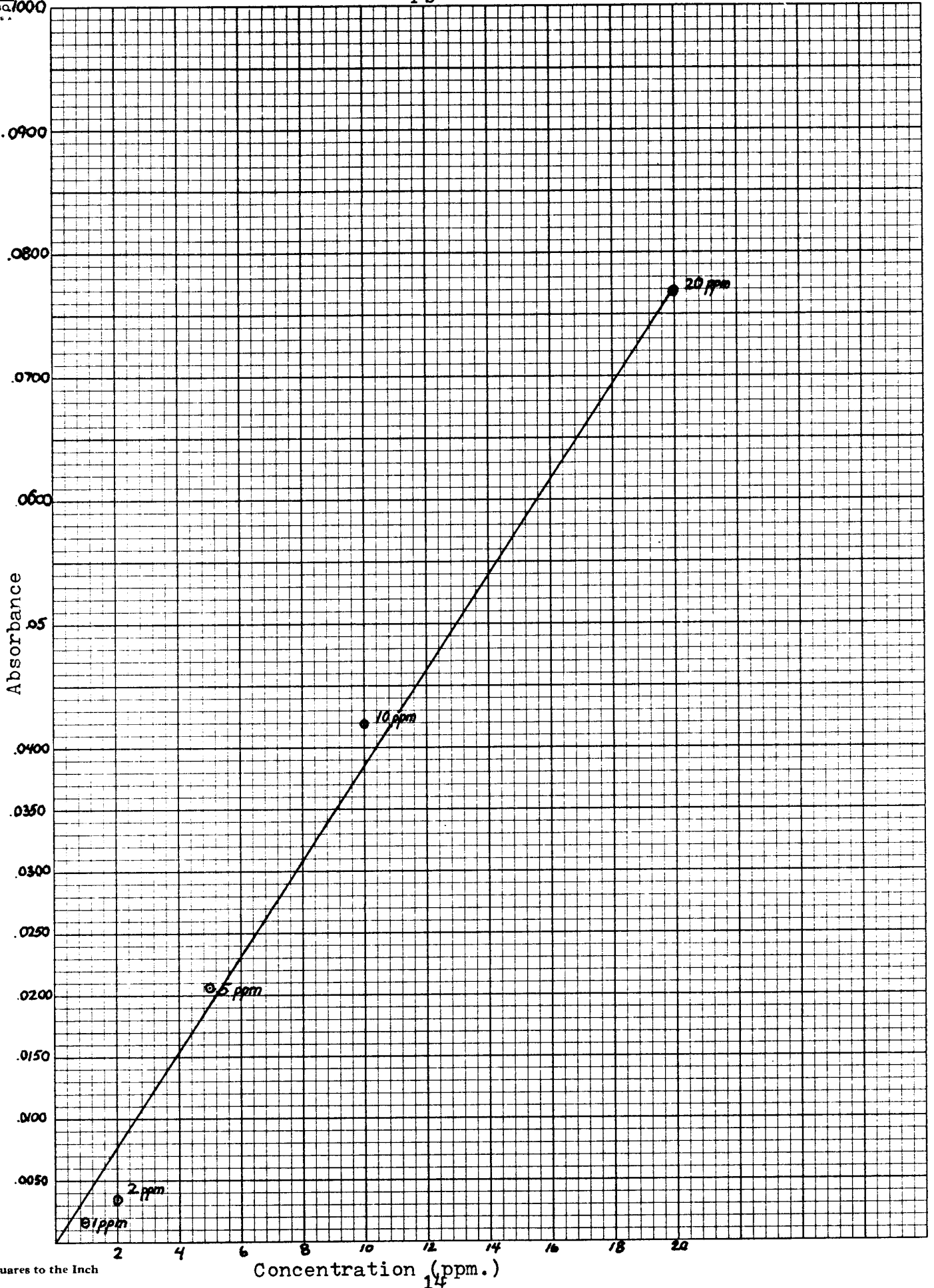
Absorbance vs. Concentration
Zn
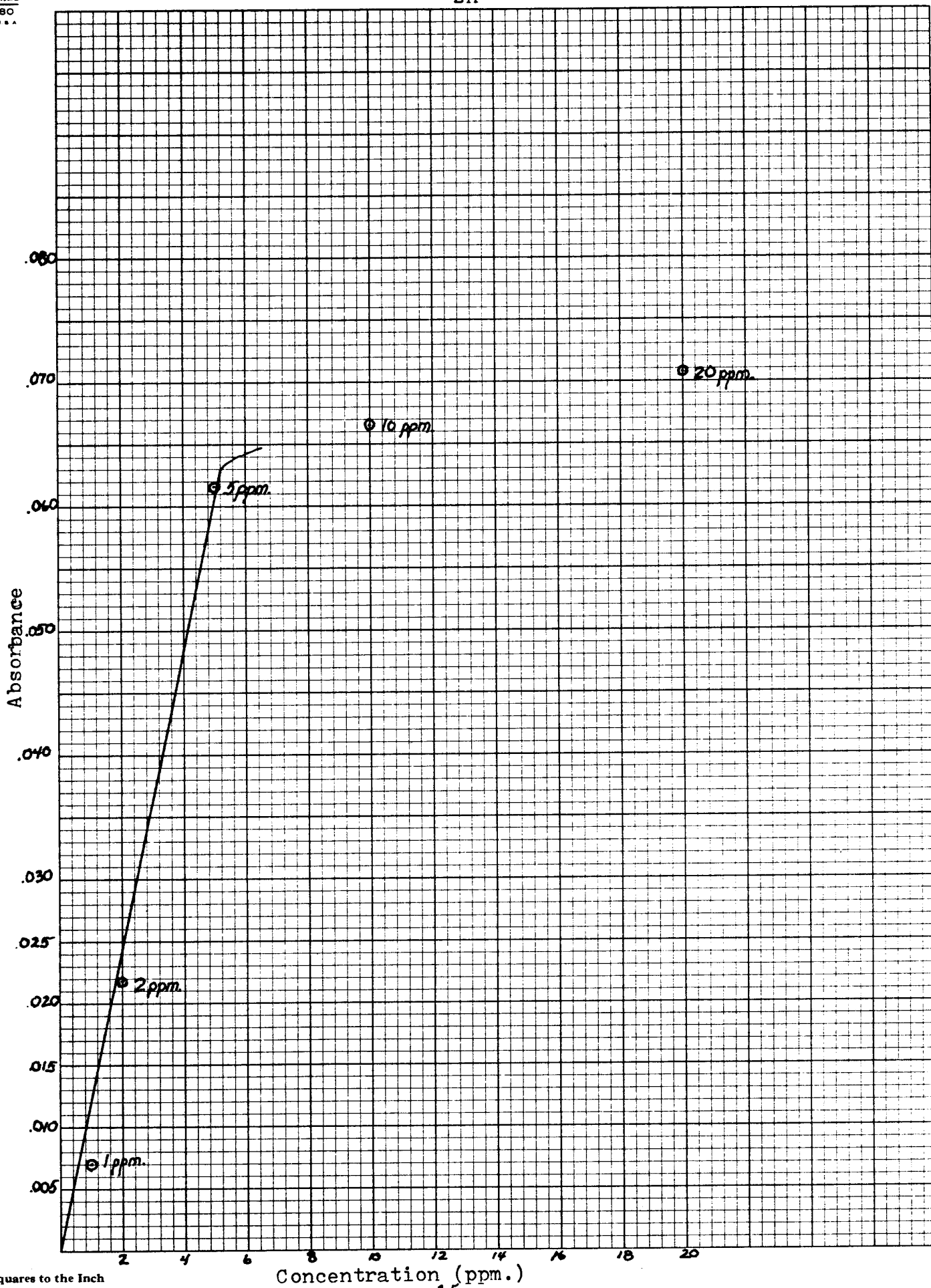
Appendix 1

Absorbance Values

Sample No.	Sample wgt. (grams)	Ag	Cu	Pb	Zn*
			Absorbance		
1	.5928	.0025	1.71	.0188	.0487
2	.6280	.0017	1.26	.0123	.0477
3	.6502	.0023	6.5	.0147	.0516
4	.4930	.0023	1.44	.0130	.0545
5	.4575	.0017	1.25	.0099	.0362
6	.6099	.0015	.92	.0107	.0391
7	.5822	.0003	.65	.0043	.0410
8	.4456	.0003	.73	.0066	.0297
9	.6031	.0018	.75	.0052	.0273
10	.4735	.0015	1.08	.0101	.0357
11	.4422	.0004	1.07	.0080	.0372
12	.4958	.0023	1.68	.0176	.0640
13	.5989	.0022	1.28	.0117	.0496
14	.5542	.0028	1.4	.0140	.0501
15	.5480	.0017	2.0	.0262	.0600
16	.5599	.0033	1.98	.0238	.0650
17	.5376	.0026	1.82	.0214	.0610
18	.5767	.0023	1.64	.0235	.0565
19	.4912	.0020	2.0	.0240	.0462
20	.5928	.0024	.97	.0122	.0496
21	.6280	.0017	.88	.0091	.0477
22	.6502	.0024	1.2	.0126	.0501
23	.4930	.0020	1.4	.0113	.0610
24	.4575	.0013	1.14	.0106	.0297

Standard Solutions

	20 ppm.	10 ppm.	5 ppm.	2 ppm.	1 ppm.
Ag	ND	.9630	.5400	.1290	.0680
Cu	.2604	.1561	.0857	.0186	.0114
Pb	.0768	.0419	.0205	.0035	.0017
Zn	.0716	.0665	.0615	.0218	.0070

*Because of very high zinc concentrations, each sample was diluted by a factor of ten. This factor of ten was then introduced into the numerator of the equation to determine concentration. 16

Appendix 2

Reservoir Geochemistry

Sample No.	Ag	Cu (ppm.) Pb		Zn	% Organics	Water Depth (ft.)	P.H.
1	2.5	97	413	3,374	8	4	5.
2	1.2	68	255	3,289	7	ND	5.
3	2.1	331	292	3,307	5	ND	5.
4	2.7	96	345	4,462	8	7	ND
5	1.6	93	273	3,388	6	6.5	ND
6	.8	49	230	2,623	5	ND	ND
7	.4	39	103	2,920	11	ND	ND
8	.6	56	202	2,917	12	19	5.
9	1.7	42	108	1,190	3	19	5.
10	1.1	74	264	3,273	14	24	4-5
11	.9	79	237	3,562	11	25	4-5
12	2.7	116	464	6,152	7	30	ND
13	2.2	72	267	3,381	5	23	ND
14	2.9	81	325	3,654	6	23	ND
15	1.4	119	630	4,384	5	3.5	4.5-5
16	3.1	116	554	6,251	5	3.5	4.5-5
17	2.8	111	530	4,650	5	7	ND
18	2.0	95	537	3,988	4	7	ND
19	2.2	132	546	3,868	7	14	ND
20	2.5	55	270	3,416	7	4	5.
21	1.2	48	191	3,105	6	ND	5.
22	2.1	62	254	3,114	4	ND	5.
23	2.2	91	304	5,070	8	7	ND
24	.9	87	306	2,842	6	6.5	ND

ND= no data

Discussion of Results and Conclusions

Though the very high zinc concentrations may be suspect, the results of the tests seem reasonable. The samples required dilution by a factor of ten because initially the readings were too high to intersect the zinc working curve. In a study by Wentz (1973), dissolved concentrations of zinc were thirty to sixty times greater than those of copper and lead respectively in Blue River. These findings would tend to reinforce the validity of the results of this study.

Based on the average concentrations of the four samples from Tenmile, and the average of the four highest concentrations of twenty samples from Blue River, the findings show in general that the higher metal concentrations are found in Tenmile Creek. The concentrations of lead and copper are appreciably higher in Tenmile than Blue River, whereas no significant differences are noted with silver. In consideration of zinc, it is noted that there are very high concentrations in both Tenmile Creek and Blue River.

Obviously, there are serious implications presented in these findings. Table 2 gives drinking water standards as supplied by the U.S. Public Health Service, and the World Health Organization. These standards are based on concentrations of trace elements either dissolved, or in suspension, and not on concentrations determined in sediments.

Table 2: Comparative Drinking Water Standards for Trace
Elements.

Water Quality Parameter	U.S. Public Health Service (1962,1970) Colorado Department of Health (1971)	World Health Organization 1961 European Standards
Copper	*1 (ppm.)	*3 (ppm.)
Lead	**.05 (ppm.)	**.1 (ppm.)
Silver	**.05 (ppm.)	-------
Zinc	*5 (ppm.)	*5 (ppm.)

*Maximum Permissable Concentration
**Recommended Limit

Source: Wentz (1972)

According to Wentz (1972), drinking water standards
are well established for humans, but not at all for
aquatic organisms. In addition, because of the associated
differences in physiology, such things as species, life-
cycle stage, and age can have considerable effect on
the response of an organism to high trace-element
concentrations. A classic example is the considerably
lower toxicity threshhold for zinc and copper to fish
than to humans. Though poeple are also at an advantage
because the water they drink is generally settled and
filtered before drinking, they are still either directly
or through consumption of affected organisms subject
to the effects of the high metal concentrations.

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