HEAVY METALS IN LAKES OF THE COEUR D'ALENE RIVER VALLEY, IDAHO

A Thesis

Presented in Partial Fullfillment of the Requirement for the DEGREE OF MASTER OF SCIENCE

Major in Zoology

in the

UNIVERSITY OF IDAHO GRADUATE SCHOOL

by

STEPHEN BERNARD BAUER

November, 1974

ACKNOWLEDGEMENTS

I wish to express my appreciation to the following:

To Dr. Fred Rabe for guidance in planning, assistance with field work, and suggestions on the writing of this paper;

To Dr. Don Johnson, Dr. George Klontz, and Dr. Doyle Anderegg for their comments and suggestion during the writing of this paper;

To my wife, Michelle, for her assistance throughout the study, and especially for proofreading and typing the final copy;

To Water Resources Research Institute for the funding of this project.

TABLE OF CONTENTS

							Page
INTRODUCTION	•	••	• •	• •	•,	• •	1
AREA DESCRIPTION .	•	• •	• •	• •	•	• •	4
METHODS	•	• •	• •	• •	•	• •	7
Field Laboratory .	•	•••	•••	•••	•	•••	7 10
RESULTS	•	• •	• •	• •	•	• •	12
Water Sediments . Fish Benthic Insect	•	• • • • • •	• • • • • •	• • • • • •	• • •	• • • •	12 15 24 32
DISCUSSION	•		• •	• •	•		41
CONCLUSION AND RECOMM	IENDA'	TIONS	• •		•	• •	50
LITERATURE CITED .	•	• •	• •		•		52

LIST OF TABLES

.

Table		Page
1.	Chemical characteristics of the Coeur d'Alene River drainage, April-June 1973	13
2.	Chemical characteristics of the Coeur d'Alene River drainage, June 1974	16
3.	Analysis of metals in sediments of the Coeur d'Alene River drainage as deter- mined by AAS, Spring 1973.	17
4.	Average concentration of metals in sediments.	20
5.	Analysis of metals in sediments of the Coeur d'Alene River drainage as deter- mined by Neutron Activation, Spring 1973	21
6.	Concentration of zinc in Yellow Perch	25
7.	Concentration of copper in Yellow Perch	28
8.	Concentration of cadmium in Yellow Perch	30
9.	Concentration of zinc in five species of fish from Coeur d'Alene River valley lakes.	33
10.	Concentration of copper in five species of fish from Coeur d'Alene River valley lakes.	35
11.	Concentration of cadmium in five species of fish from Coeur d'Alene River valley lakes.	37
12.	Zinc and copper in benthic insects and sediments from Anderson Lake, August 1973 .	40
13.	Approximate averages of metals in fish reported in other studies.	46

LIST OF FIGURES

Figure		Page
1.	Main stem of the Coeur d'Alene River	5
2.	Stations in lakes of the Coeur d'Alene River valley	8
3.	Zinc concentrations in the Coeur d'Alene lakes and river, Spring 1973	14
4.	Zinc, copper, cadmium, and lead in sediments from lakes in the Coeur d'Alene River drainage, April-June 1973	19
5.	Mean zinc concentration in Yellow Perch from the Coeur d'Alene River drainage	26
6.	Mean copper concentration in Yellow Perch from the Coeur d'Alene River drainage	29
7.	Mean cadmium concentration in Yellow Perch from the Coeur d'Alene River drainage	31
8.	The concentration of zinc in five species of fish from lakes in the Coeur d'Alene River valley	34
9.	The concentration of copper in five species of fish from lakes in the Coeur d'Alene River valley	36
10.	The concentration of cadmium in five species of fish from lakes in the Coeur d'Alene River valley	38

ABSTRACT

Heavy metal concentrations were measured in the water, sediments, and fish of nine small lakes located along the main stem of the Coeur d'Alene River. Mining wastes have been discharged into this drainage since the 1890's. Concentrations of dissolved metals were low in the lakes and did not differ significantly from lake to lake. Zn, Cu, Cd, Pb, Cs, and Sb have accumulated in lake sediments. The concentrations of these metals varied in sediments from lake to lake, and within each lake were highest at stations close to the river.

Zn, Cu, and Cd concentrations in muscle and liver of Yellow Perch were not significantly different between lakes. However, Zn and Cd concentrations in fish from several of the Coeur d'Alene lakes were significantly higher than in fish from a control area. Metal concentrations were somewhat related to trophic status, decreasing at higher trophic levels. Zn, Cu, and Cd concentrations were greater in benthic insects than in fish. The concentration of zinc in muscle was highest in Brown Bullheads (68 mg/kg), an omnivorous species, and lowest in Largemouth Bass (20 mg/kg), a piscivorous species.

INTRODUCTION

Sewage and mining wastes have been discharged into the Coeur d'Alene River since the 1890's. Rock flour and heavy metals in the mining wastes have been deposited along the river and in the lake. Ellis (1932) in an extensive survey of this pollution problem noted that the river was essentially devoid of life from the South Fork at Kellogg to the delta at Harrison, Idaho.

In 1968-1969 settling ponds for mining and milling waste waters were installed. These measures reduced the suspended solids entering the river and decreased some of the dissolved elements, such as nickel and lead (Mink, et al. 1971). However, dissolved zinc and cadmium remained above toxic limits for most aquatic organisms.

Several recent studies have investigated the effect of these wastes on the aquatic community. Sappington (1969) estimated that the 96-hour median tolerance limit for Cutthroat Trout, <u>Salmo clarki</u>, was 0.09 mg/l zinc in a static system. Savage and Rabe (1973) found low diversity values in the macrobenthic communities from polluted sections of the river. In Coeur d'Alene Lake Minter (1971) investigated the plankton population, Winner (1972) examined the macrobenthic community, Parker (1972) estimated primary production and nutrient levels, and Wissmar (1972) determined the effects of zinc, copper, and cadmium on primary production. Bartlett et al. (1974) found that growth and survival of <u>Selanastrum capricornutum</u>, a unicellular green algae, were reduced by exposure to zinc, copper, and cadmium.

However, little work has been done to examine the effect of mining wastes on nine lakes located along the lower 22 miles of the Coeur d'Alene River, or to measure metal concentrations in fish from this drainage. Ellis (1932) indicated that three of these lakes (Swan, Blue and Thompson Lakes) had sparse plankton and benthos populations which he attributed to toxic effects of mine wastes. Chupp and Dalke (1964) investigated the waterfowl mortality that had occurred regularly in the Coeur d'Alene River valley. They concluded that losses of swans and other waterfowl were due to heavy metal poisoning.

The present study was undertaken to obtain more detailed information on occurrence of heavy metals in lakes along the lower section of the river, and secondly to determine if heavy metals have accumulated in fish from this area.

Specifically, the objectives of my study were:

- 1. To determine the concentrations of zinc, copper, cadmium, and lead in the water and sediments of the lakes.
- 2. To compare concentrations of these metals in muscle and liver tissue of fish from different lakes.
- 3. To examine the concentrations of heavy metals in five species of fish and several taxa of benthic insects in relation to trophic level.

I assumed that metal values would be higher in water, sediments, and fish from areas closer to the discharge of mining wastes. Among the lateral lakes metal concentrations should be related to the extent to which river water passes into the lakes (see Area Description). Lakes that were more intimately connected to the river were expected to be higher in metal content. As a working hypothesis, the following rank in locations from high to low in metal concentrations was proposed:

- Coeur d'Alene River, main stem 1.
- 2. Killarney Lake
- 3.
- Swan Lake, Blue Lake Thompson Lake, Anderson Lake, Black Lake, 4. Medicine Lake, Cave Lake
- Rose Lake
- 5. 6. Bell's Lake (St. Joe River drainage)

The null hypothesis is one of no difference in the concentrations of metals between the river, the lateral lakes, and Bell's Lake.

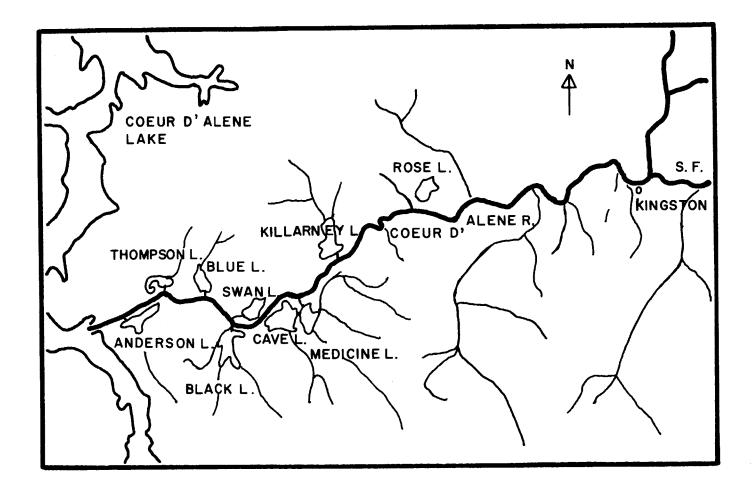
AREA DESCRIPTION

The nine lakes in this study lie along the lower 22 miles of the Coeur d'Alene River (Fig. 1). They are situated in the flood plain, and connected to the river by channels. The lakes are shallow; the deepest being only nine meters. In the summer, the bays are filled with emergent aquatic vegetation.

In the spring the lakes are usually flooded as the water table rises above the adjacent valley floor (Mink, et al. 1971). The lakes were completely flooded in 1974, but were not in the usual flooded state in 1973. Spring run-off was light in 1973, and consequently water reached bank level in the river but rose no higher. However, river water still flowed into the lakes via the inlet channels.

The dam on the Spokane River, the outlet of Lake Coeur d'Alene, enhances this flooding process. The dam backs water up the river, and in turn raises the water level in the lakes. Later in the fall, as water is released from the dam, the water level is lowered in the main stem. The water level in turn drops in the lateral lakes as water flows back into the river.

Anderson, Black, Cave, and Medicine Lakes are located on the south side of Coeur d'Alene River and are separated



.

,

.

FIG. 1: Main Stem of the Coeur d'Alene River.

٠

• • •

 \mathcal{S}

from the river by a railroad levee (Fig. 1). Three of these lakes are connected to the river by long winding inlets. Cave Lake has no direct connection to the river during periods of low water. However, at flood stage an open space in the railroad dike allows water to pass in and out. In addition, this lake is connected to Medicine Lake by a small channel.

Killarney, Rose and Thompson Lakes are located on the north side of the river. Thompson Lake is separated from the river by a dike road and Rose Lake by a state highway. However, during highwater in the spring, the river passes through a culvert and seeps across a marsh into Rose Lake. The inlet into Killarney Lake is a wide dredged out channel, approximately four meters deep.

Blue and Swan Lakes are also located on the north side of the river. No barrier separates these waters from the river. Both lakes were completely flooded in the spring of 1974 and could not be distinguished from the river.

Bell's Lake is located in the St. Joe River drainage, seventeen miles upstream from Coeur d'Alene Lake. Bell's Lake was used as a control to represent background levels of metals in water, sediments, and fish. The St. Joe River drainage and Bell's Lake have not been affected by mining or industrial wastes. This lake is similiar in size, depth, and chemical make-up to the lateral lakes off the Coeur d'Alene River, and is likewise flooded in high run-off years.

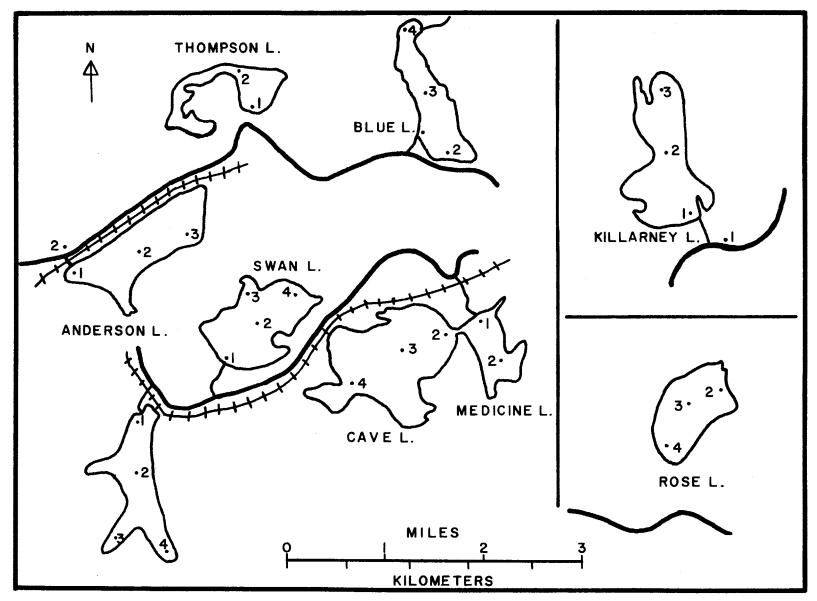
METHODS

Field:

Stations were established for the collection of water samples and bottom sediments (Fig. 2). In lakes with distinct inlets, station one (1) is located at the mouth of the inlet. The other stations were spaced at points out from the inlet to see if a gradient in metal concentrations occurred. For Cave Lake and Rose Lake which had no well defined inlets in 1973, the station numbering begins with two (2).

Water, bottom sediments, and fish were collected during May and June, 1973. Fish from Medicine, Cave, and Bell's Lakes were obtained in June, 1974. Fish from the Coeur d'Alene River were collected at Station two (2) which is 3.5 miles upstream from Lake Coeur d'Alene.

Water for heavy metal analysis was collected in acidwashed polyethylene bottles and rinsed with lake water four to five times before retaining the sample. These were kept frozen until analyzed. Dissolved oxygen and temperature were determined with a Model 51 Oxygen Meter (Yellow Springs Ins. Co.), pH with a Hellige pocket comparator, and specific conductance with a Solu Bridge conductivity meter. Alkalinity was measured by titration, and hardness by calculation according to Standard Methods (1972).



۲

٠

.

.

FIG. 2: Stations in lakes of the Coeur d'Alene River valley.

•

.

,

٠

Bottom sediments were obtained with an Eckman dredge. The top two to three centimeters of sediment was scraped from the surface of the Eckman dredge load, and retained as a sample. This portion was placed in glass jars, and kept cool until analyzed. In most lakes mixing of sediments occurs in the upper five centimeters while partial mixing occurs in the five to fifteen centimeter zone (Lee 1970). The surface sample obtained, therefore, probably represents a composite of the sedimentation that has occurred over a number of years.

Fish were obtained by using gillnets (100 feet long by 8 feet wide, bar mesh $3/8-1\frac{1}{2}$ inches) and by angling. Yellow Perch, <u>Perca flavescens</u>, and Brown Bullheads, <u>Ictalurus nebulosus</u>, were obtained in the gillnets; the Largemouth Bass, <u>Micropterus salmoides</u>, Black Crappie, <u>Pomoxis nigromaculatus</u>, and most of the Pumpkinseed, <u>Lepomis gibbosus</u>, were obtained by angling. The use of a shocker was attempted but proved to be ineffective in the soft water (14-22 mg/l CaCO₃ as total hardness).

Benthic organisms were obtained with an Eckman dredge, and strained through a 30-mesh sieve. The organisms were further separated from the bottom debris by sugar flotation (Lackey 1971). In the laboratory the benthos was separated into taxa, held in aerated glass jars containing filtered lake water for about thirty-six hours until the stomach contents were cleared, and then frozen for heavy metal analysis.

Laboratory:

The concentrations of metals were determined by a Perkin-Elmer model 303 Atomic Absorption Spectrophotometer(AAS). Detection limits for the metals considered are: zinc - 0.05 mg/l; copper - 0.02 mg/l; cadmium - 0.02 mg/l; and lead -0.5 mg/l.

Water samples were aspirated directly into the spectrophotometer without prior treatment. Many investigators recommend acidification of water sample to a low pH level to prevent adsorption of metal ions to walls of the container (King, et al. 1974; Standard Methods 1971). However, W.H. Funk (personal communication) advised that addition of acid might introduce error caused by leaching of metals from suspended solids. Water samples were frozen as an alternate method of preservation (Clement 1972).

Muscle and liver of fish were analyzed for zinc, copper, and cadmium. Muscle was selected because it is mainly utilized by higher trophic levels including man. Liver was used since it is suspected of participating in detoxification of metals, and has been commonly used in other such studies. In addition liver/muscle ratios have been used as an indicator of the pollution potential of an area (Jernelöv and Lann 1971).

Fish muscle was obtained along and above the lateral line. Cross et al. (1973) found no significant differences in heavy metal concentrations in different sections of a fillet from a Bluefish, <u>Pomatomus saltatrix</u>. It is doubtful therefore that location of the muscle sample has any effect on metal concentration.

Biological samples were wet-ashed for AAS analysis as modified from the methods of Thompson and Blanchflower (1971), as follows: Approximately one gram of desicated tissue was digested in a mixture of 3 ml of distilled concentrated nitric acid and 1 ml of 70% perchloric acid (plus two glass beads) for about two hours, then evaporated to near dryness. 5 ml of 5% HNO₃ was added to the ash. 2.5 ml of this solution was used for cadmium analysis. The remaining original solution was diluted by an equal amount of 5% HNO₃, and used for zinc and copper analysis. Two blanks were also set up with each run and the average subtracted from sample absorption before calculating the concentration in mg/kg dry weight.

Sediment samples were prepared for AAS analysis using the digestion procedures outlined in the Chemical Lab Manual for Bottom Sediments, Great Lake Region Committee (1969).

The Neutron Activation of the sediment samples was performed at the radiation center at Washington State University.

RESULTS

<u>Water</u>:

In 1973 the water in the lateral lakes was clear at the time of sampling, except near the inlets where it was turbid. This green-colored river water could be easily traced into Thompson Lake and Anderson Lake for about 100 meters. In 1974, the water in all the study lakes along the Coeur d'Alene River was turbid.

The lakes were uniform in chemical composition and contained low levels of dissolved substances (Table 1). Specific conductance ranged from 55-92 micromhos, hardness from 14-22 mg/l CaCO₃, and methyl orange alkalinity from $11-23 \text{ mg/l CaCO}_3$. The pH was between 6.8 and 7.4. Dissolved oxygen at the surface was near saturation, and was never below 4 mg/l at the bottom.

In the spring of 1973, cadmium, copper and lead concentrations in the water were below AAS detection limits (see Methods), while zinc measurements varied within lakes (Fig. 3). Dissolved zinc concentrations ranged from 0.34-0.44 mg/l at the inlet stations in Swan Lake, Thompson Lake, and Anderson Lake. This is similiar to the zinc concentration of 0.41 mg/l in the river near these lakes. Values of 0.05-0.07 mg/l zinc were recorded in the open water stations in these

4 22 7.0 8.0 60 15 16.7 3.9 1.7 Swan Lake114 7.0 $$ 80 17 18.5 3.6 2.2 2 19 7.0 $$ 75 14 17.7 3.6 2.1 3 19 7.0 $$ 75 14 17.7 3.6 2.1 4 19 7.0 $$ 78 14 17.7 3.6 2.1 Black Lake119 7.0 7.8 90 20 21.7 4.2 2.7 2 19 7.0 7.8 90 22 21.6 4.2 2.7 3 19 7.0 7.8 92 23 21.8 4.2 2.8 4 19 7.0 7.8 90 21 22.2 4.2 2.9	<0.05
Lake2207.07.0781520.64.62.2Medicine Lake1127.08.0551512.82.81.42117.010.0601110.22.11.33127.060129.61.91.2Cave Lake2227.08.0601816.73.91.73227.07.0601516.73.91.74227.08.0601516.73.91.751417.73.62.11.417.73.62.14197.0751417.73.62.19197.0781417.73.62.19197.07.8902021.74.22.73197.07.8902221.64.22.73197.07.8902221.64.22.73197.07.8902221.84.22.84197.07.8902122.24.22.9	<0.05 <0.05
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.24 0.22 0.22
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.05 0.06 0.06
Swan Lake1147.0801718.53.62.22197.0751417.73.62.13197.0751417.73.62.14197.0781417.73.62.1Black Lake1197.07.8902021.74.22.72197.07.8902221.64.22.73197.07.8922321.84.22.84197.07.8902122.24.22.9	<0.05 <0.05 <0.05
Black Lake 1 19 7.0 7.8 90 20 21.7 4.2 2.7 2 19 7.0 7.8 90 22 21.6 4.2 2.7 3 19 7.0 7.8 92 23 21.8 4.2 2.8 4 19 7.0 7.8 90 21 22.2 4.2 2.9	0.44 0.07 0.07 0.07
	0.09 0.04 0.04 0.04 0.04
Blue Lake121 7.0 7.8 73 13 15.7 3.3 1.8 221 7.0 7.3 70 14 14.2 2.9 1.7 321 7.0 7.8 70 14 14.2 2.9 1.7 421 7.0 7.8 72 14 14.3 2.9 1.7	0.12 0.06 0.07 0.06
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.41 0.06 0.34 0.05 1.10 0.41

٠

٠

.

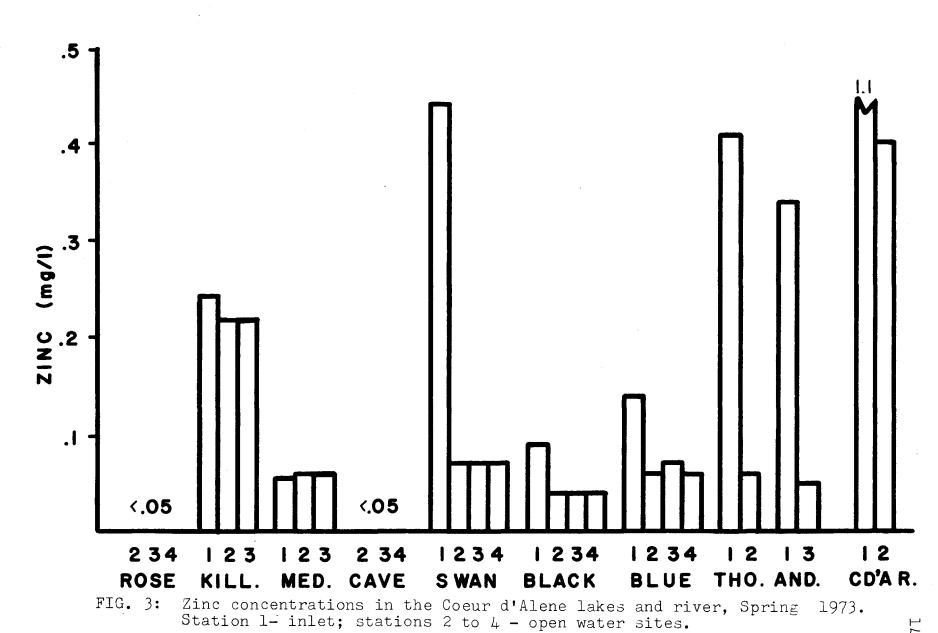
.

٠

.

TABLE 1: Chemical characteristics of the Coeur d'Alene River drainage, April-June 1973. *Station 1 - inlet; stations 2 to 4 - open water sites.

С Ц



lakes. Similiar concentrations of zinc occurred at the open water stations in Black Lake and Blue Lake while zinc increased to 0.09 and 0.12 mg/l respectively at the inlets. Zinc concentrations were as high as 1.1 mg/l in the Coeur d'Alene River, but were below detection limits in Bell's Lake which was used as a control.

The concentration of zinc at the open water stations of Killarney Lake was uniformly higher than the open water stations in other lakes. However, the zinc concentration at the inlet was much lower than in the river (Fig. 3). The wide inlet apparently transports a larger volume of river water into this lake and brings about a more thorough mixing than occurs in the other lakes.

In Rose Lake and Cave Lake zinc concentrations were below detection limits at all stations. These lakes have no direct connection to the river, but receive water from it indirectly at times of flooding in the spring.

Water chemistry data for 1974 was similiar to 1973 (Table 2). The greater dilution due to high spring run-off is apparently responsible for the decrease in conductivity and dissolved zinc.

Sediments:

The concentration of zinc, copper, cadmium, and lead in the sediments, as measured by Atomic Absorption, indicate a definite increase over background levels (Table 3).

STATION*		TEMP. (°C)	рH	COND. (<i>u</i> mhos)	M.O. ALK. (mg/l CaCO ₃)	HARDNESS (mg/l CaCO ₃)	Ca (mg/l)	Mg (mg/l)	Zn (mg/l)
Rose Lake	2	21	6.9	60	14	13.8	2.9	1.6	<0.05
	3	20	6.9	65	12	14.0	3.0	1.6	<0.05
<u> </u>	4	20	6.9	65	10	14.0	3.0	1.6	<u><0.05</u>
Killarney	1	14	7.0	60	18	14.7	3.4	1.5	0.08
Lake	2	17	7.0	60	18	11.4	3.4	1.4	0.08
	3	16	7.0	60	16	11.4	3.4	1.4	0.08
Medicine	Ţ	16	7.1	<50	14	12.8	3.0	1.3	<0.05
Lake	2	19	7.2	< 50	14	13.6	3.3	1.3	<0.05
	<u></u>	22	7.3	<50	16	11.0	2.3	<u> </u>	<0.05
Cave Lake	2	20	7.2	<50	14	12.6	2.8	1.3	<0.05 <0.05
	3	21	7.3	<50	14 12	12.4	3.0	1.2	<0.05
Swan Lake	4	<u>23</u> 17	7.4	<u> </u>	16	<u> 12.0</u> 14.9	<u> </u>	$\frac{1.1}{1.5}$	0.10
DWall Lake	1 2	17	7.0	60	18	14.9	3.3	1.6	0.10
	2	17	7.0	60	16	13.0	2.9	1.4	0.10
	1.	16	7.0	60	18	14.8	3.3	1.6	0.10
Black Lake		22	7.3	80	18	19.6	4.4	2.1	<0.05
Draon Dane	$\frac{1}{2}$	22	7.4	80	18	20.1	4.3	2.3	<0.05
	ĩ	23	7.3	90	18	24.0	5.5	2.5	<0.05
	Ĺ	25	7.3	έÕ	16	23.7	5.7	2.3	<0.05
Blue Lake	1	16	7.0	60	16	14.5	3.5	1.4	0.11
	2	16	6.8	60	16	15.3	3.5	1.6	0.09
	3	18	7.0	60	16	15.3	3.5	1.6	0.08
	4	18	7.0	60	18	14.0	3.3	1.4	0.08
Thompson	1	24	7.0	70	22	17.7	3.8	2.0	<0.05
Lake	2	24	7.0	70	20	14.9	4.0	1.2	<0.05
Anderson	1	23	7.0	65	18	14.6	3.2	1.6	<0.05
Lake	2	24	7.0	65	18	14.9	3.0	1.8	<0.05
	3	24	7.0	65	18	14.5	3.0	1.7	<0.05

.

.

•

.

TABLE 2: Chemical characteristics of the Coeur d'Alene River drainage, June 1974. *Station 1 - inlet; stations 2 to 4 - open water sites.

STATI	ON*	ZINC (mg/kg)	COPPER (mg/kg)	CADMIUM (mg/kg)	LEAD (mg/kg)	IRON (%)
Rose Lake	2(1)	240	21	2	100	0.5
	3(5)	1900	23	14	2150	3.3
	4(5)	2100	38	15	3200	3.9
Killarney Lake	1(4) 2(5) 3(2)	4000 4250 5200	140 160 87	50 55 130	4600 3950 2550	9.3 9.0 4.6
Medicine	1(1)	2550	79	30	3000	8.7
Lake	2(6)	2950	87	44	2650	6.5
Cave Lake	2(3)	2750	29	45	2300	2.2
	3(6)	2800	60	34	2700	4.0
	4(8)	3300	79	29	3850	5.5
Swan Lake	1(1)	2600	112	25	3500	10.0
	2(6)	2950	132	26	3850	9.3
	3(3)	4650	138	57	3900	6.7
	4(2)	1900	41	19	1800	7.0
Black Lake	1(1) 2(9) 3(5) 4(2)	2350 2600 2300 1750	92 38 13 8	29 29 18 11	4700 1750 800 490	8.5 4.2 2.1 1.6
Blue Lake	1(1)	2000	126	25	3400	9.2
	2(2)	6800	112	83	3400	4.2
	3(8)	3600	130	36	4200	6.1
	4(3)	2750	27	38	950	2.3
Thompson	1(1)	3000	82	23	3700	9.3
Lake	2(3)	2900	52	31	2600	4.7
Anderson Lake	1(2) 2(5) 3(3)	3250 3550 2150	76 87 34	46 42 56	2850 3350 1750	7.0 4.1 2.5
Bell's Lake**	2(4) 3(6) 4(3)	110 52 100	4 8 9	<2 <2 <2	30 <300 <300	2.2 2.4 2.0

.

TABLE 3: Analysis of metals in sediments of the Coeur d'Alene River drainage as determined by AAS, Spring 1973. *Station 1 - inlet; stations 2 to 4 - open water sites. () = depth in meters.

**Bell's Lake - control, St. Joe River drainage.

Zinc and lead concentrations were 10-40 times higher in the Coeur d'Alene lakes than in Bell's Lake sediments (Fig. 4). Copper and cadmium concentrations were not elevated to the same extent, but show a definite increase over background. Bowen (1966) lists the world-wide averages for these metals in the soil as follows: copper-20, lead-10, zinc-50, and cadmium-0.06 mg/kg. Estimates of background levels in the Coeur d'Alene soil are similiar to these world-wide averages (Canney 1959).

Within the lateral lakes there is strong agreement to the working hypothesis as relates to heavy metals in sediments (Table 4). The highest concentrations occurred in Killarney Lake and the lowest in Rose Lake. The other Coeur d'Alene lakes were intermediate between these two. Swan Lake and Blue Lake were higher than lakes in group 4 which were all separated from the river by levees.

Of the elements analyzed by Neutron Activation (Table 5) only cesium and antimony are higher than the average levels in soil. The average level of cesium in the soil was 0.3-25 mg/kg and for antimony was 2-10 mg/kg (Bowen 1966). Metal concentrations in the sediments from lateral lakes along the Coeur d'Alene River ranged from 4-1000 mg/kg for cesium and 16-121 mg/kg for antimony. Bowen (1966) indicated that antimony is moderately toxic to animals but cesium is relatively harmless.

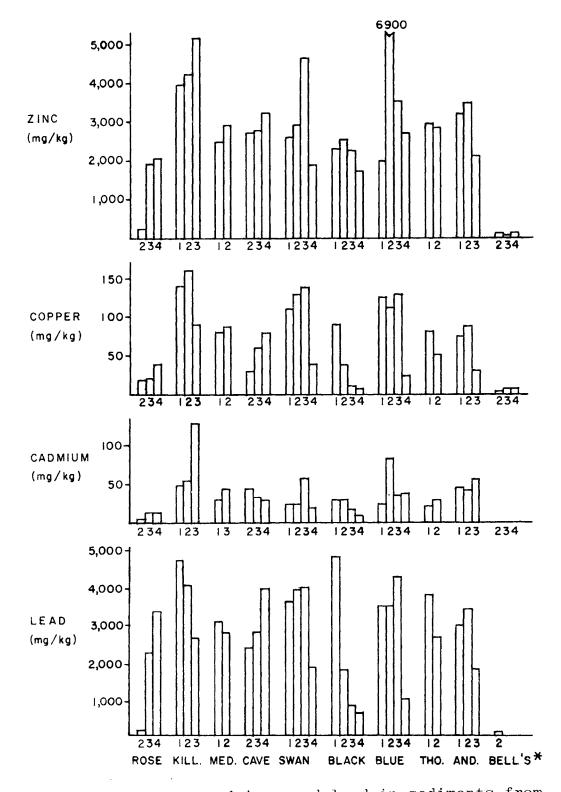


FIG. 4: Zinc, copper, cadmium, and lead in sediments from lakes in the Coeur d'Alene River drainage, April-June 1973. * Bell's Lake is in the St. Joe River drainage. Station 1 - inlet; stations 2 to 4 - oper water sites.

GROUP	LAKES	ZINC	COPPER	CADMIUM	LEAD
2.	Killarney	4483	129	78	3700
3	Swan Blue	3025 3787	105 98	32 45	3262 2987
4	Thompson Anderson Black Medicine Cave	2950 2983 2250 2750 2950	67 66 37 83 56	27 48 22 37 36	3150 2650 1935 2825 2950
5	Rose	1413	27	7	1816
6	Bell's (St. Joe River)	87	7	<2	30

TABLE 4: Average concentration of metals in sediments in mg/kg. Lakes grouped according to working hypo-thesis (see Methods).

STATION*		Ce (ppm)	Lu (ppb)	Se (ppb)	Th (ppb)	Cr (ppm)	Hf (ppm)
Killarney Lake	1(4) 2(5) 3(2)	83 99 101	698 817 696	1063 1705 1312	8,596 10,357 10,473	26.5 45.0 43.6	5.0 3.6 3.7
Medicine Lake	1(1)	86	757	918	8,214	25.0	5.1
	2(6)	104	638	1395	11,642	49.0	3.6
Cave Lake	2(3)	125	774	1679	11,756	35.7	6.2
	3(6)	103	610	1211	11,170	41.3	4.0
Swan Lake	1(1)	72	695	1221	8,140	24.7	5.9
	2(6)	77	675	1188	9,348	36.0	3.9
	3(3)	98	711	1272	10,199	44.0	3.4
	4(2)	82	593	1016	8,036	22.7	6.1
Black Lake	1(1) 2(9) 3(5) 4(2)	87 104 57 94	636 780 793 744	1012 1304 730 1379	8,283 11,514 6,728 9,805	24.0 50.0 21.1 42.0	6.2 5.7 4.5
Blue Lake	1(1)	92	664	1490	8,213	32.9	4.1
	2(2)	92	821	1436	9,593	38.3	3.6
	3(8)	140	707	1393	12,001	43.5	4.3
	4(3)	95	800	1257	10,370	41.8	3.3
Thompson Lake	1(1)	67	698	639	6,528	20.6	3.9
	2(3)	96	655	1352	11,215	42.0	3.8
Anderson Lake	1(2)	86	920	1337	8,913	27.3	6.5
	3(3)	88	690	1310	9,510	29.4	6.4
Coeur d'Alene	1(5)	72	703	559	6,195	17.6	3.7
River	2(1)	58	838	1094	6,818	22.0	5.6
		[50]	[-]	[200]	[5,000]	[100]	[3]

.

TABLE 5: Analysis of metals in sediments of the Coeur d'Alene River drainage as determined by Neutron Activation, Spring 1973.

> *Station 1 - inlet; stations 2 to 4 - open water sites. () = depth in meters. [] = average concentration in soil (Bowen 1966).

STATION*		Ba (ppm)	Zr (ppm)	Sb (ppb)	Cs (ppm)	Tb (ppb)	Sc (ppb)
Killarney Lake	1(4) 2(5) 3(2)	667 817 825	261 222 139	67,224 118,564 81,386	6,370 10,718 8,964	1476 402 1459	6,885 9,518 10,918
Medicine Lake	1(1)	640	260	59,998	5,565	2029	6,950
	2(6)	922	217	78,398	10,928	1579	12,720
Cave Lake	2(3)	725	344	28,220	7,238	677	9,839
	3(6)	740	223	44,931	9,244	458	10,586
Swan Lake	1(1)	638	345	79,125	5,138	1049	5,754
	2(6)	812	223	91,338	8,666	1728	8,695
	3(3)	1025	187	121,043	10,823	1225	9,887
	4(2)	524	278	35,660	4,653	964	6,318
Black Lake	1(1) 2(9) 3(5) 4(2)	769 578 852	311 305 238	64,994 48,823 62,150 16,458	4,950 10,116 4,789 5,993	1337 522 3358 600	5,989 16,450 6,852 13,176
Blue Lake	1(1)	640	213	107,056	6,456	1473	6,891
	2(2)	779	211	104,334	9,513	1271	9,055
	3(8)	770	240	24,750	9,460	1629	13,097
	4(3)	892	238	93,656	12,149	898	10,866
Thompson Lake	1(1)	640	191	57,978	9,521	403	10,933
	2(3)	898	261	66,301	4,712	285	4,645
Anderson Lake	1(2)	756	331	73,512	5,903	439	6,327
	3(3)	644	303	27,265	4,955	986	9,345
Coeur d'Alene	1(5)	601	178	56,380	4,300	3553	6,669
River	2(1)	619	297	62,054	4,637	1348	5,328
		[500]	[300]	[2,000- 10,000	[•3 - 25]	[]	[7,000]

TABLE 5: Continued.

•

.

.

.

-

.

•

.

.

.

.

.

STATION*		Rb (ppm)	Fe (%)	Zn (ppm)	Ta (ppb)	Co (ppm)	Eu (ppm)
Killarney Lake	1(4) 2(5) 3(2)	109 166 136	6.9 7.6 4.6	3849 4430 4984	608 775 738	11.1 23.9 16.1	2.5 2.7 2.2
Medicine Lake	1(1)	111	7.2	2710	628	13.3	2.3
	2(6)	181	5.7	2605	852	18.1	2.6
Cave Lake	2(3)	113	2.95	2373	867	11.0	2.4
	3(6)	128	4.6	2712	793	12.1	2.3
Swan Lake	1(1)	115	10.2	3152	574	15.6	2.8
	2(6)	136	8.4	3068	656	18.9	2.7
	3(3)	180	7.6	5503	726	25.5	2.6
	4(2)	82	6.1	2006	763	9.1	2.2
Black Lake	1(1)	116	8.7	2673	625	16.2	3.0
	2(9)	187	5.9	3157	996	18.3	2.5
	3(5)	119	10.2	3398	658	11.6	2.4
	4(2)	109	3.0	1760	1078	11.3	2.4
Blue Lake	1(1)	115	9.0	2094	641	14.7	2.8
	2(2)	141	5.3	8505	736	16.4	2.5
	3(8)	136	3.3	3093	902	15.0	2.4
	4(3)	177	5.9	3973	730	20.7	2.4
Thompson Lake	1(1)	147	5.9	2796	880	11.8	2.5
	2(3)	101	8.1	3611	562	13.7	2.5
Anderson Lake	1(2)	118	8.6	3215	681	16.0	2.8
	3(3)	81	2.5	2531	863	9.0	2.2
Coeur d'Alene	1(5)	112	8.6	5651	596	9.0	2.5
River	2(1)	119	10.0	3321	639	10.8	2.4
		[100]	[3.8]	[50]	[]	[8]	[]

TABLE 5: Continued.

Fish:

Yellow Perch, <u>Perca flavescens</u>, which were an abundant species in each lake, were used to compare metal concentrations in fish between lakes (Fig. 5-7). Analysis of Variance indicated significant differences in zinc, copper, and cadmium levels in muscle and liver between lakes at the 0.05 level. Duncan's Multiple Range Test at the 0.05 level was used to determine specifically which means were different. Significant differences between lakes are listed in tabular form on the corresponding figure. Values for Yellow Perch from Thompson Lake and Anderson Lake were not included in the comparison because of small sample size.

Some fish samples analyzed were below detection limits for copper and cadmium. These limits depend in part on the amount of tissue available for analysis and on the volume of 5% HNO₃ used for dilution of the ash. Only fish samples analyzed which were above detection limits are included. As a result, sample means listed for copper and cadmium are probably biased upward by a slight amount.

Mean concentration of zinc in muscle of Yellow Perch ranged from 32 to 102 mg/kg (Table 6). Except for Swan Lake, river samples showed higher zinc concentrations than the lake samples. Bell's Lake samples were lower than both river and lateral lake samples (Fig. 5).

Mean concentration of zinc in the liver ranged from 54 to 194 mg/kg. The concentration of zinc in liver of fish

LOCATIONS	TISSUE	MEAN ZINC	<u>+</u> 95% C.I.	RANGE	N
COEUR D'ALENE DRAINA	AGE	(mg/kg)		
Rose Lake	muscle	44.6	5.0	30 to 59	12
(34)*	liver	54.0	8.6	30 to 73	13
Killarney Lake	muscle		6.6	39 to 54	4
(97)	liver		20.8	134 to 182	4
Black Lake	muscle		4.6	34 to 63	13
(45)	liver		32.7	56 to 257	13
Swan Lake	muscle		14.8	70 to 119	6
(50)	liver		60.0	63 to 283	6
Blue Lake	muscle		9.3	53 to 92	8
(34)	liver		36.1	58 to 228	8
Cave Lake	muscle	34.4	10.8	22 to 63	7
(34)	liver	193.9	191	31 to 573	5
Medicine Lake	muscle		7.6	43 to 64	6
(18)	liver		28.7	133 to 186	4
Coeur d'Alene River	muscle	72.6	16.5	40 to 122	10
(40)	liver	176.9	65.5	94 to 447	10
ST. JOE RIVER DRAIN,	AGE				
Bell's Lake	muscle	31.9	6.0	25 to 53	11
(35)	liver	71.2	8.2	48 to 99	11
OVERALL MEAN					
Coeur d'Alene Lakes	muscle liver		6.3 24.0		77 74

.

.

.

.

.

.

-

•

TABLE 6: ZINC: Concentration of zinc in Yellow Perch.

* () average weight in grams
C.I. = Confidence Interval

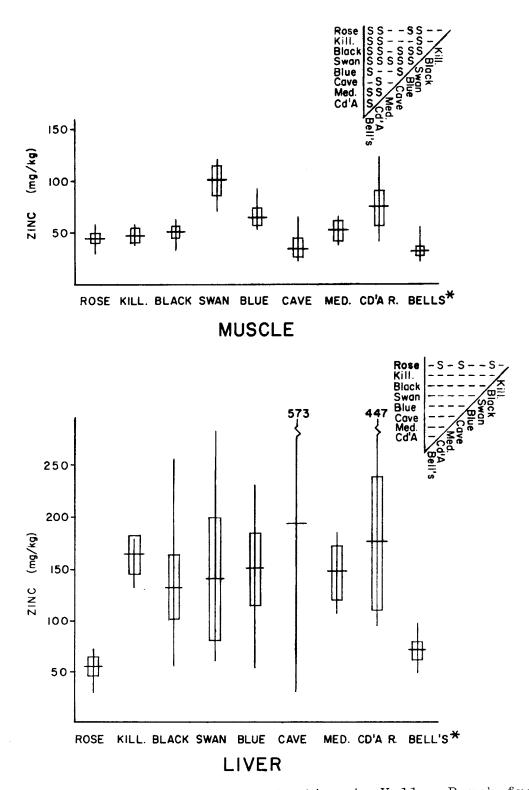


FIG. 5: ZINC. Mean zinc concentration in Yellow Perch from the Coeur d'Alene River drainage. Rectangle is 95% confidence interval, line is range. * Bell's Lake is in the St. Joe River drainage. Table above graph lists results of Duncan's Multiple Range test, S - significant difference.

from Bell's Lake and Rose Lake was lower than in fish from other locations (Fig. 5).

Mean copper concentration in muscle ranged from 0.36 to 2.6 mg/kg (Table 7, Fig. 6). The highest concentration was recorded in Yellow Perch from Cave Lake. Mean concentrations of copper in liver were 2.8 to 44.5 mg/kg (Fig. 6). Concentrations in liver of fish from Killarney Lake and Cave Lake exhibited significantly higher values. No relationship existed between the working hypothesis and copper concentrations. The mean values for Coeur d'Alene River samples were low and for Bell's Lake samples were relatively high.

Mean cadmium concentrations in muscle were 0.21 to 0.77 mg/kg (Table 8). Highest concentrations of cadmium in muscle were from Coeur d'Alene River fish. Average concentrations in the lateral lakes were similiar from lake to lake (Fig. 7).

Liver sample means ranged from 2.5 to 89 mg/kg cadmium (Table 8). Mean values were highest in Killarney Lake fish and lowest in Rose Lake fish. Values were somewhat similiar for the other lakes (Fig. 7). Cadmium concentrations in Bell's Lake fish were less than detection limits (Table 8). Generally, fish samples analyzed for cadmium fitted the working hypothesis.

Metals in Yellow Perch from the lakes were compared to metals in Pumpkinseed (<u>Lepomis gibbosus</u>), Black Crappie (<u>Pomoxis nigromaculatus</u>), Brown Bullhead (<u>Ictalurus nebulosus</u>),

LOCATIONS	TISSUE	COPPER	±95%C.I.	RANGE	N
COEUR D'ALENE DRAIN	AGE	(mg/kg)		
Rose Lake	muscle	0.44	0.04	0.35 to 0.63	12
(34)*	liver	2.8	1.00	1.7 to 5.9	7
Killarney Lake	muscle	1.1		0.68 to 1.4	4
(97)	liver	44.5		24 to 65	4
Black Lake	muscle	0.36		0.20 to 6.4	9
(45)	liver	5.0		1.9 to 7.1	4
Swan Lake	muscle	0.62		0.44 to 1.2	5
(50)	liver	5.4		4.6 to 6.9	3
Blue Lake	muscle	0.46		0.26 to 0.70	8
(34)	liver	5.9		2.8 to 11	7
Cave Lake	muscle	2.6		l.2 to 7.5	7
(34)	liver	44.4		13 to 110	5
Medicine Lake	muscle	1.2	0.19	0.96 to 1.44	5
(18)	liver	14.9	0.53	14.7 to 15.2	2
Coeur d'Alene River	muscle	0.48		0.39 to 0.54	6
(40)	liver	6.1		3.6 to 8.6	5
ST. JOE RIVER DRAIN	AGE				
Bell's Lake	muscle	0.98	0.18	0.72 to 1.5	8
(35)	liver	12.9	2.4	8.4 to 18.4	8
OVERALL MEAN					
Coeur d'Alene	muscle	0.87	0.29		50
Lakes	liver	16.5	7.3		32
TABLE 7: COPPER: Co	oncentra	tion of	copper in	Yellow Perch.	

* () average weight in grams
C.I. = Confidence Interval

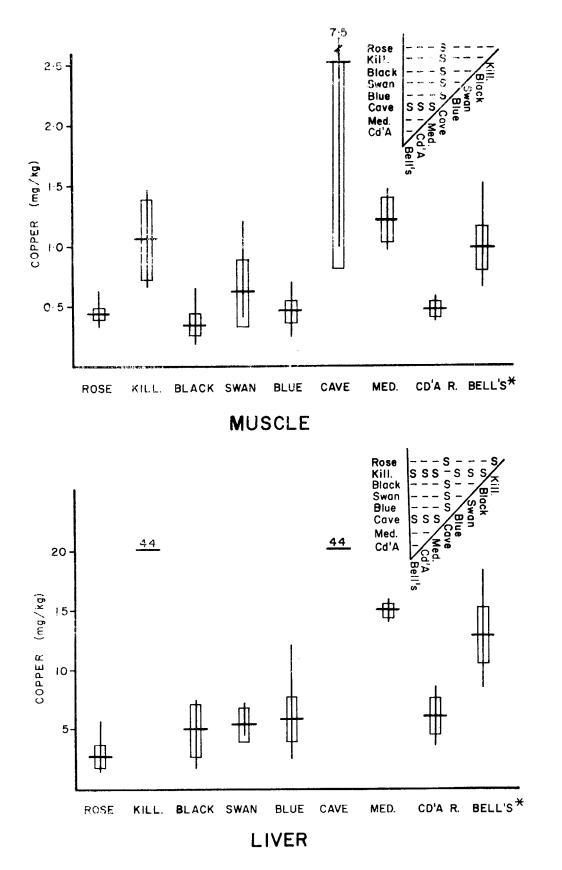


FIG. 6: COPPER. Mean copper concentration in Yellow Perch from the Coeur d'Alene River drainage. (See Fig. 5 for caption for explanation of symbols.)

29

.

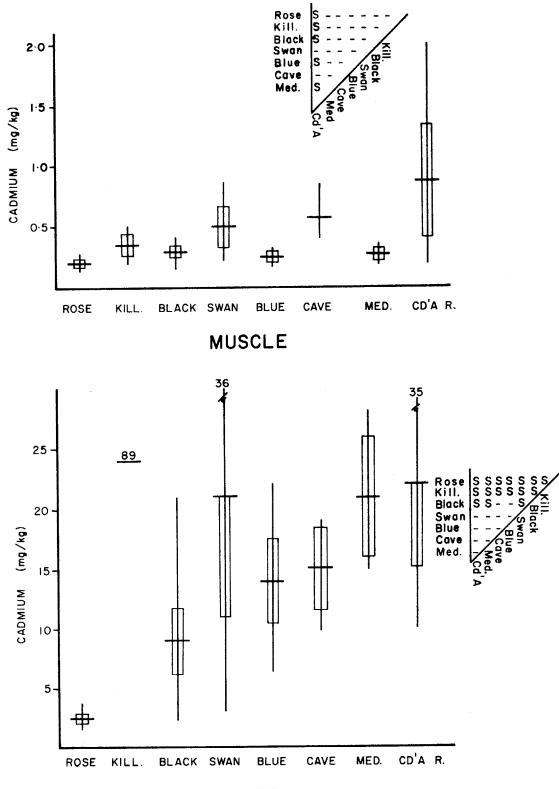
LOCATIONS	TISSUE	MEAN +	95%C.I.	RANGE		N
(mg/kg) COEUR D'ALENE DRAINAGE						
Rose Lake (34)*	muscle liver	0.21 2.5	0.02 0.38	0.17 to 1.6 to		8 12
Killarney Lake (97)	muscle liver	0.37 89.0	0.09 3.4	0.31 to 85 to		4 8
Black Lake (45)	muscle liver	0.29 8.9	0.05 3.1	0.17 to 2.3 to		9 12
Swan Lake (50)	muscle liver	-	0.18 9.8	0.22 to 5.2 to		6 6
Blue Lake (34)	muscle liver	0.26 14.2	0.04 3.6	0.21 to 6.4 to		6 7
Cave Lake (34)	muscle liver		0.33 3.5	0.41 to 9.7 to		2 5
Medicine Lake (18)	muscle liver	0.28 21.0	0.05 5.2	0.22 to 15 to		4 4
Coeur d'Alene River (40)	muscle liver	0.77 21.6	0.37 6.6	0.18 to 10 to		10 9
ST. JOE RIVER DRAINAGE						
Bell's Lake (35)	muscle liver	<0.2 <1.5				11 11
OVERALL MEAN						
Coeur d'Alene Lakes	muscle liver	0.32 16.1	0.11 5.6			39 49
TABLE 8: CADMIUM:	Concentration of		f cadmium	n in Yello	ow Per	ch.

•

-

.

* () average weight in grams
C.I. = Confidence Interval



LIVER

FIG. 7: CADMIUM. Mean cadmium concentration in Yellow Perch from the coeur d'Alene River drainage. (See Fig. 5 caption for explanation of symbols.)

and Largemouth Bass (<u>Micropterus salmoides</u>). The values for a species from different lakes were lumped together to increase sample size.

The mean zinc concentrations in muscle of the five species varied from 19.5 mg/kg in the Largemouth Bass to 67.6 mg/kg in the Brown Bullheads (Table 9, Fig. 8). The highest concentration of zinc in liver occurred in Brown Bullheads. Zinc concentration in liver of the other four species were somewhat similiar (107-147 mg/kg).

Copper concentrations in muscle of the five species were similiar, ranging from 0.87 mg/kg in Yellow Perch to 2.2 mg/kg in muscle of the Largemouth Bass (Table 10, Fig. 9). Concentrations of copper in liver of the Black Crappie and Brown Bullheads were higher than in the other three species.

Cadmium concentrations in muscle were similiar for the five species ranging from 0.32 to 1.1 mg/kg (Table 11, Fig. 10). In liver the range of values was from 3.8 to 24.5 mg/kg. Brown Bullheads contained the lowest concentration of cadmium in muscle and in liver.

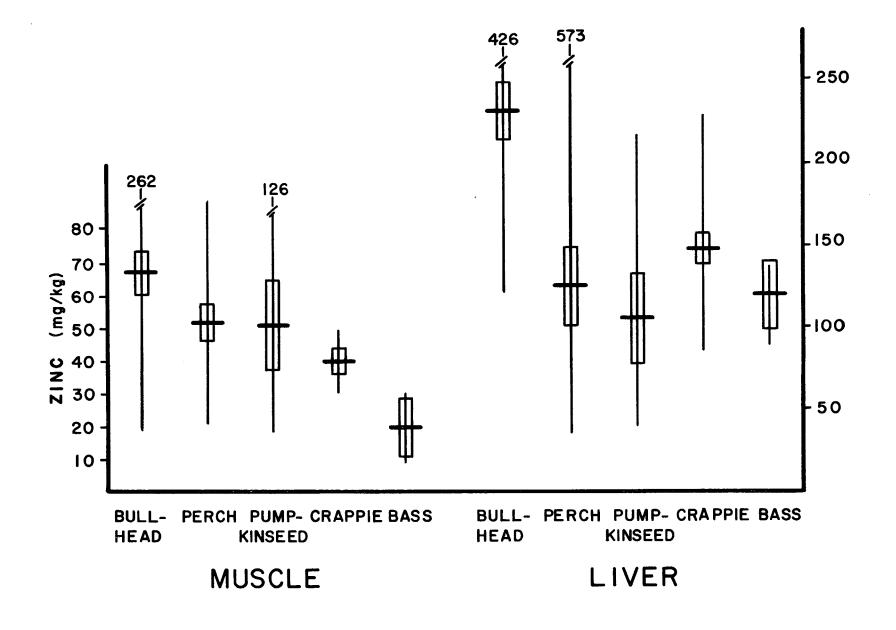
Benthic Insects:

Aquatic insects sampled from the bottom substrate of Anderson Lake were analyzed for metal concentrations (Table 12). Only Chironomids were obtained in large enough quantities for analysis at all three stations in the lake. Cadmium was below detection limits. Zinc and copper concentrations

SPECIES	SPECIES TISSUE		±95% C.I.	' RANGE	N
		(mg/kg)	***********	- <u> </u>	
Brown Bullhead	muscle	67.6	6.5	18 to 262	19
(107)*	liver	232.1	17.9	122 to 426	12
Yellow Perch	muscle	52.0	6.3	22 to 92	77
(40)	liver	126.0	24.0	30 to 573	74
Pumpkinseed	muscle	51.4	14.6	19 to 126	16
(47)	liver	107.2	29.5	37 to 219	15
Black Crappie	muscle	39.7	4.0	33 to 50	10
(128)	liver	147.9	8.6	86 to 230	10
Largemouth Bass	muscle	19.5	9.6	12 to 29	5
(516)	liver	120.5	20.1	89 to 135	5

TABLE 9: ZINC: Concentration of zinc in five species of fish from Coeur d'Alene River valley lakes.

* () average weight in grams
C. I. = Confidence Interval



ŧ

34

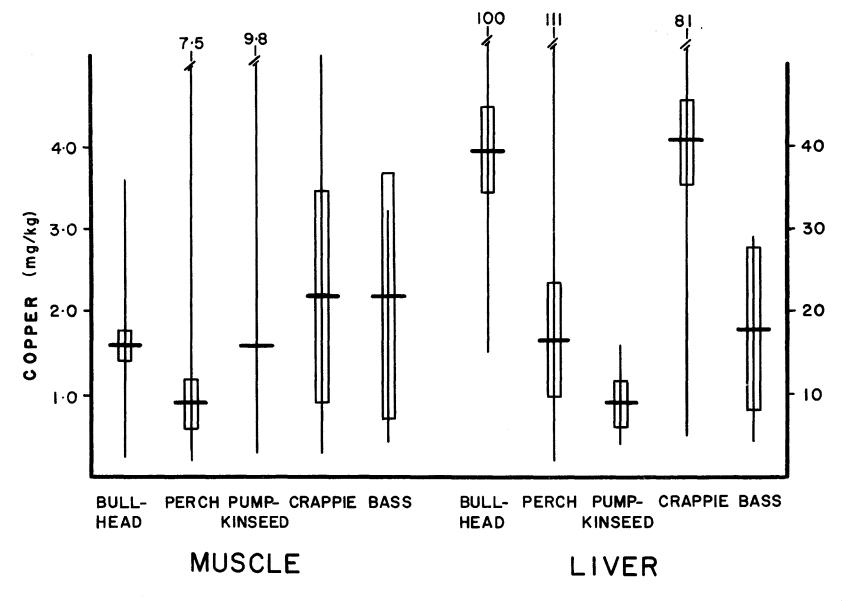
FIG. 8: ZINC. The concentration of zinc in five species of fish from lakes in the Coeur d'Alene River valley. Rectangle is 95% confidence interval, line is the range.

SPECIĘS	TISSUE	MEAN COPPER	±95% C.I.	RANGE	N
		(mg/kg)			
Brown Bullhead	muscle	1.6	0.13	0.3 to 3.6	16
(107)*	liver	39.0	4.5	13 to 100	12
Yellow Perch	muscle	0.87	0.29	0.2 to 7.5	50
(40)	liver	16.5	7.3	1.7 to 110	32
Pumpkinseed	muscle	1.6	2.8	0.3 to 9.8	8
(47)	liver	8.8	2.6	3.8 to 15	10
Black Crappie	muscle	2.2	1.3	0.3 to 5.1	10
(128)	liver	41.3	4.5	5 to 81	10
Largemouth Bass	muscle	2.2	1.5	0.4 to 3.0	5
(516)	liver	18.6	10.4	5.3 to 29	5

•

TABLE 10: COPPER: Concentration of copper in five species of fish from Coeur d'Alene River valley lakes.

* () average weight in grams
C. I. = Confidence Interval



٠

.

.

.

.

FIG. 9: COPPER. The concentration of copper in five species of fish from lakes in the Coeur d'Alene River valley. Rectangle is 95% confidence interval, line is $\stackrel{\omega}{\Leftrightarrow}$ the range.

SPECIES	TISSUE	MEAN CADMIUM	±95% C.I.	RANGE	N
<u></u>		(mg/kg)			
Brown Bullhead	muscle	0.17	2.8	0.16 to 0.17	2
(107)*	liver	3.8		1.3 to 6.4	6
Yellow Perch	muscle	0.32	0.11	0.17 to 0.85	39
(40)	liver	16.1	5.6	1.6 to 36	49
Pumpkinseed (47)	muscle	0.66	1.0	0.15 to 3.8	8
	liver	11.6	5.4	2.3 to 33	11
Black Crappie	muscle	1.1	1.8	0.33 to 3.7	5
(128)	liver	24.5	4.0	4.9 to 55	10
Largemouth Bass	muscle	0.75	1.8	0.11 to 1.9	3
(516)	liver	12.7	10.3	4.2 to 28	5

TABLE 11: CADMIUM: Concentration of cadmium in five species of fish from Coeur d'Alene River valley lakes.

* () average weight in grams
C. I. = Confidence Interval

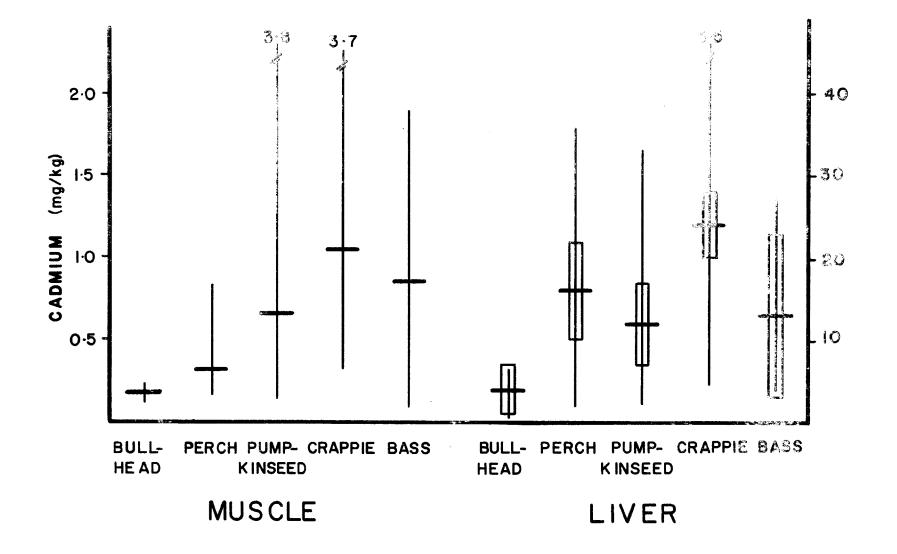


FIG. 10: CADMIUM. The concentration of cadmium in five species of fish from lakes in ω the Coeur d'Alene River valley. Rectangle is 95% confidence interval, line ∞ is the range.

in the Chironomids decreased in insects collected at stations further from the inlet, but not in direct correlation with the concentrations of zinc and copper in the sediments (Table 12).

<u>Cordulia</u> sp. (Libellulidae), a predacious dragonfly nymph, contained lower concentrations of zinc and copper than the other insects. However, <u>Chaoborus</u> sp. which is predacious on microcrustaceans and small insects contained higher concentrations than the Chironomids.

C	Т	٨	m	т	n	M	×
S	Ŧ.	н	T	⊥	U	TΛ	~

AQUATIC INSECTS

SEDIMENTS

	Chironomidae	Libellulidae	Chaoborinae	Heleidae	_
ZINC (mg/kg)					
1 2 3	858 216 50	185 	538	 188	3250 3550 2150
COPPER (mg/kg)					
1 2 3	52 13 20	37	66		76 87 34

TABLE 12: Zinc and copper in benthic insects and sediments from Anderson Lake, August 1973.

* Station 1 - inlet; stations 2 & 3 - open water sites.

DISCUSSION

Dissolved metal concentrations in the lakes change seasonally with fluctuating water levels. In the spring large volumes of river water containing dilute metal concentrations enter the lakes. Zinc concentrations at this time ranged from < 0.05 to 0.44 mg/l, and were highest near the inlets. Copper and cadmium concentrations were less than 0.02 mg/l. Once run-off ceases and suspended solids settle out, the concentration of zinc drops below detection limits (0.05 mg/l). During fall, as the water level drops in the river, dissolved metal concentrations increase but concentrated metals do not enter the lateral lakes since water is flowing out the channels. This trend continues until winter rain or spring runoff again swells the river.

Zinc concentrations present in the lakes in the spring are probably not toxic to warm water species but they may be toxic to trout. Becker and Thatcher (1973) referenced a large number of bioassay studies concerning heavy metals. The 96-hour TLm for Bluegill, <u>Lepomis macrochirus</u>, estimated under various conditions ranged from 1.9 to 20 mg/l zinc. Bioassay estimates are generally on the lower end of this range for waters of low alkalinity such as the lateral lakes.

Sappington (1969) found that the 96-hour TLm for Cutthroat Trout fingerlings in a static bioassay was only 0.09 mg/l zinc. In the spring, zinc levels at the inlets are higher than the value reported by Sappington. However, trout may avoid these higher concentrations and move to the open water sites where zinc levels are less. Salmonids exhibited an "avoidance reaction" to dissolved zinc in laboratory aquaria (Sprague 1964, 1968).

High concentrations of zinc, copper, cadmium, lead, cesium, and antimony have been deposited in the surface sediments of the lakes. Concentrations were higher than measured in the control lake or reported as background. Funk et al. (1973)reported accumulation of metals to a depth of 70-80 cm. in the Coeur d'Alene Lake delta and 20-30 cm. in the lake proper. No measurement of deposition depths was made in the lateral lakes.

The distribution of metals in the sediments reflects the mode of deposition from the river. Lakes more intimately connected to the river contain higher concentrations of metals. Within a lake there is generally a gradient of decreasing metal concentrations outward from inlet stations (Fig. 4).

However, in the inlet connected lakes the highest concentrations often occur at Station two (2). This is likely due to high adsorption of metals onto the finer sediments that occur at these locations. Thomas (1972) found that

mercury adsorbed to fine silty clays and organic sediments in greater amounts than to coarse inshore sediments. In the lateral lakes, the inlet stations contain larger quantities of sand as contrasted to the soft organic sediments at the open water stations. Thus, the composition of the sediments would tend to modify the general pattern of a decrease in metals at stations outward from the inlets.

Rose Lake and Cave Lake, which are not directly connected to the river by channels, also illustrated a gradient of metals in sediments. In Rose Lake, metal concentrations were lowest at the station which was furthest removed from the river. In Cave Lake, the metals decreased in sediments at stations further away from the opening in the railroad levee on the northwest side of the lake.

However, the concentrations of metals in sediments of Medicine and Killarney Lakes did not follow this pattern. In Medicine Lake, Station two (2) is probably situated too close to the inlet to indicate a decrease. In Killarney Lake the wide inlet probably causes an even distribution of river water within the lake, so that deposition of metals is uniform.

Heavy metals may become stabilized in the sediments by the process of adsorption. Reimer and Toth (1970) observed that complete adsorption of 0.5 ppm CuSO_4 occurred in all sediment systems tested. The adsorptive capacity was related to clay and organic matter content. Thomas (1972) found that mercury was adsorbed by clays, sulfides, and hydrated iron

oxides, and the concentration of mercury was positively correlated to organic carbon content. Quartz and sand did not adsorb mercury.

Not much information is available on the amounts of metals that can reenter water from the sediments. Maxfield and Wai (1971) demonstrated that a low equilibrium exists between water and sediment. They mixed Coeur d'Alene River sediments which contained 3200-4700 mg/kg zinc with water at different pH levels. At a pH of 7.4 the saturation concentration for the water overlying the sediment was only 1.8 mg/l zinc. The concentrations of zinc in the overlying water increased as the pH decreased. At pH levels in the lateral lakes (Table 1 & 2) dissolved zinc is maintained at low levels.

Although physical processes tend to keep metals in the sediments, biological processes may return them to the water column. For example, insoluble mercury is methylated by bacteria in the sediments and routed to fish via the water column or through the food chain (Jensen and Jernelöv 1969; Gillespie and Scott 1971).

The sediments represent a storehouse of large amounts of metals which are potentially toxic to aquatic organisms. At neutral pH levels present in the lakes, the metals are essentially trapped in the sediments and do not enter the water column. Heavy metals are more soluble in water at low pH levels (Hem 1972), consequently any decrease in pH in the poorly buffered lakes could release the trapped metals.

Metal concentrations in Yellow Perch from different locations within the Coeur d'Alene drainage did not agree closely with the working hypothesis. In muscle tissue zinc, copper, and cadmium concentrations were similiar from lake to lake. In liver tissue zinc and cadmium concentrations were noticeably lower in fish from Rose Lake. Exchange of water between this lake and the river is minimal since no direct inlet connects it to the river as in the other lakes.

In Table 13 the concentrations of metals in fish of the Coeur d'Alene lakes are compared to values reported in the literature for fish from other areas. All values were adjusted to mg/kg dry weight, and overall means were computed. The concentrations found in the Coeur d'Alene drainage fish are similiar to the values reported for other studies. Only copper and cadmium in fish from the lateral lakes appear to be higher. However, this disparity may be due to inherent differences in the studies as well as to an actual increase in concentration caused by metal pollution.

Based on comparison of values to control and to values reported for fish from other areas it appears that zinc, copper, and cadmium have not accumulated to high levels in fish from the study lakes, even though these waters annually receive metals from the river. Other studies have demonstrated that levels of zinc, copper, and cadmium in fish tissue may be a poor indicator of metal pollution.

ZINC		30	76.5	25.1	53.6	~ 10-100	52	138
COPPER	1.3	9	4.2	1.05	4.6	- 1-8	1.2	23
CADMIUM	•094	0.4		0.15	0.53		0.42	15
TISSUE	wholefish Freshwater	liver	headless, dressed	noncarn. Flesh, Freshwater	muscle Osteichthyes marine	muscle, marine	muscle	liver
METHODS	Freezedrie	d,ashed	wet ashed, AAS	wet ashed, AAS	wet ashed, AAS		wet asł	ned, AAS
AUTHOR	Lucas, et a 1970	al. ^(a)	Uthe &(b,c) Bligh 1971	Mathis &(b) Cummings 1973	Windom (c) et al. 1973	Cross et al.(a,d) 1973	present	t study

· • •

•

- TABLE 13: Approximate averages of metals in fish reported in other studies, in mg/kg dry weight.

٠

, . .

- a) mg/kg, ash weight
 b) Data reported as mg/kg (ug/g, ppm) wet weight was converted to mg/kg dry weight by multiplying by five (Lagler 1962, reported the average water content as 80%, so dry weight is approximately one-fifth of the wet weight).
 c) Overall average was approximated from data presented in publication.
 d) Derived from data points on a graph.

Uthe and Bligh (1971) compared metals in fish from the Lower Great Lakes Basin, a highly industrialized area, to those from a non-industrialized lake in Manitoba. Values for zinc, copper, and cadmium in liver tissue of Lake Whitefish, <u>Coregonus clupeaformis</u>, and Northern Pike, <u>Esox lucius</u>, were not significantly different between the two areas. Lucas et al. (1970) found that copper and zinc concentrations in ten species of fish varied little between different Great Lakes. Cadmium concentrations did vary slightly with species between lakes, ranging from 0.06 to 1.4 ppm, wet weight.

Van Meter (1974) determined metal concentrations in salmonids, suckers, and sculpins from various sections of the Clark Fork River drainage in Montana. He observed little difference in zinc, copper, and cadmium concentrations between fish from locations unaffected by mining wastes and fish from those stretches exposed to mining effluents.

Among adult fish there appears to be a relationship between trophic level and zinc concentration in muscle. Marcusen (1966) in studying Round Lake, located in the same drainage as my study, found that Bullheads are omnivorous feeding on plankton, benthic insects, and plant matter; Yellow Perch, Pumpkinseed, and Black Crappie are largely carnivorous on plankton, benthic organisms, and surface insects; and Largemouth Bass feed almost exclusively on fish. These species can be ranked generally according to trophic level from omnivorous to carnivorous in the following order: Brown Bullhead > Yellow Perch, Pumpkinseed, Black Crappie > Largemouth

Bass. Zinc concentrations in muscle decreased along this rank from Brown Bullhead to Largemouth Bass (Fig. 8). However, this trend was not evident in copper and cadmium concentrations (Fig. 9 & 10).

Zinc concentrations may decrease in muscle from omnivorous species to predacious fish due to differences in metal content of the food they consume. An omnivorous fish feeds on detrital material, which likely contains high levels of metals. Among predacious fish, piscivores consume material that contains lower levels than fish which feed primarily on invertebrates.

Differences in metal concentrations between species may also be related to the size of the fish. Heavy metals, other than mercury, tend to decrease with an increase in size or age. Cross et al. (1973) observed either no change or a decrease in concentration of metals with increasing size in two marine species. O'Rear (1971) found a decrease in zinc and copper concentrations with size in Striped Bass, <u>Morone</u> <u>saxatilis</u>. The specimens of Largemouth Bass analyzed in this study were much larger in size than the other species (Table 9).

In general most metals have been shown to decrease at higher trophic levels. The few bottom invertebrates that I examined contained higher concentrations of zinc, copper, and cadmium than measured in fish fillets. Also, the omnivorous insects showed higher metal values than the predacious forms. Accumulation coefficients for manganese, copper and zinc decreased from plankton to benthic organisms to fish in a marine food chain (Rozhanskaya 1969). Windom (1973) also noticed a decrease in levels of zinc, copper, and cadmium from plankton to planktivorous fish in the ocean. Baptist and Lewis (1969) described the decrease of zinc-65 up an estuarine food chain. The concentration of copper, lead, and cadmium decreased from tubificids to clams to fish (fillet) in the Illinois River (Mathis and Cummings 1973).

The most important factor in the relation of metals to food chains is probably the physiological differences in uptake and excretion rates between major groups of organisms. Concentration may occur by bioaccumulation, which is direct uptake from water, or by biomagnification, which is build up via the food chain. If uptake of metals from water involves only passive diffusion, small organisms would be expected to have higher accumulation rates than larger organisms since accumulation would depend on the ratio of surface area to volume. Estimates of uptake rates may also be altered by adsorption. Cushing and Rose (1970) showed that uptake of zinc-65 in periphyton was dependent on an adsorptive mechanism.

Excretion of metals occurs in aquatic organisms, but, little is known about the specific mechanism or rate for each metal (Pentreath 1971). To maintain homeostasis, excretion must keep up with accumulation. If it does not, then storage into tissues will occur. Apparently homeostatic processes in fish from the lateral lakes are able to control metal concentrations at these exposure levels.

CONCLUSION AND RECOMMENDATIONS

1. The Coeur d'Alene River transports heavy metals into the lateral lakes especially during highwater in the spring. However, since dilution is greatest during this time of year the concentration of dissolved metals is low. Zinc concentrations may be toxic to trout at the lake inlets, however, dissolved metals are below toxic levels in the open water areas of the lakes.

2. Heavy metals have accumulated to high concentrations in sediments of lakes in the Coeur d'Alene River valley. However, these metals are probably strongly adsorbed to sediments and apparently have little effect on the biota of the lakes.

3. Metal concentrations in fish from several of the lakes were higher than values for fish from a control area. However in general, the levels found were not excessive and illustrate that fish are not accumulating these contaminants from the lake environment. Determination of zinc, copper, and cadmium in tissues of fish then appears to be a poor indicator of heavy metal pollution.

4. In order to clarify these points, further studies should examine other species of fish in the drainage especially Salmonids which support the bulk of the sport fishery. In addition.fish should be analyzed for other metals which

occur in the mining wastes such as lead and antimony.

Many physiological changes in fish have been demonstrated at concentrations that are well below documented lethal limits. Such sublethal effects need to be assessed before the impact of metals on these fish populations can be fully understood.

LITERATURE CITED

- Baptist, J. P. and C. W. Lewis. 1969. Transfer of zinc-65 and chromium-51 through an estuarine food chain. Proc. 2nd Nat. Sym. Radioecol., Ann Arbor, Mich., 420-430.
- Bartlett, L., F. W. Rabe, and W. H. Funk. 1974. Effects of copper, zinc, and cadmium on <u>Selanastrum</u> <u>capricornutum</u>. Water Research 8: 179-185.
- Becker, C. D. and T. O. Thatcher. 1973. Toxicity of power plant chemicals to aquatic life. Batelle: Pacific Northwest Laboratories, Richland, Washington, WASH-1249.
- Bowen, H. J. M. 1966. Trace elements in biochemistry. Academic Press, London & New York. 241 p.
- Canney, F. C. 1959. Geochemical study of soil contamination in the Coeur d'Alene district, Shoshone County, Idaho. Mining Engineering 214: 205-210.
- Chupp, N. R. and P. D. Dalke. 1964. Waterfowl mortality in the Coeur d'Alene River Valley, Idaho. J. of Wildlife Mang. 28 (4): 692-702.
- Clement, J. L. 1972. Preservation and storage of water samples for trace element determinations. M.S.C. Thesis, U. of Illinois, Urbana, Illinois. <u>In</u> Water Res. Abstracts 1972, 6 (1): 464, #25-070.
- Cross, F. A., L. H. Hardy, N. Y. Jones, and R. T. Barnes. 1973. Relation between total body weight and concentrations of manganese, iron, copper, zinc, and mercury in white muscle of Bluefish (<u>Pomatomus saltatrix</u>) and a bathyl-demersal fish <u>Antimora rostrata</u>. J. Fish. Res. Bd. Can. 30: 1287-1291.
- Cushing, C. E. and F. L. Rose. 1970. Cycling of zinc-65 by Columbia River periphyton in a closed lotic microcosm. Limnol. and Oceanogr. 15 (5): 762-767.
- Ellis, M. M. 1932. Pollution of the Coeur d'Alene River and adjacent waters by mine wastes. Report to US Bur. of Fish. 55 p.

- Funk, W. H., F. W. Rabe, and R. Filby. 1973. The biological impact of combined metallic and organic pollution in the Coeur d'Alene-Spokane River drainage system. OWRR, Joint Project Completion Report (B-044 Wash, & B-015 Ida). 187 p.
- Gillespie, D. C. and D. P. Scott. 1971. Mobilization of mercuric sulfide from sediment into fish under aerobic conditions. J. Fish. Res. Bd. Can. 28 (11):1807-1808.
- Great Lake Region Committee on Analytical Techniques. 1969. Chemical laboratory manual for bottom sediments.
- Hem, J. D. 1972. Chemistry and occurrence of cadmium and zinc in surface water and groundwater. Water Resources Research 8 (3): 661-679.
- Jensen, S. and A. Jernelöv. 1969. Biological methylation of mercury in aquatic organisms. Science 223: 753-754.
- Jernelöv, A. and H. Lann. 1971. Mercury accumulation in food chains. Oikos 22 (3): 403-405.
- King, W. G., J. M. Rodriquez, and C. M. Wai. 1974. Losses of trace concentrations of cadmium from aqueous solution during storage in glass containers. Analytical Chemistry 46 (6): 771-773.
- Lackey, R. T. and B. E. May. 1971. Use of sugar flotation and dye to sort benthic samples. Trans. of Amer. Fish. Soc. 100 (4): 794-797.
- Lee, F. G. 1970. Factors affecting the transfer of materials between water and sediments. U. of Wisconsin Water Resources Cen., Eutrophication Infor. Pro., Lit. Review 1. 50 p.
- Lucas, H. F., D. N. Edington, and P. J. Colby. 1970. Concentrations of trace elements in Great Lakes fishes. J. Fish. Res. Bd. Can. 27: 677-684.
- Marcuson, P. E. 1966. Limnology and fish food abundance in Round Lake, Idaho. M. S. Thesis, U. of Idaho, Moscow, Idaho. 22 p.
- Mathis, B. J. and T. F. Cummings. 1973. Selected metals in sediments, water, and biota in the Illinois River. J. Wat. Pol. Con. Fed. 45 (7): 1573-1583.

- Maxfield, D. and C. M. Wai. 1971. Heavy metal pollution in the sediments of the Coeur d'Alene River delta. NSF-Student Originated Studies Project. 47 p.
- Mink, L. L., R. E. Williams and A. T. Wallace. 1971. Effect of industrial and domestic effluents on the water quality of the Coeur d'Alene River Basin. Idaho Bur. of Mines and Geology, Pamphlet #49. 30 p.
- Minter, R. F. 1971. Plankton population structure in the lower Coeur d'Alene River, Delta, and Lake. M. S. Thesis, U. of Idaho, Moscow, Idaho. 70 p.
- O'Rear, C. W., Jr. 1971. Some environmental influences on the zinc and copper content of Striped Bass, <u>Morone</u> <u>saxatilis</u>. Ph.D. Dissertation, Virginia Polytech. and State U., Blacksburg, Va. 70 p.
- Parker, J. I. 1972. Algae production and nutrient enrichment in Lake Coeur d'Alene, Idaho. M. S. Thesis, U. of Idaho, Moscow, Idaho. 39 p.
- Pentreath, R. J. 1971. The metabolism of radionuclides, p. 97-118. <u>In Marine radioecology</u>, the cycling of artificial radionuclides through marine food chains. Proc. 2nd ENEA Seminar, Hamburg. 213 p.
- Reimer, D. N. and S. J. Toth. 1970. Adsorption of copper by clay minerals, humic acids, and bottom muds. J. Amer. Water Works Assoc. 62 (3): 195-197.
- Rozhanskaya, L. I. 1969. Biogenic movement of manganese, copper, and zinc in the sea of Azov. Hydrobiological J. (USSR) 5: 43-47.
- Sappington, C. W. 1969. The acute toxicity of zinc to cutthroat trout (<u>Salmo clarki</u>). M. S. Thesis, U. of Idaho, Moscow Idaho. 22 p.
- Savage, N. L. and F. W. Rabe. 1973. The effects of mine and domestic wastes on macroinvertebrate community structure in the Coeur d'Alene River. Northwest Science 47 (3): 159-168.
- Sprague, J. B. 1964. Avoidance of copper-zinc solutions by young salmon in the laboratory. J. Wat. Pol. Con. Fed. 36 (8): 990-1004.
- Sprague, J. B. 1968. Avoidance reactions of Rainbow Trout to zinc sulphate solutions. Water Research 2:367-372.

- Standard methods for the examination of water and wastewater. 1972. American Public Health Assoc., 13th ed. 874 p.
- Thomas, R. L. 1972. The distribution of mercury in the sediments of Lake Ontario. Can. J. of Earth Sciences 9 (6): 636-651.
- Thompson, R. H. and W. J. Blanchflower. 1971. Wet-ashing apparatus to prepare biological materials for atomic absorption spectrophotometry. Laboratory Practice 20 (11): 859-861.
- Uthe, J. F. and E. G. Bligh. 1971. Preliminary survey of heavy metal contamination of Canadian freshwater fish. J. Fish. Res. Bd. Can. 28: 786-788.
- Van Meter, W. P. 1974. Heavy metal concentrations in fish tissue of the upper Clark Fork River. Montana U. Joint Water Resources Research Center, Report #551. 37p.
- Winner, J. E. 1972. Macrobenthic communities in the Coeur d'Alene Lake system. M. S. Thesis, U. of Idaho, Moscow, Idaho. 41 p.
- Windom, H.,R. Stickney, R. Smith, D. White, and F. Taylor. 1973. Arsenic, cadmium, copper, mercury and zinc in some species of North Atlantic Fin fish. J. Fish. Res. Bd. Can. 30 (2): 275-279.
- Wissmar, R. C. 1972. Some effects of mine drainage on primary production in Coeur d'Alene River and Lake, Idaho. Ph. D. Dissertation, U. of Idaho, Moscow, Idaho. 61 p.